

Terahertz Nonlinear Optics & III-V Semiconductor Nanowires



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A thesis submitted for the degree of

Doctor of Philosophy

Michaelmas 2019

This thesis is dedicated to
my parents, my brothers, and all of my teachers especially
my spiritual master, al-Shaykh al-Sayyid Muhammad Abul Huda
al-Ya'qoubi al-Hassani al-Idrissi

Acknowledgements

My DPhil journey began in 2016, and throughout those 3 years, I have undoubtedly achieved a lot. There are countless people I would like to thank but first are my supervisors, Professor Michael B. Johnston and Professor Laura M. Herz who have been incredibly supportive of my work. Often times, you hear condescending comments from doctoral students from other research groups and they stem mainly from the fact that they barely get to discuss their projects and results with their supervisor or even in most cases, they barely see them at all. I am utterly grateful for the weekly meetings held on Mondays with group presentations that help in shaping and improving communication skills. Lest we forget the great British culture of holding tea times at 11.00 am and 16.30 pm where group members would get an opportunity to discuss further with both Michael and Laura. Michael's support in choosing my career options has been crucial and seeing his ambitions and achievements have contributed to my choice in staying in academia. In Islamic Tradition, teachers are held in high respect, second to one's parents, and I would like to take this opportunity to mention that they have been great mentors.

I do not think that I would have been able to pass through those 3 years without the help and company of many brilliant and amazing people in my lab. Thank you all for being there:

1. Dr. Timothy Crothers who has been sitting next to my desk, the Matlab warrior, the "wannabe" Wehrenfennig (ha!) but who eventually snaked all of us for Python. We spent a lot of time discussing about projects, experiments, electronics, data analysis, figures, life problems and many more, especially over tea/coffee;
2. Sabrina Sterzl for being very nice to me and helping me out with a lot of experiments, system aligning, some dry German jokes and dealing with difficult situations in the lab;
3. Dr. Jay Patel (fellow brown guy on the group) for his very candid behaviour and dealing with things in the least number of steps, his very gentle nature of always asking how my experiments are going and

potentially finding a solution if need be, and without forgetting him being the master of the FTIR;

4. Dr. Adam Wright, a pleasant young Sheldon Cooper (this is a compliment, don't worry!), keen scientist, fun friend and someone who understood my jokes (great minds think alike);
5. DPhil student Alexander Knight for his genius mind in solving puzzles, helping out with Matlab issues, and allowing me to use his microscope in the Johnston lab;
6. Hannah Eggimann, for her fine Swiss manners, always perfecting things and baking cakes (cinnamon stars!) and bringing chocolates for me from Switzerland;
7. Kimberley Savill for her great company during late hours when I was writing this thesis.

I would also like to thank my teachers in Islamic Sciences who have been amazing support:

1. Shaykh Muhammad Abul Huda al-Ya'qoubi for his excellent spiritual support;
2. Shaykh Muhammad Hassani for his countless advice on how to approach science and to be always honest in my dealings.

I would also like to acknowledge the various people involved in the different projects I have been doing during my DPhil:

1. Dr. Hannah Joyce and her PhD student, Chawit Ustwachoke, at the University of Cambridge for providing the polariser samples;
 2. Prof. Chennupati Jagadish and his group at the Australian National University (ANU) for growing the nanowires;
 3. Dr. Mohammad Rashidi Shahgoli at the Australian National University for growing the indium phosphide nanowires for a length dependence study;
 4. Dr. Tuomas Hagrren at the Australian National University (ANU) for fabrication the wire grid polariser device;
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5. Dr. Simonas Kicas, and his PhD student, Simas Melnikas at the Centre for Physical Sciences and Technology (FTMC) in Lithuania for providing the spintronic emitters with coatings;
 6. Dr. Sudha Mokkalapati at the University of Monash for doing the simulations for the nanowire samples;
 7. Dr. Nicole Grobert and her DPhil student, Eoin O'Sullivan, at the University of Oxford for growing the hexagonal boron nitride samples and carrying out Raman measurements on them;
 8. Mr. Dipankar Chugh who is a PhD student at ANU (Department of Electronic Materials Engineering) for making the *h*BN thin films.

Finally, I cannot stress enough the great support I received from my parents and my two brothers.

Abstract

MOST commercially available terahertz spectrometers make use of resonant and non-resonant methods to generate and detect THz radiation. This allows only the low frequency spectrum to be accessed, usually from 0.1 THz to 8 THz, severely limiting the range over which dynamics can be observed. In this thesis, the physics of non-linear optics is exploited and a state-of-the-art terahertz air-plasma generation and detection setup is showcased. THz radiation is generated through non-linear interaction of a two-colour laser field under a dry nitrogen atmosphere producing a plasma, while the detection is accomplished with an Air Biased Coherent Detection (ABCD) technique. The issue of phonon resonances, damage threshold, etalon effects and dispersion of crystals in the THz region are effectively bypassed. The system was specifically designed and built to ensure a robust experimental setup is obtained with several components being made by our physics workshop. Furthermore, significant improvements have been put in place to increase data acquisition speed and maximising signal-to-noise ratio for better results.

III-V semiconductor nanowires are playing an increasingly important role in the field of condensed matter physics. From nanoscale components to highly efficient photovoltaic devices, there is a strong urge to have a solid fundamental understanding of their optoelectronic properties. The air plasma system was used to demonstrate two novel ultrafast THz modulators based on GaAs semiconductor nanowires operating at very high THz bandwidth (up to 40 THz). A significant improvement in modulation depth was achieved, up to 45%, together with picosecond modulation speed. Additionally, to further widen the study of III-V nanowires, this thesis presents a study showing a direct relation between the nanowire length and the frequency of surface plasmon resonance in the terahertz regime. Theoretical calculations have been done to further strengthen this study with the simulations revealing higher electron mobilities than the previously reported values.

Finally, two smaller chapters were dedicated to the study of the temperature-dependence of the refractive index of *c*-cut sapphire in the ter-

ahertz regime and the optoelectronic properties of hexagonal boron nitride (*h*BN) at equilibrium state. These provide fundamental insights into the potential usage of sapphire substrates as a replacement to quartz substrates as they are more robust and can support higher temperatures during growth and with the *h*BN laying the foundation for further avenues of research.

List of Publications Associated with this Thesis

Manuscripts

- **D. A. Damry**, S. Mokkapati, M. R. Shahgoli, H. H. Tan, M. Hejda, A. Hurtado, L. M. Herz, M. B. Johnston, *Length Dependent Plasmon Resonance in GaAs and InP Nanowires*, (Manuscript in preparation)
- **D. A. Damry**, C. Uswachoke, H. H. Tan, T. Haggren, L. M. Herz, H. J. Joyce, M. B. Johnston, *An Ultrafast Switchable Terahertz Polarization Modulator Based on III–V Semiconductor Nanowires Operating at High Bandwidth*, (Manuscript in preparation)
- **D. A. Damry**, S. Melnikas, S. Kicas, M. B. Johnston, *Increasing THz Emission Efficiency of Spintronic Emitters*, (Manuscript in preparation)
- **D. A. Damry**, M. B. Johnston, *Temperature-Dependent Refractive Index of c-Sapphire at Terahertz Frequencies*, (Manuscript in preparation)
- K. Peng, D. Jevtics, F. Zhang, S. Sterzl, **D. A. Damry**, M. U. Rothmann, H. H. Tan, L. M. Herz, L. Fu, A. Hurtado, C. Jagadish, M. B. Johnston, *3D-Cross Nanowire Networks Recover Full Terahertz State*, **Submitted to Science**
- J. L. Boland, S. A. Baig, **D. A. Damry**, H. Hoe Tan, C. Jagadish, H. J. Joyce, M. B. Johnston, *An Ultrafast Switchable Terahertz Polarization Modulator Based on III–V Semiconductor Nanowires*, *Nano Letters*, **17**, 4, 2603-2610 (2017)
- S. A. Baig, J. L. Boland, **D. A. Damry**, H. Hoe Tan, C. Jagadish, H. J. Joyce, M. B. Johnston, *Choice of Polymer Matrix for a Fast Switchable III-V Nanowire Terahertz Modulator*, *MRS Advances*, 1-6 (2017)

Conference Proceedings

- H. J. Joyce, C. Uswachoke, S. Adeyemo, S. Kar, **D. A. Damry**, K. Peng, M. B. Johnston, J. Wong-Leung, H. H. Tan, C. Jagadish, *Engineering III–V Nanowires for*

Optoelectronics: From Visible to Terahertz, Conference: Novel Optical Materials and Applications, (2019)

- J. L. Boland, K. Peng, S. Baig, **D. A. Damry**, P. Parkinson, L. Fu, H. H. Tan, C. Jagadish, L. M. Herz, H. J. Joyce, M. B. Johnston, *The Route to Nanoscale Terahertz Technology: Nanowire-based Terahertz Detectors and Terahertz Modulators*, 43rd International Conference on Infrared, Millimeter, and Terahertz Waves (IRMMW-THz) (2018)
- S. A. Baig, J. L. Boland, **D. A. Damry**, H. Hoe Tan, C. Jagadish, H. J. Joyce, M. B. Johnston, *Modulation of Terahertz Polarisation on Picosecond Timescales using Polymer-Encapsulated Semiconductor Nanowires*, CLEO: Science and Innovations (2017)

Conference Presentations

- **Oral:** An Ultrafast Switchable Terahertz Polarization Modulator Based on III–V Semiconductor Nanowires Operating at High Bandwidths, *IRMMW, Maison de la Chimie, Paris, France*, (2019)
 - **Oral:** An Ultrafast Switchable Terahertz Polarization Modulator Based on III–V Semiconductor Nanowires, *OTST, UCL, London*, (2017)
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Fundamental Constants

$$g = 9.80 \text{ m s}^{-2}$$

$$c = \text{speed of light in vacuum} = 3.00 \times 10^8 \text{ ms}^{-1}$$

$$e = \text{charge of electron} = 1.60 \times 10^{-19} \text{ C}$$

$$m_e = \text{mass of electron} = 9.11 \times 10^{-31} \text{ kg}$$

$$m_n = \text{mass of neutron or proton} = 1.67 \times 10^{-27} \text{ kg}$$

$$N_A = \text{Avogadro's number} = 6.022 \times 10^{23} \text{ molecules/mol}$$

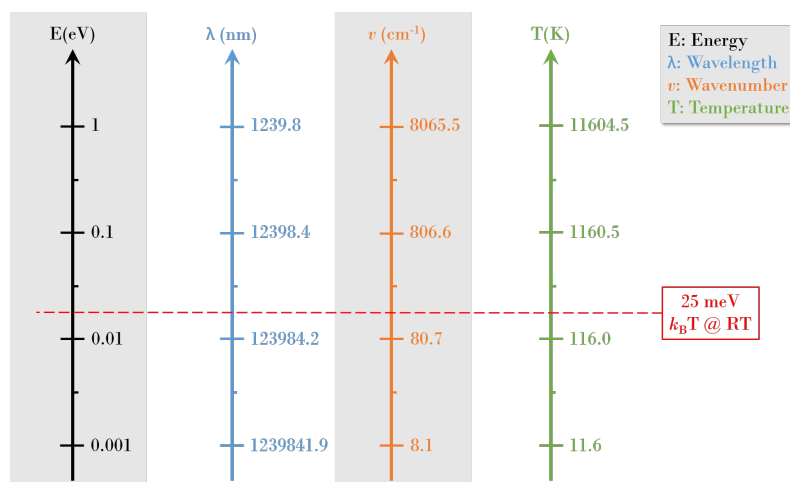
$$k_B = \text{Boltzmann's constant} = 1.38 \times 10^{-23} \text{ J/K}$$

$$R = \text{universal gas constant} = 8.31 \text{ J/(mol K)} = 0.0821 \text{ atm/(mol K)}$$

$$c_W = \text{specific heat of water} = 1 \text{ cal/(g K)}$$

$$1 \text{ cal} = 4.186 \text{ J}$$

$$\sigma = \text{Stefan-Boltzmann constant} = 5.67 \times 10^{-8} \text{ W/(m}^2\text{K}^4\text{)}$$



List of Abbreviations

ABCD: Air-Biased Coherent Detection	OPTP(S): Optical-Pump Terahertz-Probe (Spectroscopy)
BBO: Barium Borate	OR: Optical Rectification
BNNT: Boron Nitride NanoTube	PCA: Photoconductive Antenna
cBN: cubic Boron Nitride	PCD: Photoconductive Detection
CNT: Carbon NanoTube	PECVD: Plasma-Enhanced Chemical Vapour Deposition
DAST: 4-N,N-Dimethylamino-4'-N'-Methyl-Stilbazolium Tosylate	PMMA: Poly(Methyl Methacrylate)
EBL: Electron Beam Lithography	SAE: Selective Area Epitaxy
EMT: Effective Medium Theory	SEM: Scanning Electron Microscopy
EO: Electro Optic	SHG: Second Harmonic Generation
FDTD: Finite Difference Time Domain	TA: Transient Absorption
FS-EOS: Free-Space Electro Optic Sampling	TDS: Time-Domain Spectroscopy
FTO: Fluorine-doped Tin Oxide	TFISH: Terahertz-Field Induced Second Harmonic
FWHM: Full Width Half Maximum	TFSF: Total Field Scattered Field
FWM: Four Wave Mixing	TO: Transverse Optical
GVM: Group Velocity Mismatch	THzTDS: Terahertz Time-Domain Spectroscopy
hBN: hexagonal Boron Nitride	THzTRS: Terahertz Time-Resolved Spectroscopy
HRFZ: High Resistivity Float Zone	TI: Tunnel Ionization
IR: Infra-Red	TP: Transfer Printing
MOCVD: Metal-Organic Chemical Vapour Deposition	TRS: Time-Resolved Spectroscopy
MOVPE: Metal-Organic Vapour Phase Epitaxy	VDP: Vapour Deposition Polymerization
MPI: Multi-Photon Ionization	VIS: Visible
ND: Neutral Density	wBN: wurtzite Boron Nitride
NW: Nanowire	WZ: Wurtzite
OAP: Off-Axis Parabolic	ZB: Zinc Blende

INTRODUCTION

SPECTROSCOPY has been a crucial field of study in condensed matter physics. It is principally the investigation of the interaction of light with matter, such as the absorption and emission of electromagnetic radiation as it goes through a particular material as a function of the wavelength of the waves. More recently, with the advancement of classical and quantum mechanics, the definition has been expanded to include the study of the interactions between particles such as electrons, protons, and ions, as well as their interaction with other particles as a function of their collision energy. Spectroscopic analysis has been key in the development of the most fundamental theories in physics, including quantum mechanics, the special and general theories of relativity, and quantum electrodynamics. On an astronomical scale, spectroscopy has been applied to high-energy collisions and has been a resourceful tool in developing scientific understanding not only of the electromagnetic force but also of the strong and weak nuclear forces.

Spectroscopic techniques have been applied in virtually all technical fields of science and technology. A key frequency range has sparked huge research in semiconductor physics and this field has been termed as Terahertz Photonics. Previously, this frequency regime has been unexplored due to a lack of sources, methods and detection techniques. However, the ground-breaking work of Auston *et al.* [1] in 1984 has allowed scientists to bridge the so-called “Terahertz Gap.” Auston pioneered in the generation, transmission and detection of electromagnetic (EM) radiation for applications in high-speed electronics. In 1989, Fattinger and Grischkowsky transformed the idea and went one step further: generating and detecting THz radiation coherently. [2,3] This major leap allowed scientists to develop a new technique - Terahertz Time-Domain Spectroscopy (THz-TDS). The

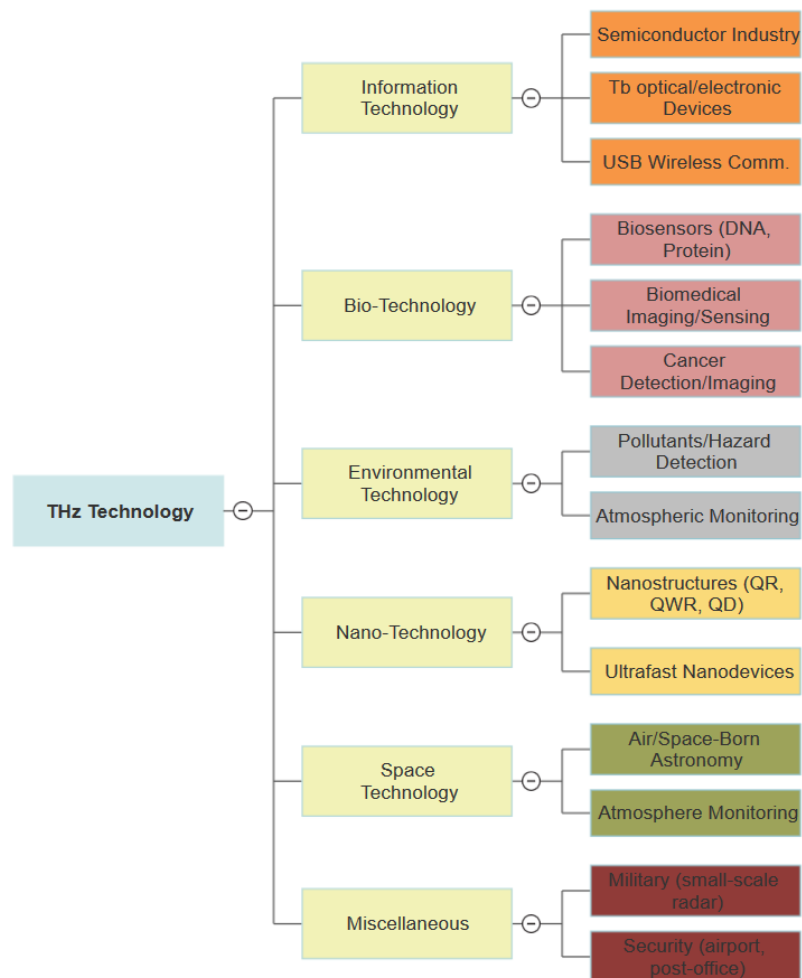


Figure 1.1: **THz Technology**: Prominent areas where THz technology has played an important role.

implications that ensued meant that when studying a material, coherent THz emitters and detectors would allow one to measure both the amplitude and phase of THz pulses as opposed to just the intensity. The extraction of the complex refractive index - real and imaginary parts - of samples is then straightforward, bypassing a major bottleneck, the complex *Kramers-Kronig* relations.

The terahertz spectral range is from ≈ 0.1 THz to ≈ 30 THz. In other units for a better perspective:

$$1 \text{ THz} \approx 1 \text{ ps} \approx 33 \text{ cm}^{-1} \approx 0.3 \text{ mm} \approx 48 \text{ K} \approx 4.1 \text{ meV}$$

This means that this frequency regime sits between the high-frequency optical side and the low-frequency electronic side of the EM spectrum. 1 THz in photon energy is about 4 meV and the THz energies are much less than the electronic state transitions in atoms and molecules. THz therefore will allow one to access the vibrational and rotational modes of molecules which will include insight into phonons, plasmons, and magnons amongst other quasiparticles.

Charge carrier dynamics for nanostructured materials can vary drastically in comparison with those of their bulk counterparts, due to their unique morphology and material properties, such as crystal structure, electronic bandstructure, optical bandgap and electron-phonon coupling. [4] Thus, it is crucial to investigate the following key qualities of semiconductor nanowires (NW) and nanoparticles: the degree of confinement, including possible quantum confinement; the large surface-to-volume ratio intrinsic to NWs; the length scale defined by the NW diameter, which has dramatic consequences for the excitation and emission of the NW electronic states; and finally, the quality of growth and NW crystal structure. By gaining a deeper understanding of these NW qualities and their effect on the charge carrier dynamics, NWs can then be grown and specifically engineered to optimise performance for future specific NW-based devices.

1.1 Thesis Overview

This thesis is three-fold in its theme: (1) ultrafast spectroscopy, (2) optoelectronics and (3) applications of semiconductors. Chapters 2-4 deal with an introduction to semiconductors and terahertz spectroscopy, while Chapters 5-7 deal with using pump-probe techniques to study various condensed matter systems.

Thesis Themes

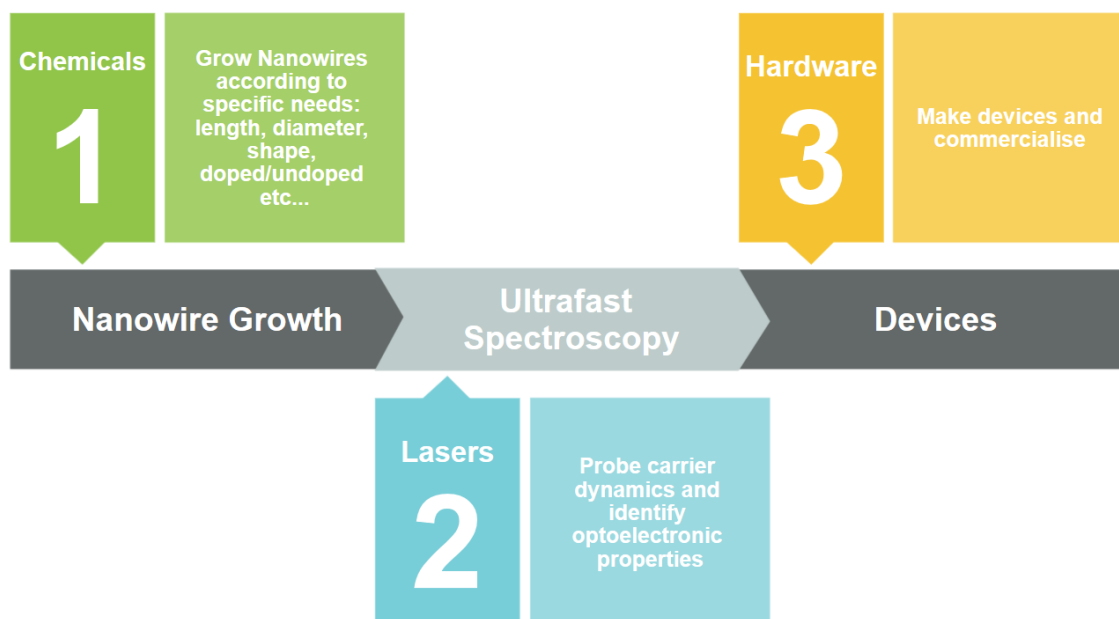


Figure 1.2: **Themes within this thesis:** Schematic diagram showing an overview of the topics covered within this work.

1.1.1 Ultrafast Spectroscopy

Chapter 3 gives an overview of terahertz spectroscopy which is a non-contact technique used to study various materials. Terahertz (THz) radiation is non-ionizing, non-invasive, and penetrable to many materials with a depth of penetration lower than that of microwave radiation. Being on the lower end of the energy scale, THz waves also tend to be very sensitive to various kinds of low-energy resonances such as vibrational, translational, rotational, torsional, and conformational states, thus providing crucial information on molecules that would otherwise be inaccessible via other analytical and imaging techniques. These unique characteristics make THz suitable for identifying, analyzing, or imaging a variety of materials.

Much effort has gone into developing this technique, ranging from THz emission, to THz detection through THz wave propagation in various media. Two main techniques that are heavily employed are THz time-domain spectroscopy, and optical-pump THz-probe spectroscopy. Throughout this thesis, these two methods have been used for the study of samples. Therefore it is important to have a broad in-depth knowledge of how the systems work. I have also spent a lot of time in the optimisation of the experimental setups and chapter 3 goes into details regarding the various methods of generating and detecting THz pulses. Although this technique is quite powerful, there are some

compromises that need to be taken into consideration. Often times, one would need a high signal to study materials that have, for instance, low mobilities whereas at other times, a large bandwidth would take precedence over a high signal typically when looking at photoconductivity spectra. Therefore an overview is given of the different crystals that would meet the desired characteristics.

Chapter 3 also describes the various systems I have built during my DPhil. Particular emphasis is given to system alignment which is fundamental to having an ultrafast spectroscopic system that is both robust and stable. These points will hopefully help future students to have a good understanding of how things operate and should there be any issues, they will know how to probe and troubleshoot. The chapter addresses in a detailed section the data extraction methods from experimental measurements with the last section dedicated to the temperature-dependence of the complex refractive index of *c*-Sapphire substrates at terahertz frequencies.

Chapter 4 is entirely dedicated to the physics of air-plasma photonics. As new materials come to light, we are in dire need of new ways to generate high powered radiation with large bandwidths to be able to probe how various systems operate in an ultra-broadband regime. As the reader goes through this thesis, it will be clear that most of the semiconductors that have been studied have characteristic features/resonances in the 0.1 – 4 THz range. Prior to this thesis, the THz spectrometers did not allow us to go beyond 8 – 9 THz owing to the emitter and detector types. One of the routes for broadband THz generation is high power laser plasma interaction.

This technique requires sophisticated methods and both Chapters 3 and 4 expound on these several aspects. A state-of-the-art experimental setup was built and tested. The chapter begins by giving short introductions into the theory behind plasma filamentation and the field of non-linear optics. Although THz generation from an air-plasma is not yet fully understood, two theories are described that have been put forward and their respective successes and failures are presented. This was then followed by a description of the setup and the various intricacies and subtleties that were considered during this building-up process. A detailed section is dedicated to extracting and correcting for electro-optic detection and we go on to show some results we got when characterising the system. The final setup is still being built and a schematic with the different parts is shown.

Boron * B 10.81 5	Carbon * C 12.01 6	Nitrogen *** N 14.01 7
Aluminium * Al 26.98 13	Silicon * Si 28.09 14	Phosphorus * P 30.97 15
Gallium * Ga 69.72 31	Germanium * Ge 72.63 32	Arsenic * As 74.92 33
Indium * In 114.82 49	Tin * Sn 118.71 50	Antimony * Sb 121.76 51
Thallium * Tl 204.38 81	Lead * Pb 207.2 82	Bismuth * Bi 208.98 83

Figure 1.3: **III-V Compounds:** Periodic table showcasing the various elements used in III-V semiconductors. Gallium arsenide (GaAs), indium phosphide (InP), boron nitride (BN) are the materials we study in this thesis.

1.1.2 Optoelectronics and Applications of Semiconductors

Over the past century, scientific research has grown ever so challenging with materials displaying unique behaviours and properties. This ultimately led to a renaissance of novel effects and potentially disruptive technologies observed in and designed from materials with nanoscale dimensions. Our knowledge of how systems function had to be revamped with new effects being at play. At this scale, classical Newtonian mechanics do not apply and instead quantum effects dominate and the confinement of electrons along one, two, or three dimensions will undoubtedly alter the density of states of the materials yielding discrete energy levels that differ from their bulk counterparts. These effects confer special properties to such systems enabling new and uncharted avenues to be explored. Furthermore, nanostructured materials have enormous surface area-to-volume ratios that enable highly efficient processes allowing surface states to play a major role.

One interesting family of materials which have attracted much research and development interest is III – V compound semiconductor nanowires due to their excellent physical properties for high-performance nanoelectronics, photodetectors, photovoltaics, transistors, ferroelectrics, catalysis, batteries and many more. [5–13] They behave as quasi 1D-structures but are unlike them in many respects: for instance, compared with other one-dimensional (1D) nanostructures such as silicon (Si) NWs or carbon nanotubes (CNTs), III – V NWs typically exhibit higher intrinsic carrier concentration and mobilities, [14] and these properties are coveted for high-performance and high-speed electronic

devices which would otherwise not be easily achieved solely by Si or other nanostructured materials. [15, 16] Additionally, most III – V NWs have direct bandgaps which is essential in light absorption and by optimising the material stoichiometry, the bandgaps can be engineered over a wide range expanding their optoelectronic properties. Another yet desirable property these materials possess is their natural tendency to be mechanically flexible and optically transparent for which they are considered as active materials for high-performance flexible electronics for the development of next-generation display technologies, including “see-through” and conformable products. [17–22] Furthermore, their extraordinarily large surface area-to-volume ratio make the NWs perfect contenders for high-performance sensors. All these attractive combinations of the properties of III – V NWs have made them superior candidates for next-generation nanoscale electronics, photonics and sensors, and they can be cheaply manufactured over a large scale and deposited on flexible substrates. [23]

Chapter 2 will give an introduction to the physics of III-V nanowire semiconductors, Figure 1.3, their growth techniques and the various electronic and optical properties they possess. The two materials studied in this thesis are gallium arsenide and indium phosphide, and therefore a brief background is given on these two. Dr. Jessica Boland’s thesis [24] goes into great detail about various nanowires and methods used to study them. The reader is highly encouraged to go through her thesis should he/she be interested in learning more.

Chapter 5 deals with nanowire polarisers. In 2016, highly aligned, unpassivated gallium arsenide nanowires embedded in a parylene-c host matrix were used as THz polarisers (all the devices were fabricated at the university of Cambridge). It is well-known that nanowires have high anisotropic THz absorption along their long axis and by rotating them, it is possible to modulate the intensity of the THz. The modulation depths were increased through stacking several layers and the lifetimes of these stacked devices were on the picosecond scale, allowing ultrafast switching speeds. However, the devices were shown to operate in the range of 0.1 – 4 THz. The air-plasma system goes beyond what we previously could achieve: a staggering 40 THz ultrawide bandwidth. New and improved devices were tested and assessed whether the modulation is still significant at these frequencies. Through better stacking techniques, the overall nanowire density was also increased resulting in higher modulation depths. We also show the performance of a wire-grid polariser based on a patterned thin sheet of GaAs ($\approx 300\text{ nm}$). The device was fabricated at the Australian National University using epitaxial lift-off and electron beam lithography and the modulation depth observed was as high as the champion device for the highest stacked layered devices from Cambridge. Although the lifetime of the

charge carriers increased by ten-fold, it was still on the order of picoseconds which is very promising for applications in high speed communication devices.

Chapter 6 looks at the length-dependent plasmonic resonance in both GaAs and InP nanowires. Dr. Hannah Joyce and Dr. Jessica Boland previously performed in-depth studies of nanowires and how their optoelectronic properties behave with temperature, doping densities and types, surface passivation, and core-shell structures amongst others. [14,24–33] They concluded that the plasmon resonance, which is a characteristic feature of these quasi-1D structures due to strong quantum confinement, is dependent on the charge-carrier density after photoexcitation. Simulations by Dr. Sudha Mokkalapati have shown a length-dependence as well, with the plasmon mode shifting to higher frequencies for short nanowires. By using various methods, nanowires can be engineered to grow up to different lengths and we used them as part of this study. As for the GaAs nanowires, the samples were transferred onto z -cut quartz substrates via the conventional method of rubbing. Although this gives decent nanowire alignment, it is not ideal. The samples gave very good results, although a bit noisy owing to the fact that the nanowire density was poor. As for the InP nanowires, they were grown and transferred onto z -cut quartz substrates via a more sophisticated method: transfer-printing. This ensures that most nanowires are aligned in one direction and as closely packed together as possible. This meant that the nanowire density was much greater resulting in better signal-to-noise ratio. The transfer-printing was done at the university of Strathclyde and the method is described in detail. The results of this chapter showed amazing correlation with the simulated data and this hopefully will ensure we use the correct nanowire lengths for device fabrication.

Going back to **Chapter 3**, it has an extra section that deals with the complex refractive index of c -cut sapphire at terahertz frequencies. Earlier on, Davies *et al.* presented a work on the temperature-dependence of the refractive index of z -cut quartz in the terahertz regime. This work was essential as z -cut quartz discs are highly used as substrates and windows in regards to optical-pump terahertz-probe (OPTP) spectroscopy. However, sapphire is another potential substrate which is more robust than quartz and scratch-resistant. In addition Sapphire is also a better thermal conductor which means heat is dissipated quicker during experiments keeping the sample deposited on them at a lower temperature. Therefore an optical characterisation of how the complex refractive index changes with temperature is important. Crothers *et al.* demonstrated that in order to extract the maximum information from an OPTP experiment, knowledge of the refractive indices of the substrate which dictate the internal Fabry-Perot reflections is required. Here, we go on to present how the complex refractive index of c -Sapphire change with

temperature in a broadband regime between 0.5 THz and 7.0 THz taken at 6, 14, 46, 80, 120, 160, 200, 300, 350, and 420 K.

Chapter 7 examines the optoelectronic properties of a wide bandgap, Van der Waals material hexagonal boron nitride nanotubes and films using THz spectroscopy. This project was done in collaboration with material scientists at Oxford University and the Australian National University who provided the nanotubes and films respectively. Boron nitride features an enormous bandgap of 5.9 eV. This is about 4 times the energy provided by our laser amplifier which sits at roughly 1.5 eV. To photoexcite these samples, fourth harmonic generation is necessary and unfortunately this was not possible given the very high cost of crystals capable of such frequency conversion and their efficiency ($\lll 1\%$). Instead we opted to study their dark conductivity properties that is essential as a breakthrough to more advanced characterisation methods and sample fabrication. In making these samples, the use of precursors such as carbon or magnesium will undoubtedly introduce dopants and we show that these materials display a Drude conductivity at equilibrium.

1.2 The Conclusion

The thesis is concluded with an overview of possible avenues for projects in the future. Although quite a lot of work has been done for this thesis, there are nevertheless countless other research ideas that can be further pursued. For instance the work on air-plasma photonics in Chapter 4 can be delved much deeper into the understanding of plasma physics and the generation of terahertz radiation which is currently subjected to a lot of debates. Overall, it would be near-impossible to include every single detail I have learnt or explored throughout my DPhil in this thesis.

SEMICONDUCTOR NANOWIRES:

Fundamentals, Principles, Growth & Optoelectronic Properties

SEMICONDUCTOR nanowires (NWs) were first proposed in the 1960s, [34] and since then there has been a huge outpouring in research into the growth techniques and device applications of these nanoscaled materials owing to their usage as active components in devices. [35,36] Moreover, in order to facilitate their usage, it is imperative to know their electrical and optical properties and despite huge progress in the field since its inception, the charge carrier dynamics and effects of NW size and morphology on their optoelectronic properties are yet to be unveiled.

As mentioned briefly, owing to their quasi 1D nature, nanowires are known to exhibit particularly distinctive and interesting phenomenological properties, namely discrete quantized energy levels, Coulomb blockades, and single-electron tunnelling. These quantum mechanical effects tend to play an important role in such small structures. To tailor the optoelectronic properties of semiconductor NWs for device applications, an in-depth understanding of the carrier transport and recombination dynamics within the NWs are required. For instance, fast switching speed devices for high speed telecommunications require the carrier lifetime to be as short as possible.

This chapter deals with the physics of semiconducting nanowires, their growth techniques, applications and a literature review of the work that has been done so far to understand their optoelectronic properties. The list of works mentioned here is not an exhaustive one and the reader is encouraged to read further materials which are not presented here. [37–46]

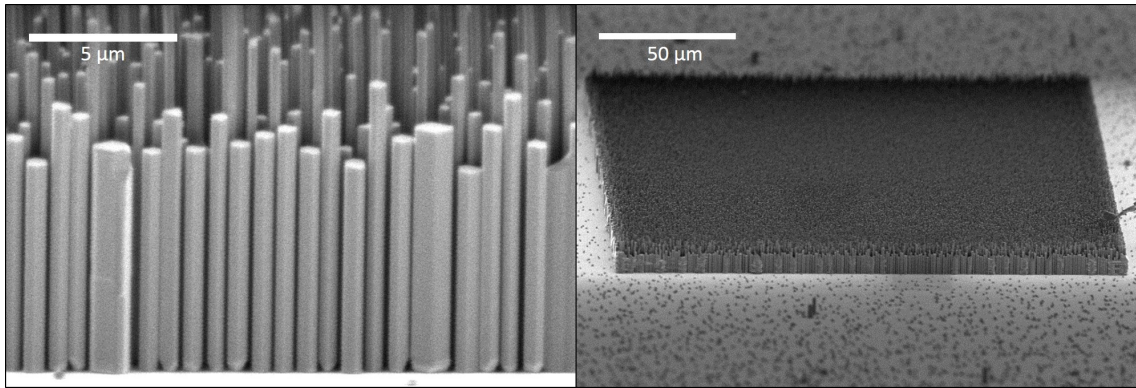


Figure 2.1: **SEM of InP Nanowires:** Scanning-electron-microscope (SEM) of InP nanowires grown via metal-organic-chemical vapour deposition (MOCVD) at the Australian National University. The nanowires are unidirectional and densely packed together. The length of a nanowire is approximately 7-8 microns.

2.1 Nanowire Growth Techniques

Nanowires, Figure 2.1, described as sub-micron structures having diameters on the order of nanometres ($1\text{ nm} = 10^{-9}\text{ m}$) and varying lengths, are intensely researched and sought-after due to their capability to interface with other nano-micro scale systems, realization of nano-bio devices due to their size regime being similar to biological macromolecules, and single nanowire-based device integration. They also have a higher surface area-to-volume ratio with long axial morphology for applications in light detection, sensors, and catalytic functionalities. By nature, they have incredible properties that can be tailored to specific functionalities.

The field of NW fabrication has emerged in an effort to study them using various electronic and spectroscopic techniques. Indeed the fabrication process is a prerequisite for tailoring the optoelectronic properties of semiconductor NWs for devices as different techniques will induce several characteristic features that will affect how they behave. From morphology to chemical composition, even on the nanoscale regime, these small variations will drastically influence carrier properties and device performance. Therefore, NW growth with well-controlled dimensions, orientations, structures, phase purities and chemical composition is essential.

Due to their inherently small dimensions, NWs have a quasi-1D geometry. This introduces degrees of confinement and localisation of charge carriers thereby exhibiting special peculiarities. [47,48] Furthermore, the crystallographic phase of the material, such zinc-blende (ZB) or wurzite (WZ), will directly affect the bandstructure and electronic properties of the NW. This is due to the fact that combinations of atomic orbitals result in a multitude of eigenfunctions possessing different energy levels. Even more critical are

the crystallographic defects, such as stacking faults and twin planes, which will generate non-radiative recombination routes and trap states, leading to a reduction in carrier lifetimes and mobilities. [49,50] Therefore, achieving the desired phase purity is crucial when choosing the NW growth technique. [27,51,52] Finally, chemical composition and stoichiometry must also be considered, in order to produce intrinsic or doped NWs and achieve unique heterostructures that are essential for future NW-based devices. [53]

A plethora of approaches have been developed over time to grow nanowires [54] and they can broadly be classified into two categories: (1) top-down approach and (2) bottom-up approach. The top-down method begins with the bulk material and pattern the NWs into the material via a combination of lithographic and etching techniques. However, although previously dominating the microelectronics industry, these methods have been found to be resolution limited and expensive when scaling down for the emerging nanoelectronics industry. On nanoscale lengths, definition is lost and surface defects are abundant, which are detrimental to the NW optoelectronic properties. [55] In comparison, the bottom-up method chemically synthesises the NWs by combining constituent adatoms, allowing for increased control over NW growth. Atomically precise NW device structures can be fabricated [56] and hence bottom-up methods currently dominate the nanoelectronics industry. The nanowire samples used in this thesis have been grown by epitaxial metal-organic-chemical-vapour-deposition (MOCVD).

Epitaxial Growth. Epitaxy, coming from the Greek roots *Epi* meaning “above” and *Taxis* meaning “deposition in ordered manner”, refers to the method of the ordered growth of one crystalline film deposited onto a crystalline substrate. The crystal orientation planes and sizes are dependent on the growth substrate of choice. Epitaxial growth can be subdivided into two categories: (1) *homoepitaxy*, where the crystal is grown onto a like substrate; and (2) *heteroepitaxy*, where the crystal is grown onto a substrate of a different material. The potential for crystal growth is then determined by thermodynamics, where a chemical potential difference must exist between the precursors and the growth material. For growth to occur, a steady-state non-equilibrium condition is established by continuous replenishing of the precursor materials, to produce the thermodynamic driving force.

Epitaxial growth therefore depends on many factors, such as the concentrations of the precursors and crystalline materials and their temperatures. To be able to control the NW geometry and crystal structure during growth, the effects of these growth parameters must be understood. At present, there are two main epitaxial growth methods that are of interest for NW growth: template-directed and free-standing NW growth. Template-directed growth methods use a template, defined via lithographic techniques such as photolithography or electron beam lithography, to confine the crystal growth in one

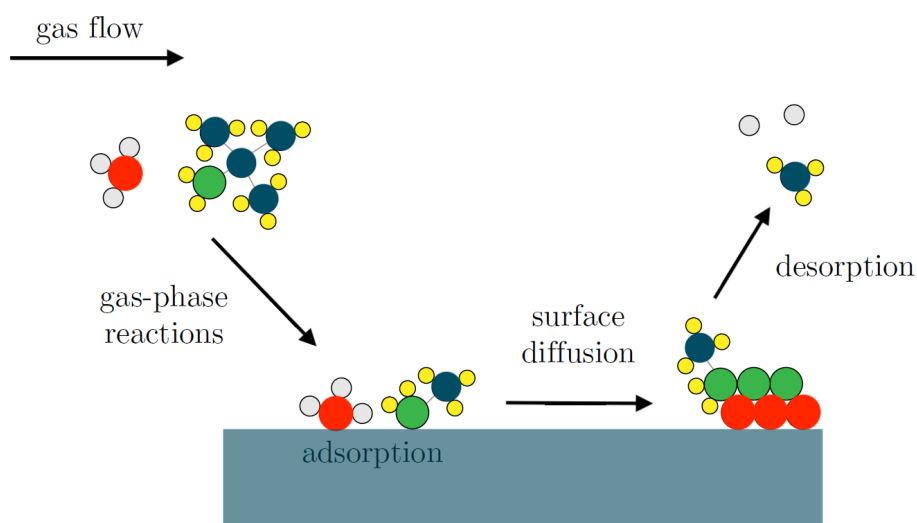


Figure 2.2: **MOCVD**: Schematic diagram showing the steps of the MOCVD process. Reproduced with permission from [58]

direction and produce a 1D geometry. [57] Free-standing NW growth mechanisms, in contrast to template-directed methods, rely on the anisotropy of growth rates to produce a 1D NW geometry.

2.1.1 Metal-Organic Chemical Vapour Deposition

Metal-organic Chemical Vapour Deposition or MOCVD is a technique for semiconductor growth using a chemical reaction of a metal-organic and vapour-phase precursors. This is in stark contrast to other methods that rely primarily on physical deposition. The whole process, illustrated in Figure 2.2, can be simplified into a number of smaller steps as follows:

1. Precursor molecules are heated to high temperatures and transported as a gas into a reaction chamber,
2. Chemical reaction of the precursors in the gas-phase,
3. Transport of reactants to the substrate surface,
4. Adsorption of reactants onto the substrate surface,
5. Diffusion along the surface towards nucleation sites,
6. Desorption of products alongside excess reagents.

In this process, the group III elements are added to the system as vapour phase organometallic precursors and the group V elements as vapour phase hydrides. A substrate of the same material is chosen to allow for homoepitaxial growth and gold

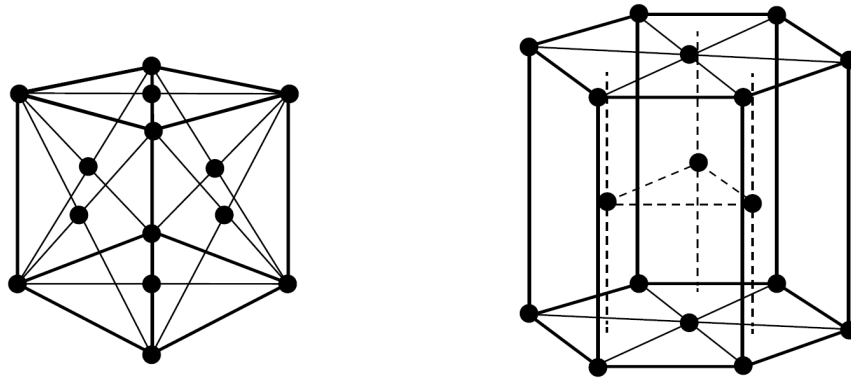
(Au) nanoparticles are deposited on the surface. Thereafter the substrate is heated and annealed to desorb any surface contaminants. At a certain growth temperature, the precursors decompose to release the group III and V elements, with which the Au nanoparticle forms a eutectic alloy. The Au nanoparticle acts to reduce the activation barrier and provide another pathway for the chemical reaction to take place, while not being consumed by the reaction, thus acting as a catalyst for growth. The liquid surface has a high accommodation coefficient and becomes a preferred deposition site for the precursors, promoting NW nucleation at the NW-substrate interface. With a constant supply of reactants, deposition continues at the nanoparticle-NW interface, with the nanoparticle driving the highly anisotropic NW growth, [59] as shown in Figure 2.2. The NW diameter is thus dictated by the nanoparticle diameter and the radial growth rate of the material. Accuracy in NW dimensions can therefore easily be obtained by tailoring the seed particle dimension, allowing NWs to be designed with well-defined length and diameter. NW arrays can also be grown onto substrates, depending only on the number of seed particles and substrate size, highlighting the potential for scaling this growth method for use in industry. [60]

Furthermore, for Au-assisted NW growth, there are two growth modes that can take place: axial growth, which refers to the Au-assisted elongation of the crystal structure; and radial growth, which refers to the lateral or conformal growth of the NW that does not directly involve the Au nanoparticle. The rate at which the growth proceeds is dependent on the temperature of the substrate, the pressure of the reaction chamber and the chemistry of the gas phase. A major consideration in MOCVD processes is that these precursors and the subsequent exhaust gases are often highly toxic. Other common growth techniques include vapour-liquid-solid growth, and molecular beam epitaxy.

2.1.2 Nanowire Morphology and Crystal Structure

Although the abovementioned growth methods are well-known, one factor that must be taken into account when growing nanowires is their crystal structure and morphology. Crystallographic defects and small variations in shape introduce grain boundaries, trap states and other forms of undesirable defects that can have a drastic effect on the NW electronic properties.

Solids are among the three basic states of matter that include liquids and gases. Most of the semiconductor materials studied in condensed matter physics are solids, characterized by a rigid structure of atoms, molecules or ions arranged in an orderly or non-orderly fashion. Using X-ray crystallography, these orderly or non-orderly arrangements have led to the categorization of solids as amorphous and crystalline structures. The nanowire



face-centred cubic

hexagonal close-packed

Figure 2.3: **Bravais Lattice:** In three-dimensional space, there are 14 Bravais lattices and 2 of the most relevant ones are shown in this diagram. Reproduced with permission from [58]

morphology belongs to the crystalline nature and the following section gives an overview of the various elements used to describe this particular structure.

Crystal Structure: In crystallography, any crystal structure can be described using a basis and a lattice, the former being attached to the latter. The lattice is a geometrical arrangement of points in vector space, each point having identical surroundings, whilst a basis represents atoms and their spacing. If one combines both of them, we get a crystal structure. Atoms come in different sizes and therefore to quantify their optimal arrangement, we would need a measure of how far they stand apart in a lattice. This spacing between individual lattice points is called the lattice constant. There are fourteen so-called Bravais lattices that represent all possible lattice arrangements, and the most common and relevant to this work are the face-centred cubic (fcc) and hexagonal close-packed (hcp) as shown in Figure 2.3.

The crystal structure a material adopts is the one that is the most thermodynamically favourable to achieve the lowest energy stability conformation, and therefore the one that has the closest packed atoms: an equilibrium compromise between strong repelling forces if they are too close together and weak attractive forces if they are too far apart. Accordingly, most bulk III-V semiconductor materials depending on the growth technique, including GaAs and InP, usually adopt a zinc blende (ZB) crystal structure which has a modified face-centred cubic lattice formed from two interpenetrating face-centred cubic lattices. Sometimes, they also form a modified hexagonal close-packed structure, known as wurtzite (WZ), as do III-nitrides semiconductors. This structure, which is more closely packed than zinc-blende, is achievable by III-V nitrides due to the nitrogen atom being considerably smaller than the atoms of other group V elements. Both ZB and WZ

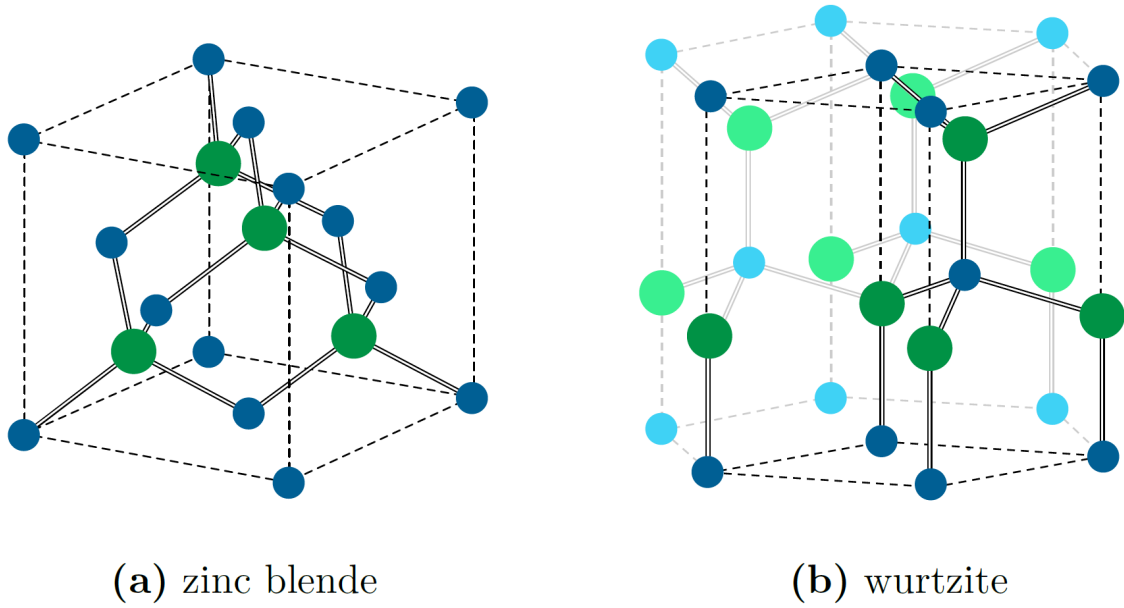


Figure 2.4: Crystal Structures: The two most important crystal structures for semiconductors. (a) Zincblende is characterized as a cubic closet packing (ccp), also known as face-centered cubic, structure. (b) Wurtzite has a hexagonal closest packing structure (hcp), which is characterized by 12 ions in the corners of each unit that create a hexagonal prism. Reproduced with permission from [58]

structures are shown in Figure 2.4.

Unfortunately, the optical and electronic properties of the same material either in wurtzite or zinc-blende structures will be different due to the different arrangement of atoms. Some directions and planes have a higher density of atoms and these dense planes have an influence on the behaviour of the material. This necessitates an understanding of the crystallographic planes defining the planes on which the atoms lie.

Crystallographic Planes and Miller Indices: The optoelectronic properties of semiconductors are anisotropic in that they are dependent on the direction through a crystal for which they are measured. This is most easily seen in THz detectors using electro-optic crystals such as gallium phosphide (GaP). The next two chapters deal with the fundamental concepts of this detector in great detail. It is therefore important to know the relevant directions or planes to consider when undertaking experiments.

Miller indices form a set of notations in crystallography for defining planes in crystal lattices. (hkl) is the Miller index of a plane, where the h , k and l components are integers that can be derived by finding the intercepts on the 3D lattice axes in terms of the lattice constants and taking their reciprocals. As an example, consider a plane running parallel to the k and l axes and intercepts the h -axis a distance of one lattice constant away from the origin (i.e., the plane $h = 1$), then the Miller index of the plane is (100) . Figure 2.5 gives

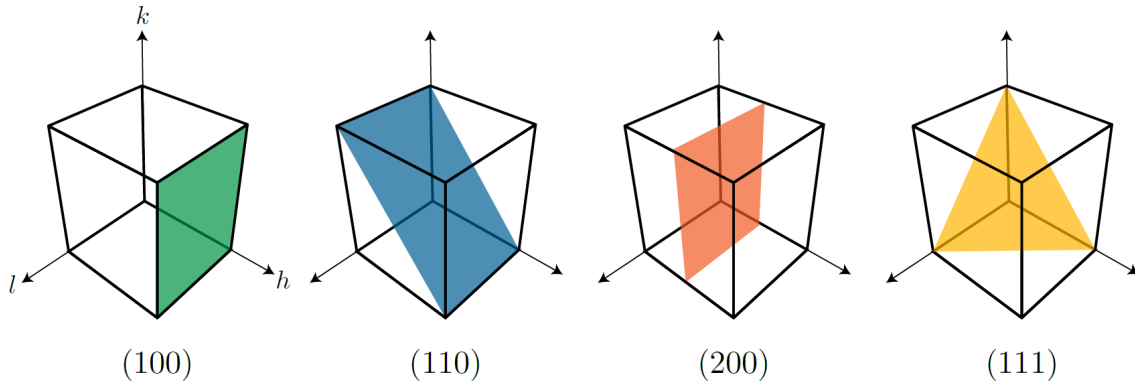


Figure 2.5: **Miller Indices:** Schematic diagram showing a few Miller indices used in crystallography. The indices are a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface. Reproduced with permission from [58]

some examples for several different planes. A bar above one of the numbers indicates a negative intercept. Using Miller indices for the hexagonal close-packed (and hence wurtzite) structure results in crystallographically-equivalent planes having different indices. To make this more apparent, it is useful to introduce a fourth axis and an accompanying four-index system ($hkil$), such that $h + k + i = 0$. These are known as the Miller-Bravais indices and is shown in Figure 2.6.

The distinct stacking of plane sequences results in the optical and electronic properties for ZB and WZ NWs to be different as indeed with different crystal structures comes different density of states and therefore different electronic band structures (explained in the next section). Therefore, to create the desired properties, the crystal structure must be well-controlled. III-V NWs have been successfully grown with both the ZB and WZ crystal phases: MOCVD-grown GaPs [61] and GaAs [62] have been shown to predominantly exhibit ZB structures, while MOCVD-grown InP [49] and MBE-grown GaAs NWs [63] normally exhibit WZ structures. Up till recently, the breadth of knowledge in nanowire growth has allowed the optimisation of growth parameters to precisely control ZB and WZ growth in III-V NWs, with the demonstration of pure-phase materials [26, 64, 65] and type-II QW systems based on ZB/WZ interfaces. [66, 67]

However, there are still challenges associated with crystal structure in NW growth, as planar defects, namely twin planes and stacking faults, are often created and catalyst-free, pure-phase NW growth, in particular, remains difficult. This variation in morphology has huge effects on the electronic properties of the NWs, as surface states are either created or destroyed. [68] Therefore, the growth parameters must be optimised to produce the necessary crystal structure and morphology with as few defects as possible for the desired NW application.

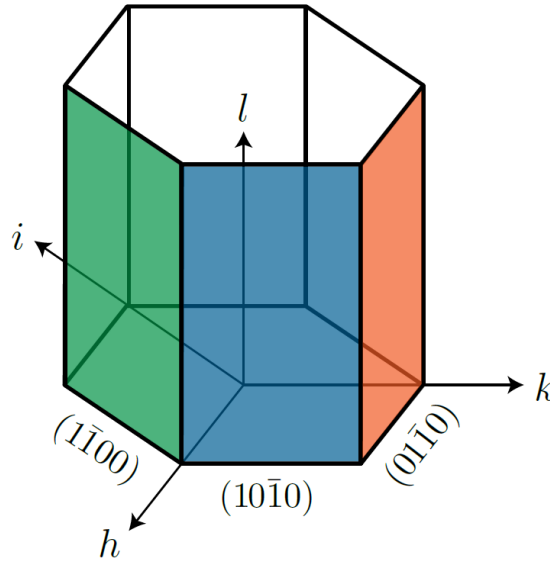


Figure 2.6: **Miller-Bravais Index:** Schematic diagram showing the Bravais-Miller index used to identify planes in a hexagonal structure. This is particularly useful as in 3D, as issues arise for hexagonal systems where some crystallographic equivalent directions will not have the same set of indices. Reproduced with permission from [58]

2.2 Electronic Structure Theory

In order to understand the optoelectronic properties of the NW semiconductors, it is imperative to be able to quantify the various energy levels of the interacting electrons in the material. In solid-state physics, the electronic band structure of a solid describes the range of energies an electron within the solid may have (called energy bands, allowed bands, or simply bands) and ranges of energy that it may not have (called band gaps or forbidden bands).

Band theory derives these bands and band gaps by examining the allowed quantum mechanical wave functions for an electron in a large, periodic lattice of atoms or molecules. Band theory has been successfully used to explain many physical properties of solids, such as electrical resistivity and optical absorption, and forms the foundation of the understanding of all solid-state devices (transistors, solar cells, etc.).

Quantum mechanics dictate that electrons orbiting individual atoms do so at discrete energy levels in orbitals. When these atoms are brought close together to form molecules, the electrons interact with each other. The linear combination of atomic orbitals and the Pauli exclusion principle which states that no two electrons can occupy the same energy level, the individual energy levels combine and split into a new set of energy levels. For an infinite number of atoms, these energy levels become so closely spaced that they can be described as continuous energy bands instead. This series of bands

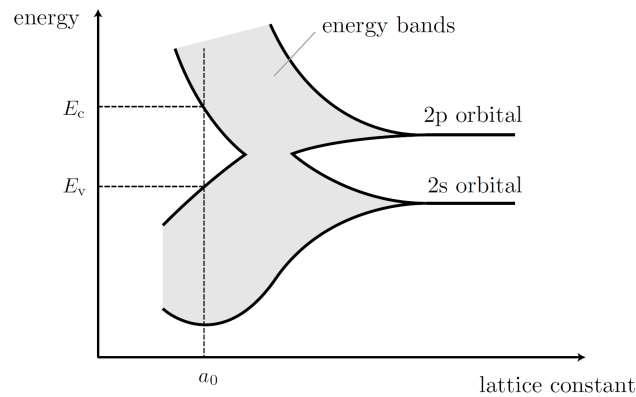


Figure 2.7: **Band Diagram:** Schematic diagram of the band diagram of diamond.

and their accompanying band gaps (forbidden energies) is termed the band structure. Figure 2.7 shows how the formation of these bands occurs as atoms are brought from very far apart to typical-crystal atomic spacing for the case of diamond. The electron filling of these bands is fundamental to a crystal's conductance. Bands that are partially full have higher energy levels available and hence electrons can gain energy and move in an applied electric field (i.e. they can conduct). Bands that are completely full have no higher energy levels available and therefore do not contribute to the conductance while bands that are empty do have available energy levels, but no electrons to fill them and hence they also do not contribute to the conductance.

Mind the Gap. The most important bands are the valence and conduction bands. The valence band is made up of the energy levels of valence electrons in the outermost atomic energy shells, the conduction band is the band that lies above this (at a higher energy) and the gap between them is the so-called band gap. In metals, these bands either overlap, or in the case of metals with only one valence electron per atom (e.g. copper), the valence band is only partially filled. In both cases, electrons can move freely and hence metals have a high conductance. In insulators, the band gap is too large such that a prohibitively large amount of energy is needed to move electrons from the valence to the conduction band. Semiconductors are an intermediate case; they have a band gap, but it is small enough that given some external energy (e.g. photon absorption or heating to room temperature), electrons can be promoted to the conduction band and they can conduct electricity. The differences in energy bands between metals, semiconductors and insulators is shown in Figure 2.8. The band gap value at which a semiconductor becomes an insulator is not strictly defined, but values between 1 and 3 eV seems to be a widely accepted range in the semiconductor community.

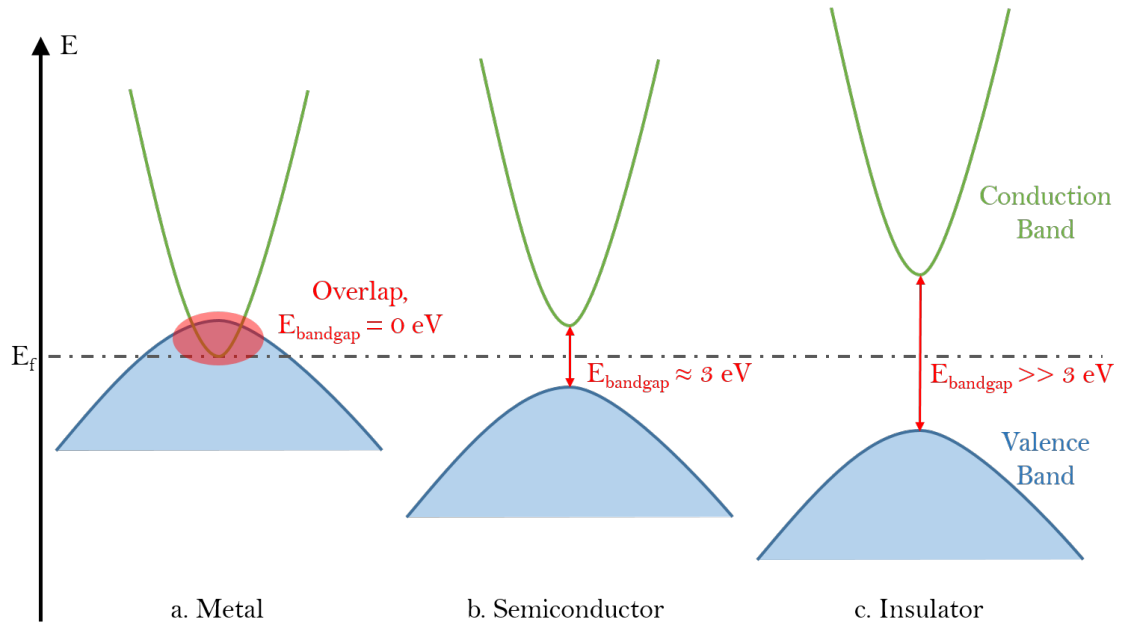


Figure 2.8: **Various Band Diagrams:** Schematic of the band diagrams for a metal, semiconductor and insulator. In metals, the conduction band and the valence band come very close to each other and may even overlap, with the Fermi energy (E_f) somewhere inside. This means that the metal always has electrons that can move freely and so can always carry current. Such electrons are known as free electrons. These free electrons are responsible for current that flows through a metal. In semiconductors and insulators, the valence band and conduction band are separated by a forbidden energy gap (E_g) of sufficient width, and the Fermi energy (E_f) is between the valence and conduction band. To get to the conduction band, the electron has to gain enough energy to jump the band gap. Once this is done, it can conduct. In semiconductors at room temperature, the band gap is smaller, there is enough thermal energy to allow electrons to jump the gap fairly easily and make the transitions in conduction band, given the semiconductor limited conductivity. At low temperature, no electron possesses sufficient energy to occupy the conduction band and thus no movement of charge is possible. At absolute zero, semiconductors are perfect insulators. The density of electrons in conduction band at room temperature is not as high as in metals, thus cannot conduct current as good as metal. The electrical conductivity of semiconductor is not as high as metal but also not as poor as electrical insulator.

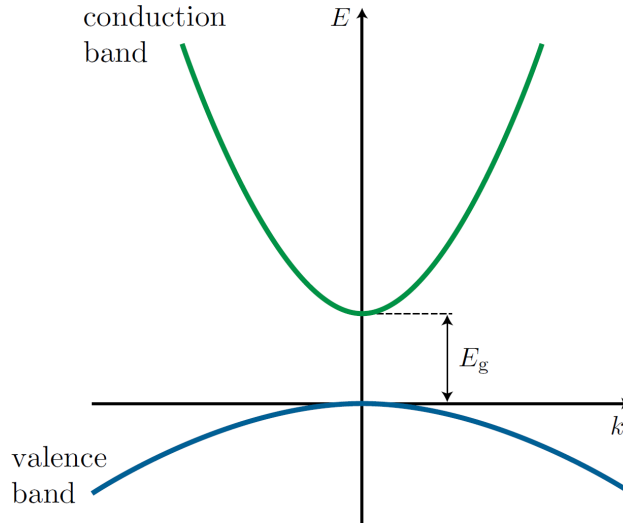


Figure 2.9: **Band Diagram 1:** A simplified diagram of the band structure of a semiconductor showing the band gap, E_g . Reproduced with permission from [58]

2.2.1 Band Structure in the Energy-Momentum Space

$E - \hat{k}$ diagrams are a common way to depict band structures of materials by exploiting the relation between the particle/molecule/atom energy E and its momentum $\hat{k}$. The $\hat{k}$ is the particle's wave vector and is related to carrier's momentum via the de Broglie's relation, $\mathbf{p} = \hbar\hat{k}$. These $E - \hat{k}$ diagrams demonstrate how energy states are distributed in momentum space which will be very useful when looking at the interaction with electromagnetic radiation. Figure 2.9 shows a simplified $E - \hat{k}$ diagram for a 1D momentum space with wave number $\hat{k}$. The diagram consists of two parabolas, the conduction band, and the valence band. The conduction band possesses a minimum while the valence band has a maximum at $\hat{k} = 0$. Around these extrema, the bands appear approximately parabolic, similar to the behaviour of free electrons, for which

$$E = \frac{\hbar^2 \mathbf{k}^2}{2m_0}, \quad (2.1)$$

where m_0 is the free electron rest mass with a value of 9.11×10^{-31} kg. The gap in between the parabolas appears as the $E - \hat{k}$ relationship needs to satisfy the Kronig-Penney mathematical model. Physically, this is due to the interference within the crystal lattice structures: constructive and destructive. The repetitive nature of the wave vector implies that one can concentrate mainly around $\hat{k} = 0$.

The curvature of the band is inversely proportional to the mass of the carrier. From the diagram, the conduction band has a lower curvature than the valence band due to the higher mass of the electrons compared to the holes. For electrons in semiconductors, the curvature of the bands near to the minima can be far higher than the free electron case,

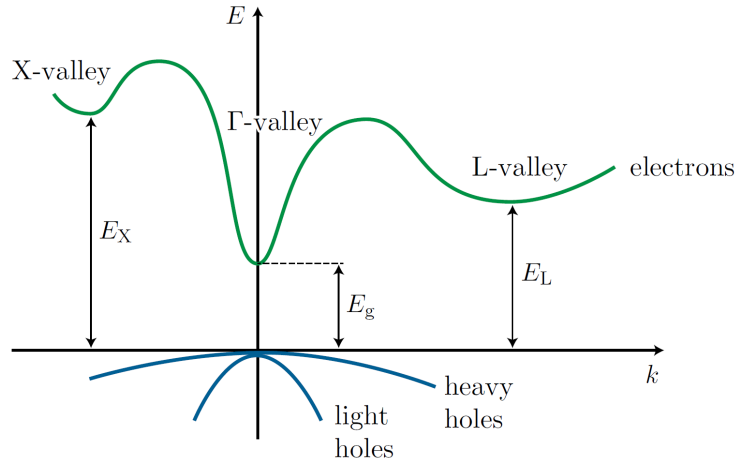


Figure 2.10: **Band Diagram 2:** A more realistic depiction the band structure of gallium arsenide with multiple valleys and parabolas. Reproduced with permission from [58]

and therefore it seems as though the semiconductor electron mass is much smaller than the free electron mass. This mass the semiconductor electrons appear to have is called the *effective mass* and we can use it to re-write Equation 2.1 for the conduction and valence bands in Figure 2.8:

$$\begin{aligned} E_c &= E_g + \frac{2\hbar^2 \mathbf{k}^2}{2m_e^*} \\ E_v &= -\frac{2\hbar^2 \mathbf{k}^2}{2m_h^*}, \end{aligned} \quad (2.2)$$

where m_e^* and m_h^* are the electron and hole effective mass respectively. In reality, it is not uncommon to find band diagrams being more complicated than the one shown above. Gallium arsenide has a band diagram as shown in Figure 2.10 where the valence band possesses two parabolas depicting the light holes and heavy holes. The conduction band has several minima but it is important to note that the band gap is always the difference between minimum energy of the conduction band and the highest energy of the valence band.

2.2.2 Fermi Level & Fermi-Dirac Distribution

The Fermi energy E_f is defined as the chemical potential at absolute zero temperature ($E_f = \mu(T = 0)$), i.e. the energy of a state which has a 50% probability of being occupied at absolute zero (0 K), and arises from the Fermi-Dirac statistics where electrons are Fermions. The Pauli exclusion principle states that Fermions cannot exist in identical energy states and therefore at absolute zero, they pack into the lowest available energy states and build up a "Fermi sea" of electron energy states. This chemical potential, sometimes called the Fermi level, is temperature-dependent and at higher temperatures,

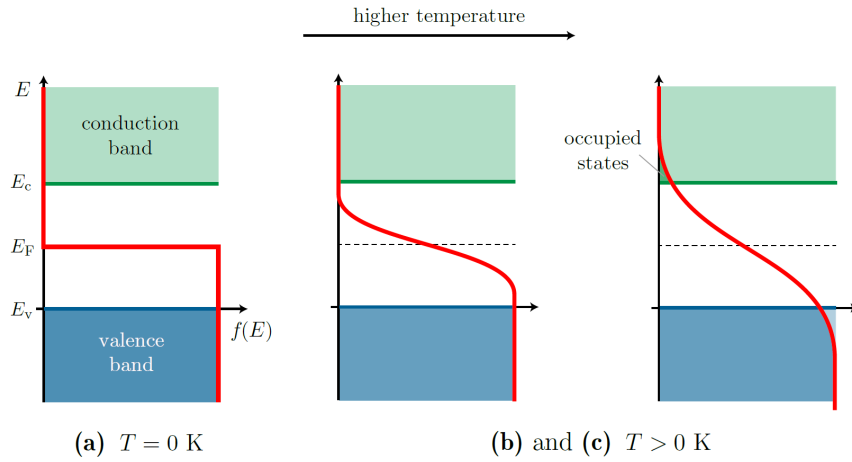


Figure 2.11: **Fermi-Dirac Distribution:** Schematic diagram showing the Fermi-Dirac distribution at various temperatures. Reproduced with permission from [58]

thermal excitation will cause higher energy states to be populated. In semiconductors (and insulators), the Fermi level lies within the band gap and is hence a hypothetical energy level that no electron can actually occupy. In metals, it sits within the conduction band, availing free electrons that contribute towards a high conductance.

The Fermi function or the Fermi-Dirac distribution $f(E)$, gives the probability that a Fermion will occupy an available energy state E_i at a given temperature:

$$f(E) = \frac{1}{\exp((E_i - E_F)/k_B T) + 1}. \quad (2.3)$$

At ordinary temperatures, most of the levels up to the Fermi level are filled, and relatively few electrons have energies above the Fermi level owing to their low thermal energies. The illustration in Figure 2.11 shows the implications of the Fermi function for the electrical conductivity of a semiconductor. As mentioned previously, semiconductors possess a sizeable bandgap, at around 3 eV, and the Fermi level sits right in between the two bands. At higher temperatures, the high thermal energy means that a larger fraction of the electrons can bridge this gap and participate in electrical conduction. Note that although the Fermi function has a finite value in the gap, there is no electron population at those energies (that's what you mean by a gap). The population depends upon the product of the Fermi function and the electron density of states. So in the gap there are no electrons because the density of states is zero. In the conduction band at 0 K, there are no electrons even though there are plenty of available states, but the Fermi function is zero. At high temperatures, both the density of states and the Fermi function have finite values in the conduction band, so there is a finite conducting population.

The actual population of electrons in the conduction band for a semiconductor is given

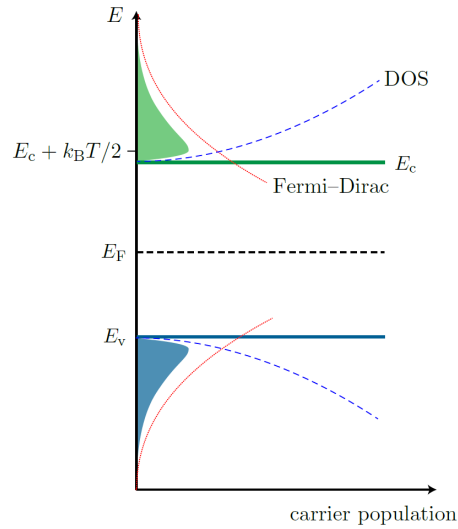


Figure 2.12: **Carrier Distribution:** Charge carrier distribution for electrons in the conduction band and holes in the valence band, green and blue regions respectively, at an elevated temperature. This is obtained by computing the product of the DOS represented by the blue dashed lines and the Fermi-Dirac distribution represented by the red lines. Equation 2.4 suggests that the largest number of carriers are concentrated at $\pm k_B T / 2$ from the band edges. Reproduced with permission from [58]

by the product of the Fermi-Dirac function and the density of states (DOS):

$$n = \int_{E_c}^{\infty} g_c(E) f(E) dE, \quad (2.4)$$

where $g_c(E)$ is the DOS defined as the number of energy states available per unit energy in the conduction band. Figure 2.12 shows the distribution of electrons in the valence and conduction bands in a bulk semiconductor at a finite temperature that is high enough that thermally-excited electrons have enough energy to populate conduction band states.

2.2.3 Light-Matter Interaction

The only way for carriers to be promoted from the valence band into the conduction band is through absorption of radiation. In doing so, an electron-hole plasma is created with energy higher than the bandgap (the concept of electrons and holes is touched upon later in this chapter). Initially, this immediate excited state is unstable (sometimes also referred to as a transition state) owing to its high energy and will relax back to the equilibrium state via charge-carrier recombination pathways imparting energy as this happens. This section gives a brief overview of the resulting processes that may happen in semiconductor materials, especially nanowires.

Direct & Indirect Bandgaps: Figure 2.13 depicts schematically both a direct (a) and an indirect (b) bandgap semiconductor. In (a), at $\hat{k} = 0$, there is a valence band maximum

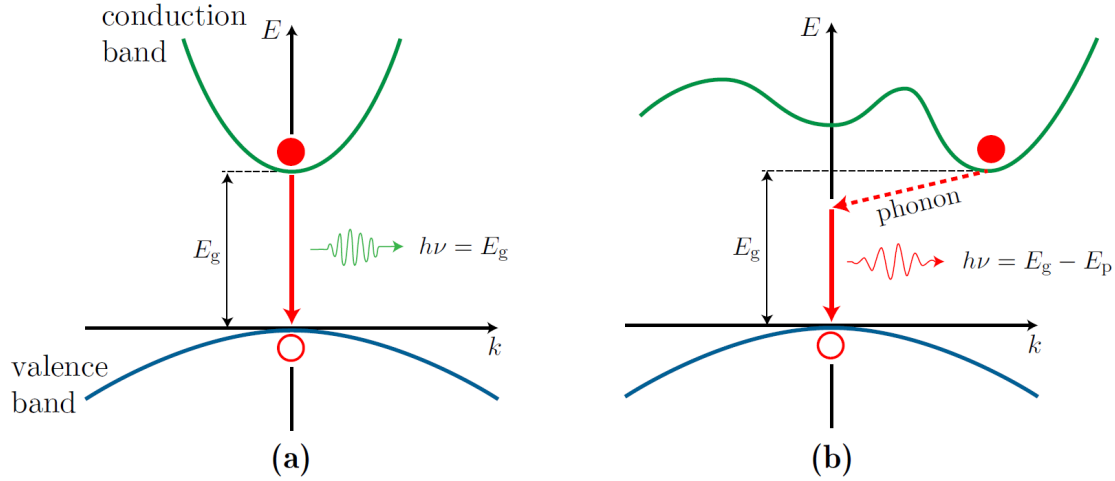


Figure 2.13: **Direct & Indirect Bandgap:** Schematic diagram depicting the $E - \hat{k}$ band diagram for a direct (a) and an indirect (b) bandgap semiconductor. Reproduced with permission from [58]

and a conduction band minimum. In this case, energy transition between the bottom of the conduction band and the top of the valence band happens “vertically” and does not require any momentum change along the $\hat{k}$ axis. A photon with energy $E = h\nu = E_g$ can photoexcite an electron from the top of the valence band to the bottom of the conduction band. As the electron relaxes back to the equilibrium state, it drops down from the bottom of the conduction band to the top of the valence band generating a photon with energy exactly equal to the band gap, $h\nu = E_g$.

In (b), the top of the valence band and the bottom of the conduction are not aligned at $\hat{k} = 0$. In this case, energy transition between the bottom of the conduction band and the top of the valence band requires a photon in addition to a lattice vibration, or ‘phonon’, to either gain or lose momentum for an absorption or emission event to take place. As this indirect process involves three quasiparticles, a photon, a phonon and an electron, recombination and emission usually occurs at a much slower rate in indirect bandgap materials. As such, in an indirect semiconductor, a photon with energy $E = h\nu = E_g$ cannot photoexcite an electron from the top of the valence band to the bottom of the conduction band, an extra momentum change is required for this transition. Indirect semiconductors such as silicon therefore cannot be used to make semiconductor lasers and LEDs.

Absorption, Relaxation & Recombination Dynamics: The key to unravelling the optoelectronic properties of semiconductors lies in quantum mechanics and photophysics. These processes occur by virtue of the quantisation of electromagnetic radiation, transferring their energy into the formation of electron-hole plasmas and the latter recombining

to give out energy. It should be noted that only specific amounts of energies can be absorbed by materials owing to this quantisation as illustrated in Figure 2.14.

For example, electron-hole separation will induce a photocurrent, whereas electron-hole recombination can lead to photon emission, or other niche effects such as photon re-absorption. As a result, the electronic properties of a material, such as the free charge carrier density and the carrier mobility, are determined by its electronic bandstructure whereas the optical properties, such as the carrier lifetime and the radiative efficiency, are determined by the type of free carrier and the optical bandgap of the material, i.e. the threshold for photons to be absorbed. These material properties must therefore be well understood, in order to control the electrical conductivity and optical properties of semiconductor NWs.

Recombination Processes are the processes by which electrons and holes annihilate each other. Electrons occupy the empty state associated with a hole, releasing the energy difference between the initial and final state of the electron. This annihilation can happen in either one step or via multiple steps, involving carrier cooling via phonons. The three main processes by which recombination occurs are: radiative, Shockley-Read-Hall and Auger recombination.

1. **Radiative** recombination occurs when the energy difference between the electron and hole is released as a photon resulting in light emission. Various mechanisms for radiative recombination exist, which all exhibit different associated lifetimes, depending on the number of interactions required for radiative recombination to occur.
2. **Shockley-Read-Hall** recombination, shown in Figure 2.15(a), occurs via mid-gap energy states, called traps due to impurities and crystal defects left behind from the growth process. These trap levels constitute of either ‘deep’ donor defect levels that lie far away from the band edge deep within the forbidden band or ‘shallow’ ‘hydrogenic’ defect states that lie close to the conduction band edge. An electron can become trapped by these mid-gap states and a hole moves up from the valence band to recombine with the electron.
3. **Auger** recombination, shown in Figure 2.15(b), is the recombination of an electron in the conduction band with a hole in the valence band (or, the recombination of an exciton) with the subsequent transfer of the energy lost to a third charge carrier, promoting that to a higher energy level. For example, the third carrier may be an electron which is promoted to a higher-energy conduction band state, or it may

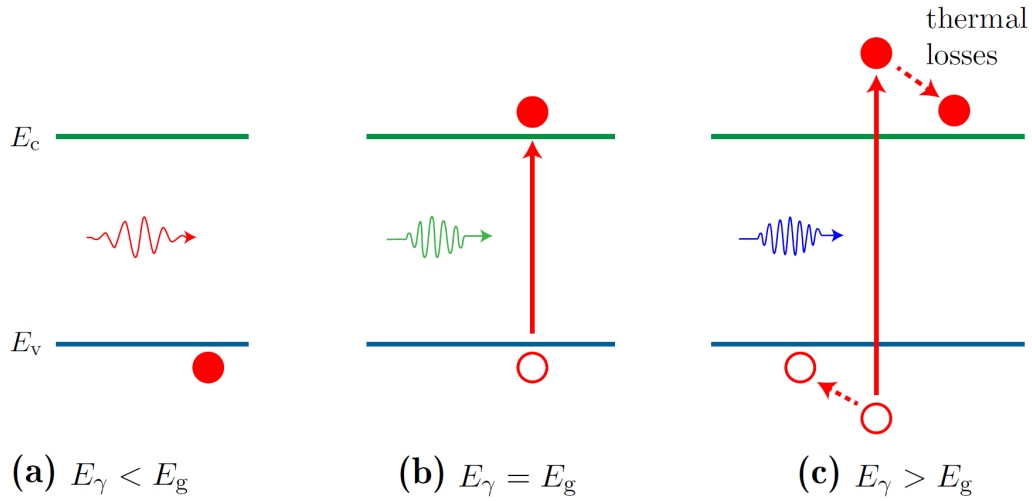


Figure 2.14: Excitation via Photon Absorption: In (a) $E_\gamma < E_g$, photons with energy less than the band gap only interact weakly with the semiconductor and most will pass straight through. In (b) $E_\gamma = E_g$, The ideal case is photons having the same energy as the band gap, in which case they are absorbed without the loss of any excess energy. In (c) $E_\gamma > E_g$, Photons with energy greater than the band gap can be absorbed (depending on the thickness of the semiconductor), but any energy above the band gap is wasted as conduction electrons quickly thermalise to the band edge. Reproduced with permission from [58]

be a hole with some non-zero $\hat{k}$ -value that is promoted from the heavy hole to the light hole band.

Charge Carriers & Quasiparticles:

1. **Electrons and Holes:** As mentioned above, electrons can be made mobile by photoexciting them into the conduction band or via selective doping which intrinsically fill the conduction band partially. In doing so, the conductivity can be increased by over an order of magnitude. For the case of photoexcitation, the excited electron leaves behind a vacancy or 'gap' state in the valence band, which can also become

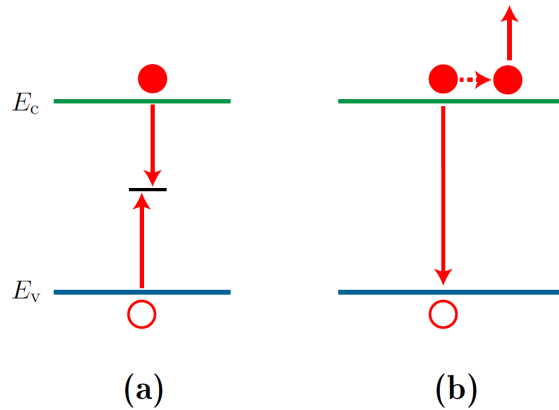


Figure 2.15: Recombination: Schematic diagram indicating recombination mechanisms, (a) Shockley-Read-Hall, and (b) Auger. Reproduced with permission from [58]

mobile. This 'gap' state acts like a positively charged electron, forming a quasiparticle, which is referred to as a 'hole'. These mobile holes can also contribute to the material's conductivity and are of great importance for use in electronic devices, particularly transistors. It is important to note that just above or below the bandgap, these mobile electrons and holes no longer behave as in a vacuum, as the electron or hole wavefunction experiences interference due to its interaction with the periodic crystal potential. To address this, an effective mass is introduced, which describes the mass that an electron or hole appears to have when moving through a crystal. The size of this effective mass has a direct effect on the mobility of the particle through the material. For example, for holes heavier than electrons, the former move more slowly through the material and thereby possess a lower mobility. The electron and hole effective masses also vary from material to material, as they are purely dependent on the crystal structure and band structure. This leads to an inherent difference in mobilities for different semiconducting materials, with a limit placed on the mobility dependent on the material's crystal structure.

2. **Plasmons:** Plasmons are quasiparticles that arise from the quantisation of collective oscillations of the free electron density with respect to fixed positive ions in a material. Plasmons can be either of two types: surface plasmons or bulk plasmons depending on where the oscillations occur. The best way to visualise plasmons is when an electric field is applied to a material such as a metal. The mobile electrons respond to the electric field, and will move in the direction opposite to the electric field, cancelling out the field and exposing positive ions on one side of the material. If the electric field is an oscillating one, at some point in time, it will be instantaneously zero and at that point the electrons are repelled by each other and attracted to the positive ions, causing them to change direction. Having an inertia, the electrons will overshoot their equilibrium position and move in the other direction and back again to the other side and so on and so forth. The frequency at which the electrons oscillate is labelled the plasma frequency, ω_p . The value of this plasma frequency determines whether light is either transmitted or reflected through the material. If the incident light possesses a frequency lower than the plasma frequency, the electrons screen the electric field of the light and it is reflected; whereas if the incident light has a frequency greater than the plasma frequency, the electrons cannot respond fast enough to screen the light's electric field and it is transmitted. Therefore, a material's optical properties are determined by its plasma frequency.

3. **Phonons:** Like plasmons, phonons are quasiparticles. The only difference is that while plasmons are collective oscillations of the free electron densities in the lattice, phonons are the oscillations of the lattice itself arising from the quantisation of the lattice's mechanical vibrations and is therefore crystal structure-dependent. They are easily visualised as atoms/ions connected via springs. When energy is supplied to a material, the displacement of atoms about their equilibrium positions produces lattice waves within the crystal, for which the wave amplitude is equal to the magnitude of the displacement. In 3D, when the unit cell contains more than one atom, the crystal will contain two types of phonons: acoustic and optical both containing transverse and longitudinal modes as illustrated in Figure 2.16. In the optical mode, two adjacent atoms move in the opposite direction to each other, whereas in the acoustic mode, they move together. Mobile charge carriers can interact or 'scatter' off these phonon modes, causing a drastic change in their optoelectronic properties. For instance, as we will see later in this thesis, crystals such as gallium phosphide (GaP) are used as terahertz detectors. GaP contains a phonon mode at around 8 THz and therefore the amplitude spectrum contains a dip at this frequency causing signal beyond 8 THz to be unreliable. Hence, probing the various types of phonon scattering in semiconductor crystals is an important task for determining the limiting factors on carrier mobility as will also be explained in later chapters of this thesis. In particular, optical phonons are of interest, as they are the dominant scatterers in III-V semiconducting NWs at room temperature. As optical phonons require out-of-phase movement, they are usually promoted by either infrared radiation or Raman scattering, so THz spectroscopy is ideal for probing the dynamics of these phonon types.
4. **Polarons:** Another type of quasiparticle is the polaron which is sometimes referred to as 'self-trapped electrons.' They are predominantly found in polarisable semiconductors where the charges are important or even conjugated polymers where torsional modes play a key role in the liquid state. In the former case, the atoms retain a partial ionic positive or negative charge, so that mobile negatively charged electrons or positively charged holes can interact with the crystal lattice via repulsive or attractive Coulomb interactions to induce a polarisation within the lattice. The electron or hole can then couple with its self-induced polarisation in the lattice to form a quasiparticle, known as the 'polaron'. In the latter case, as an electron propagates along a conjugated polymer backbone, the torsional modes induced by Brownian motion of the surrounding will cause the wavefunction to localise at particular sites, distorting the energy landscape around it. Polaron size depends very much on the coupling strength: for weak coupling, large polarons

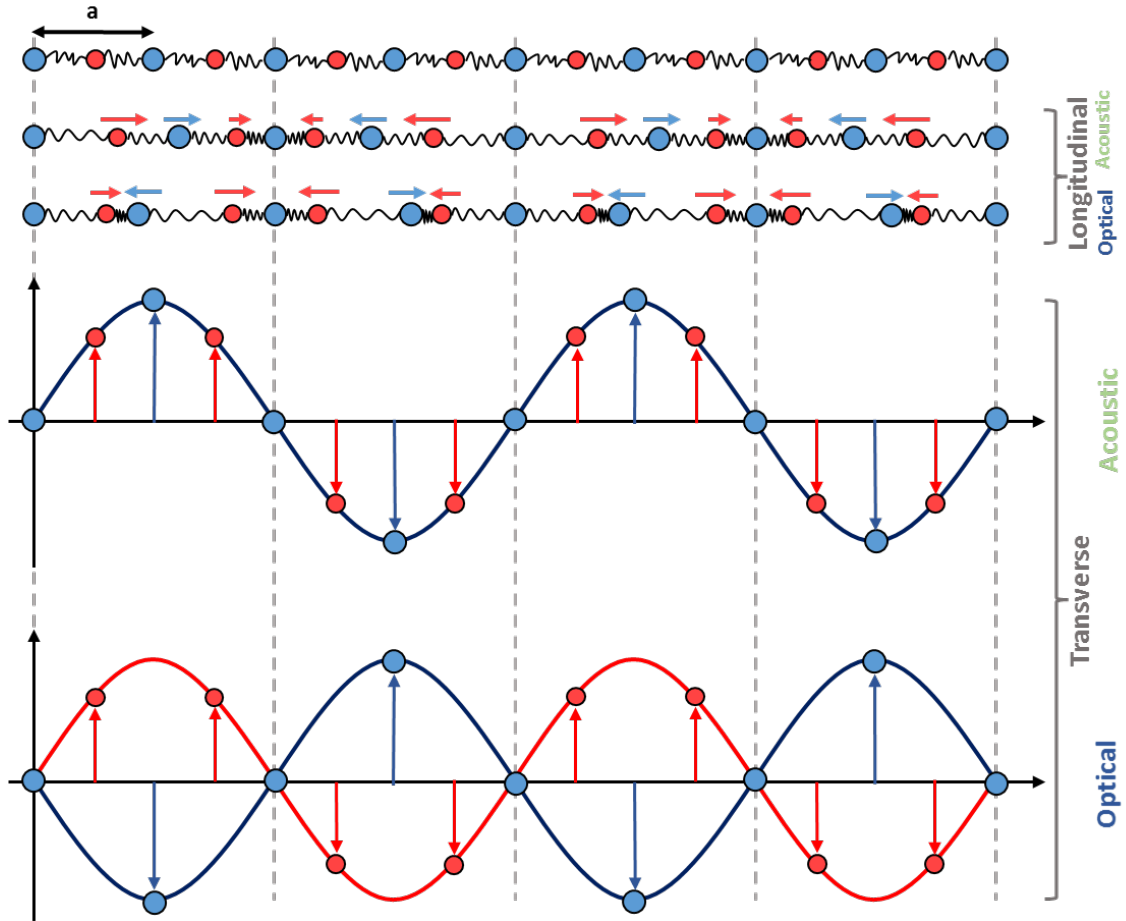


Figure 2.16: **Acoustic & Optical Phonons:** Cartoon illustration for the two types of phonon modes. Both are present as longitudinal and transverse waves. For the acoustic branch, the two types of atoms (here represented by two distinct colours) oscillate in phase, effectively “riding” the same wave. This is the same pattern that a sound wave in a fluid medium would follow. as for the optical branch, the two types of atoms oscillate with opposite phase. If the two types of atoms have opposite charges as well as different masses, the wave causes a charge separation because the positive charges are always displaced in the opposite direction to the negative charges. This is the kind of wave which can be excited using electromagnetic radiation, hence the name optical branch.

with spatially extended wavefunctions are formed. In this case, electrons draw in the lattice, creating polarons with an effective mass greater than the band mass and for strong coupling, small polarons are formed that cause self-trapping of electrons within the potential well formed by the lattice deformation. In this case, charge transport only occurs via tunnelling or hopping between lattice sites and small polarons contribute to very low material conductivities, reducing device mobility in highly polarisable ionic materials due to polaron formation. Polar semiconductors such as GaAs and other III-V compounds, possess large polarons due to what is called the Frolich interaction. This happens due to the LO phonons, producing a macroscopic electric field which in turn strongly interacts with the electrons. [69]

5. **Excitons:** Excitons are “collective excitations” - usually an entity consisting of an electron coupled to a hole - that emerge predominantly in non-metallic systems. The electrostatic forces due to the particles cancel out and as such an exciton is considered as an electrically neutral quantum of electronic excitation energy, travelling in the periodic structure of a crystal. It can essentially be viewed as a bound electron-hole pair that involves the transport of energy, but not of a net charge and hence no net current flows. As the exciton arises just in the presence of both the electron and the hole, its existence is generally related to the absorption of a light field at a given frequency. Single-particle optical transitions are different in nature, in which only one single particle state gets excited by the incident light field and all the other states do not participate. On the other hand, the excitonic transition is a “collective” one, which involves many states of the electronic band structure. In effect, the electron-hole pair forms its own hydrogenic energy levels in the excited materials. For materials possessing a low dielectric constant, the exciton binding energy is stronger, for example in most organic semiconductors. They are stable as long as the binding energy is higher than the thermal energy.

Depending on the value of the binding energy and the spread of the wavefunction in the lattice, excitons in condensed matter can be classified under two generic types, Figure 2.17: Frenkel excitons where the exciton is small and tightly bound; and Mott-Wannier excitons, which are lightly bound and have an electron-hole separation greater than the lattice constant. Mott-Wannier excitons are usually created in polarisable lattices with high dielectric functions, as the electron-hole attraction is screened and exciton binding energies are typically less than 0.1 eV. The electron-hole is delocalized over several unit cells and therefore the effect of the lattice potential creates a low exciton effective mass. In contrast, Frenkel excitons form in materials which are not so easily polarised and therefore possess low

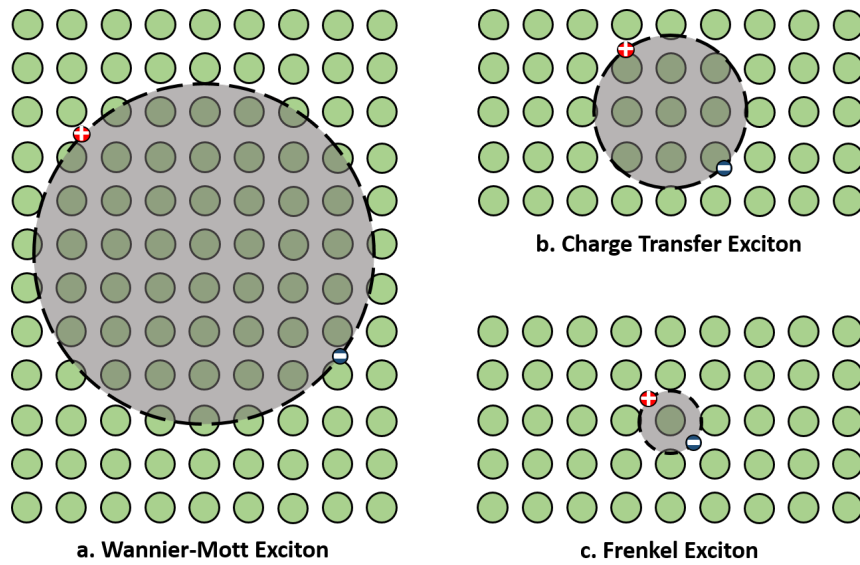


Figure 2.17: **Exciton types:** Cartoon illustration for three different types of excitons. (a) Wannier-Mott excitons represent hydrogenic electron-hole pairs delocalized over several unit cells of the lattice and arise in semiconductors with high dielectric constant. (c) The other extreme is represented by Frenkel excitons, which correspond to a correlated electron-hole pair localized on a single lattice site and mostly prevail in solid rare gases and molecular solids. (b) Intermediate between these two regimes is a number of exotic excitations that are typically called charge-transfer excitons.

dielectric values. [70] The small size separation, usually on the order of interatomic spacing, means a high exciton binding energy and for these strongly bound excitons, discrete energy levels with large energy level spacings are observed. As the electron-hole separation increases due to the decreasing coupling, the excitons become more weakly bound, with the energy level structure becoming more dense. At this stage they behave as free carriers and the energy level density increases recovering the band structure one would normally see. Excitonic materials are particularly desirable for optical devices and solar cells, as the energy threshold for photon absorption is lowered by the exciton binding energy. Their strong electron-hole correlation also leads to a high radiative recombination probability, with electrons dropping into their corresponding hole to recombine. This produces a strong luminescence yield, which is desirable for optical displays and LEDs. On the other hand excitonic materials are less desirable for electronic devices, as even though excitons can move freely through the crystal and effectively transport energy, they are electrically neutral and do not contribute to the DC conductivity. Nonetheless, when the bandgap is indirect, excitons near the direct gap are unstable and can easily decay into free electrons and holes and thereby contribute to the conductivity. [24]

2.3 Nanowires: A Brief Literature Review

The main III-V elements used to grow the nanowires used in this thesis are gallium (Ga), arsenic (As), indium (In), and phosphorus (P). We therefore give a brief overview of the work that has been done so far on gallium arsenide (GaAs) and indium phosphide (InP) nanowires, although the list is not an exhaustive one.

2.3.1 GaAs Nanowires

III-V semiconductor NWs have been at the forefront on most research pertaining to semiconductor materials. GaAs has been of particular interest due to its direct bandgap, low Auger recombination rate, high absorption coefficient, picosecond carrier lifetime and high electron mobility. Over the course of the years, fabrication methods have been improved and the growth of nanostructures is very well controlled. GaAs NWs have been grown to high quality via either MBE or MOVCD using gold nanoparticle catalysts and provide an easy, scalable alternative to current semiconductor technology that uses bulk GaAs for carrier transport. More importantly, it has now been possible to interface the nanowire with other materials creating novel structures known as core-shell NWs. [27,28,71–74]

GaAs NWs have been highly investigated using THz spectroscopy. In 2013, Joyce *et al.* [14] studied the photoconductivity via OPTP spectroscopy on MOVCD grown GaAs NWs with an average diameter of 50 nm. The photoconductivity spectra displayed a strong plasmonic response with the plasmon resonance exhibiting a red-shift with decreasing photoexcitation fluence and electron density, as previously predicted for localised surface plasmon (LSP) modes. This study allowed for NW surface states to be determined, a key factor in tailoring the NW for device fabrication and performance.

To further investigate the optoelectronics of GaAs, the Lorentzian plasmon model, described in the next chapter, was fitted to the photoconductivity spectra. The electron mobility extracted was a factor of 6 lower than bulk GaAs and the reduction was attributed to electron scattering at the NW surface due to surface defects. The photoconductivity decay traces were also measured for these GaAs NWs, displaying a very short photoconductivity lifetime of less than 10 ps due to rapid charge trapping at the NW surface, [75] and this proved to be very useful when it comes to devices requiring fast switching speeds as has been demonstrated in 2016. [76–78] Joyce *et al.* went on to study the effect of NW diameter on photocarrier lifetime. By comparing the photoconductivity decays of bare GaAs NWs with varying diameters, the surface recombination velocity was determined to be extremely high at $5.4 \times 10^5 \text{ cm s}^{-1}$. The photoconductivity featured

a monoexponential decay behaviour with the carrier lifetime decreasing with decreasing diameters. This was attributed to the effect of the higher the surface area-to-volume ratio, which allows for saturable carrier trapping at the NW surface. [14]

Furthermore, investigations into the surface passivation of GaAs NWs have also been carried out, [79] with numerous experiments on the effect of overcoating of GaAs NWs with AlGaAs shells. Various mobilities were obtained which indicated that there was a reduction in the surface-related scattering. This also pointed to the fact that the carrier lifetimes of the passivated layers increased in addition to increasing the fluence of the photoexcitation pulse. [79] Further studies have shown that through the optimisation of the AlGaAs shell growth conditions and thickness, the surface-related scattering can be reduced to optimise the electron mobility to reach up to 3000, comparable with bulk values. [31] This increase in mobility is consistent with an increase in photoconductivity lifetime of up to 1.6 ns with the thickest AlGaAs shells. [14,30,32,33,75]

Boland *et al.* went even further to investigate the effects of dopants in GaAs NWs. Both n - and p - type doping were studied revealing lower carrier mobilities than undoped ones. However, there was an increase in the carrier lifetime demonstrating a strong suppression of non-radiative surface and defect-mediated recombination. p - type doping also showed an ultrafast decay within the first 25 ps after photoexcitation which was a result of band bending. [33] All these effects offered great insights into the optoelectronic properties of GaAs which have been key to using them in many devices such as lasers and solar cells.

2.3.2 InP Nanowires

Besides GaAs, another III-V material that has attracted a lot of attention is InP. They have been extensively studied, owing to their very long carrier lifetimes. High quality MOCVD-grown InP NWs with the wurtzite crystal structure can now be grown successfully. Similar to the above-mentioned GaAs diameter dependence, the InP samples were analysed using an OPTP system. The carrier decays exhibited long lifetimes of over 1 ns and were independent of the NW diameter, suggesting that the lifetime is predominately dominated by trapping at planar crystallographic defects rather than at the NW surface. Through fitting of the lifetimes for different average diameters, a low surface recombination velocity of 170 cm s^{-1} was determined. Its low value was attributed to the spatial separation of electrons and holes, which prevents carrier recombination and leads to a much longer lived photoconductivity lifetime. [14,79]

Photoconductivity spectra were also measured for all InP NWs with a similar Lorentzian response observed as for InAs and GaAs NWs. By fitting a plasmon model to the spectra

for all NWs, an unintentional n -type doping of $(10 \pm 3) \times 10^{15} \text{cm}^{-3}$ was determined and electron mobilities between 120 and 660 extracted. The mobility was also found to be independent of NW diameter, thereby suggesting the dominant scattering mechanism for these NWs to be scattering from ZB-WZ boundaries rather than from the surface. [29]

Ponseca *et al.* in 2014 [80] investigated p-doped InP NWs. Recently NW-based tandem solar cells have been shown to have reasonable efficiency and therefore doped InP NWs have also been investigated owing to their long carrier lifetime, a p-n junction must be created within the NW. More specifically, periodic arrays of heavily n-type doped InP NWs embedded in a PDMS polymer matrix have been examined. These NWs were grown via Au-seeded MOVPE and the transverse conductivity measured via OPTP with the NW axis aligned parallel to the THz wave propagation direction and perpendicular to the polarisation of the THz field. Photoconductivity spectra were measured at 10 ps after photoexcitation and fitted with a Monte Carlo model to account for electron localisation and heavy doping. A long scattering time of 150 fs and a transverse electron mobility of over $3000 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, significantly higher than those measured for the longitudinal mode, as electrons are unaffected by stacking faults in the growth direction. [80]

Additionally, novel photoconductive antenna based on single nanowire for THz detection has been demonstrated using InP as the active element. The high material quality, coupled with the relatively short carrier lifetime and high mobility made the material very attractive. This has facilitated the design and fabrication of yet another novel device based on two orthogonal InP NWs for polarization-resolved THz detection. [81–84]

2.4 Conclusion

In summary, semiconductor NWs have been in the limelight for quite some time and THz spectroscopy measurements have revealed some of the fundamentals of their optoelectronic properties. NW growth has been optimised for best results with varying degrees of doping, defects, lengths, thicknesses and heterostructures. The carrier mobilities and lifetimes are important for tailoring their use in devices and this thesis looks at incorporating III-V NWs as polarisation modulation of THz radiation. Furthermore, as THz technology continues to amplify, the need for nanoscale THz-active components are becoming crucial and we hope that through the various studies done, it will be possible to make this a reality.

Table 2.1: Photoconductivity lifetimes (τ) and surface recombination velocities (S) measured via OPTP. '-' labels unreported values. [24]

NW	Diameter (nm)	Fabrication Method	τ (ps)	S (cm s^{-1})	Ref.
ZnO	100-200	Chemical Bath Deposition	$\tau_1 = 160$ $\tau_2 = 5600$	-	[85]
Ge	80	Au-catalysed, CVD	75-125	-	[86]
Si	30	Au-catalysed, CVD, annealed and etched	-	1700	[87]
Si	90	Au-catalysed, CVD, annealed	-	1800	[87]
Si	90	Au-catalysed, CVD	-	1100	[87]
Si	(110 $\pm$ 60)	Au-catalysed, CVD	$\tau_1 = 2 - 4$ $\tau_2 = 4 - 10$	-	[88]
n-Si	(90 $\pm$ 40)	Au-catalysed, CVD	$\tau_1 = 0.6 - 1.4$ $\tau_2 = 16 - 37$	-	[88]
InAs	27		200		
	45	Au-catalysed, MOVPE	290	3×10^3	[14]
	95		470		
	195		660		
InP	50		1180		
	85	Au-catalysed, MOVPE	1270	170	[14, 29]
	135		1300		
	160		1340		
GaAs	30	Au-catalysed, MOVPE	1.3		
	50	Au-catalysed, MOVPE	2.4	5.4×10^5	[31, 89]
	80	Au-catalysed, MOVPE	1.3		
GaAs/AlGaAs	50 nm core	Au-catalysed, MOVPE	5-1600	-	[14, 75]
n-GaAs	105		(3800 $\pm$ 100)	-	
p-GaAs	110	MBE	(2500 $\pm$ 20)	-	[33]
GaAs	115		130	-	
GaN	310	PAMBE	(2500 $\pm$ 500)	-	[90]

Table 2.2: Charge carrier scattering times, γ^{-1} , mobilities, μ , and equilibrium electron concentrations, N_{eq} in NWs measured by THz-TDS and OPTP spectroscopy with the model used for data analysis displayed. A symbol ‘-’ indicates values that are unreported. [24]

NW	Diameter (nm)	Technique	γ^{-1} (fs)	μ ()	N_{eq} (cm ⁻³)	Model	Ref.
ZnO	100-200	THz-TDS	28	16	19×10^{17}	Drude-Smith	
ZnO	100-200	OPTP	84	138	-	Drude-Smith	[85]
ZnO annealed	100-200	OPTP	88	189	-	Drude-Smith	
SnO ₂	50-100	OPTP	(75 ± 7)	(72 ± 10)	3.3×10^{16}	Drude-Smith	[91]
SnO ₂	100	THz-TDS	50	20	8×10^{16}	Drude-Smith	[92]
InSnO	50-100	THz-TDS	60-69	2-26	7×10^{19}	Drude-Smith	[93]
Ge	80	OPTP	(70 ± 15)	1590	-	Plasmon	[86]
Si annealed	30	OPTP	-	(60 ± 0.5)	-	Drude-Smith	
Si annealed	90	OPTP	-	(38 ± 0.4)	-	Drude-Smith	[87]
Si	90	OPTP	-	(13 ± 0.2)	-	Drude-Smith	
p-Si	90	THz-TDS	23.6-113.9	-	-	Drude-Smith	[94]
Si	(110 ± 60)	OPTP	(28 ± 6)	(190 ± 40)	-	Plasmon	[88]
n-Si	(90 ± 40)	OPTP	(14 ± 4)	(95 ± 25)	5×10^{17}	Plasmon	
GaAs	50	OPTP	(38 ± 4)	(1000 ± 100)	$\leq 10^{15}$	Plasmon	[14,75]
GaAs/AlGaAs	50 nm core	OPTP	46-115	1200-3000	-	Plasmon	[30,32]
InAs	45	OPTP	(75 ± 12)	(6000 ± 1000)	5×10^{15}	Plasmon	[14]
InAs	-	OPTP	22-71	-	-	Plasmon	[95]
InP	50	OPTP	(32 ± 5)	(700 ± 100)	10×10^{15}	Plasmon	
InP	85	OPTP	5.5	120	-	Plasmon	[14,29]
InP	135	OPTP	10	220	-	Plasmon	
InP	160	OPTP	22	480	-	Plasmon	
n-InP	150	OPTP	≥ 150	≥ 3000	-	Monte Carlo	[80]
GaN	310	OPTP	-	(820 ± 120)	-	Plasmon	[90]
InN	130	THz-TDS	(1.3 ± 0.2)	(80 ± 5)	5×10^{19}	Drude-Smith	[96]

TERAHERTZ SPECTROSCOPY

ULTRAFAST laser spectroscopy is a non-linear optical spectroscopic technique that uses ultrashort amplified laser pulses for the study of dynamics on extremely short time scales (attosecond (10^{-18} s) to picosecond (10^{-12} s)). Over the course of time, many different methods have been developed spanning different time scales and photon energy ranges and they have all been used to examine dynamics of charge carriers, atoms and molecules. Some of the current known methods include: (1) photoluminescence, (2) VIS pump - IR probe, and (3) VIS pump - THz probe among others. Our focus for this thesis will be centered around *terahertz spectroscopy*, and this chapter will try to capture the essence of this technique and its superiority over other conventional methods used to study semiconductors.

3.1 Introduction

Historically, THz spectroscopy grew out of efforts to generate and detect ultrashort electrical transients as they propagated down a transmission line. The breakthrough was done by research groups led by Dan Grischkowsky, David Auston, and Martin Nuss and since then they became very active in this area. Maxwell's equations dictate that a time-varying electric current should radiate an electromagnetic (EM) pulse. Therefore, it became evident that these transmission lines should be radiating short bursts of EM radiation. In 1988/1989 a major shift in research happened when reports were being published wherein these radiated pulses were propagated in free space from a generator to a detector. [3,97] At this point, one could now envision using these elements in a way

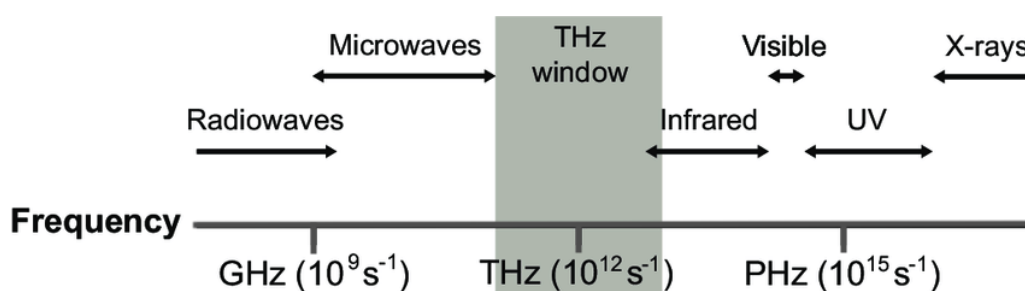


Figure 3.1: **Electromagnetic Spectrum:** from radio waves to X-rays. The THz region is shown in shaded grey. Typical energy regions for molecular rotations and vibrations, intraband electronic motion, and interband transitions are also shown. Adapted from [118]

to study materials in transmission mode. As a far-IR light source and detector pair, one could additionally place a sample between the two of them and with the correct tools, one would be able to analyse the data. THz spectroscopy was born. Since its inception, THz spectroscopy has been widely used in a plethora of fields with topics spanning gas-phase spectroscopy, [98–101] THz and 3D imaging, [102–106] solid state physics (optoelectronic properties of materials), [107–114], and biological media. [14, 29, 115–117] THz technology/spectroscopy exploits various nonlinear optical techniques such as difference-frequency generation (or more commonly known as optical rectification) and the Pockels effect amongst others.

Moreover, in the past few years, advances in intense ultrafast lasers coupled with strong nonlinear optics have made it possible to produce intense single-cycle (half-cycle) THz pulses with peak field amplitudes on the order of megavolts per metre. The strong field of the THz pulse provides new avenues to explore deeper novel phenomena in condensed matter physics in the terahertz range. All of the work done so far allows us to probe the various optoelectronic properties of materials in order to better use them for devices.

Why terahertz radiation? The terahertz spectral region is an interesting yet elusive part of the electromagnetic spectrum covering a frequency range of 0.1 THz to ≈ 100 THz. In semiconductor technology, this range sits nicely between transport-based electronics and quantum-transition-based photonics which suggests the possibility of combining both of these two realms to gain further insight into the fundamental physics governing various materials. This is what this work is hoping to achieve and throughout the rest of this chapter, we will go into the finer details of this experimental approach starting with an overview of what THz radiation is, how they are generated and detected, how the radiation is used and finally how to extract information from a spectroscopic viewpoint.

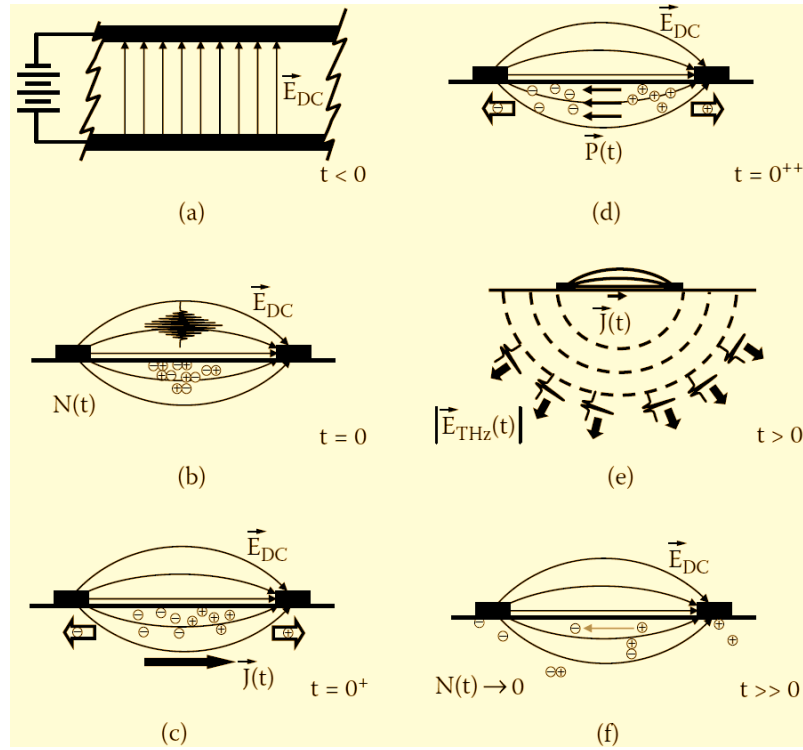


Figure 3.2: **Photoconductive Antenna:** Underlying principle of a photoconductive antenna. (a) Top view of the coplanar transmission lines before photoexcitation. The E-field is provided by an external device. In (b) the optical pulse pumps electrons into the conduction band of the material and in the presence of the electric field, are accelerated (c). In (d) the charge carriers create an opposing field and the induced polarisation generates a transient current radiating THz pulses. Finally in (e) the charge carriers recombine and return to steady state. Adapted from [146]

3.2 THz Generation

THz pulses can be generated via different methods. Common to all these methods is an ultrafast change in polarisation triggered by a femtosecond laser pulse. One approach to getting a fast polarisation change is by using non-linear optical effects in crystals also known as *optical rectification*. [1, 119–128] The second method is via *photoconductive emission* [97, 108, 128–132] when optical excitation induces conductivity changes in a semiconductor. Photoconductive emitters are particularly useful for systems with low power lasers which cannot efficiently access the second order non-linearities required for optical rectification. Other methods have very recently been developed and include THz generation via spintronic emitters [133] and via air-plasma filamentation. [134–145] The next few sections will give a brief overview of these different methods.

3.2.1 Photoconductive Antenna

Photoconductive THz generation occurs when an optical excitation induces conductivity changes in a semiconductor. This is a resonant interaction and the photons are absorbed through inter-band transitions. The second mechanism is non-resonant interaction arising from nonlinear frequency mixing or optical rectification. Transient photoconductivity is used for both the generation and detection of THz radiation, with THz generation discussed first.

A simplified representation of the process of photoconductive THz generation is illustrated in Figure 3.2. [146] The six frames of Figure 3.2 represent different steps in pulse generation and are discussed below. The geometry of a basic photoconductive THz source is shown in a top-down view in Figure 3.2. A coplanar transmission line is fabricated on a semiconductor substrate with high mobility, usually GaAs or low temperature-grown GaAs. The geometric design is such that it is able to support large electric fields across the surface. Intense ultrashort laser pulses from an amplifier are then focused onto the area in between the electrodes which will then generate hot carriers proportional to the local intensity of the incident optical pulse which will effectively close the switch. It is important to note that the energy of the laser pulses should be above the bandgap of the semiconductor material. Under an electric bias, the charges are accelerated in opposite directions which will cause a rapid change in the current density. The accompanying change in dipole then produces a THz transient. [146,147]

Although PC antennae have been widely employed, the shape and frequency components of the THz transients are highly dependent on the antenna structure/geometry and the carrier dynamics of the semiconductor material used. [147] Furthermore, the exact nature of THz generation in PCAs is not universally agreed upon. [148] As such, a great deal of research is still ongoing in order to have a better understanding of the physics underlying THz pulse generation from transient photoconductivity. This area encompasses a great deal of interdisciplinary aspects and not limiting to: optical generation of hot carriers, their subsequent rapid motion to reach thermal equilibrium, ballistic transport on a femtosecond time scale with collisions and restoring forces from nearby atoms/ions, rapid screening of generated fields due to charge accumulation at the edges, design of high bandwidth antenna structures, and propagation of single cycle pulses in dispersive media. [148–158]

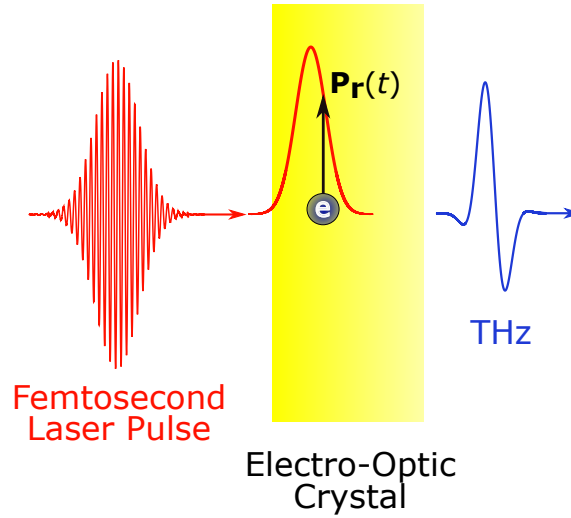


Figure 3.3: **Optical Rectification** Illustration demonstrating the conversion of an optical pulse at 800 nm to a THz transient through an electro-optic crystal. The carrier frequency of the optical pulse is rectified while the envelope is retained. The optical pulse width is on the order of femtoseconds while the THz pulse is on the order of picoseconds. The pulse broadening is due to the non-instantaneous response of the EO crystal.

3.2.2 Optical Rectification

Optical rectification (OR), [159] one of the most popular methods of generating THz radiation in addition to PC antennae, is a second order nonlinear process or more commonly referred to as a difference frequency generation and can only occur in non-centrosymmetric nonlinear materials. In this particular setup, when a monochromatic wave plane wave of the form $E(t) = E_0 \cos(\omega t)$ travels through a nonlinear crystal with non-zero second order susceptibility ($\chi_2 \neq 0$), it induces a polarisation given by [160]

$$\begin{aligned} P_2(t) &= \epsilon_0 \chi_2 E_0^2 \cos(\omega t) \\ &= \frac{\epsilon_0 \chi_2 E_0^2}{2} - \frac{\epsilon_0 \chi_2 E_0^2 \cos(2\omega t)}{2}. \end{aligned} \quad (3.1)$$

By Maxwell's equations, the polarisation $\mathbf{P}$ will act as a source term, radiating off a single cycle electro-magnetic pulse in the far field. If the laser pulse has a duration of less than a picosecond, the result will be a very short electromagnetic pulse with frequency contents in the terahertz range.

In order to generate strong THz electric field, we would need to fully exploit the material properties of the generation crystal. Efficient optical rectification requires considering three major factors: using materials with large second-order nonlinear susceptibilities, well-suited phase-matching properties for THz generation, and low absorption of both the optical pump and the THz waves. The most common crystals used are gallium phosphide (GaP), zinc telluride (ZnTe), and for large bandwidth gallium selenide (GaSe).

Material	Structure	Point Group Symmetry	EO Coefficient (pm/V)	Dielectric Constant	GVM (ps/mm)
ZnTe	Zincblende	$\bar{4}3m$	$r_{41} = 3.90$	10.1	1.1
GaP	Zincblende	$\bar{4}3m$	$r_{41} = 0.97$	-	-
GaSe	Hexagonal	$\bar{6}2m$	$r_{41} = 14.4$	-	0.10
CdTe	Zincblende	$\bar{4}3m$	$r_{41} = 4.50$	9.4	0.75
GaAs	Zincblende	$\bar{4}3m$	$r_{41} = 1.43$	13	0.015
LiTaO ₃	Trigonal	3m	$r_{33} = 30.5$ $r_{13} = 8.40$	$\begin{smallmatrix} 41 \\ 43 \end{smallmatrix}$	14.1
LiNbO ₃	Trigonal	3m	$r_{33} = 30.9$	43	14.2
ZnO	Wurtzite	6m	$r_{33} = 2.60$	-	-

Table 3.1: Electro Optic Coefficients of some commonly used terahertz emitters and detectors. EO = ElectroOptic, GVM = Group Velocity Mismatch. [170]

THz emission from a variety of other nonlinear materials have been reported: lithium niobate (LiNbO₃), lithium tantalate (LiTaO₃), cadmium telluride (CdTe), cadmium zinc telluride (CdZnTe), organic crystals such as DAST, and metals. [120,159,161–169] Table 3.1 gives a brief overview of common materials and their respective properties which make them attractive for OR. The reverse process of OR is used for detecting THz radiation and because of the numerous applications of THz pulses, obtaining a good signal-to-noise ratio (SNR) in the electro-optic detection of a THz electric field is essential. Improving the signal detection allows one to reduce the measurement time. Taking into considerations all of these conditions, ZnTe is very suitable for both generation and detection because its refractive index in the far IR is comparable to the near-IR refractive index, resulting in relatively efficient THz generation and detection.

3.2.3 Spintronic Emitters

The field of spintronics revolutionised numerous areas in experimental physics. Siefert *et al.* [133] pioneered in the field of spintronic emitters, making the first device capable of generating ultrashort pulses covering the 1 – 30 THz range. Being able to exploit an intrinsic quantum characteristic of electrons was a major leap and today terahertz radiation can be produced through this method. The spintronic emitter used on our setups consists of a 1.8 nm thick non-ferromagnetic material, Co₂₀Fe₄₀B₂₀, sandwiched between two 2 nm thick ferromagnetic materials, W and Pt, all sitting on a fused silica substrate.

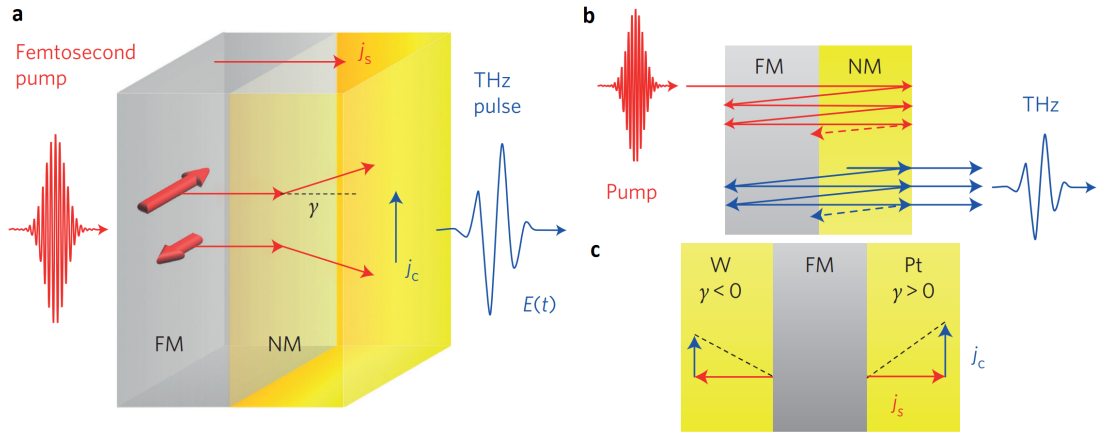


Figure 3.4: **Spintronic Emitter** Underlying principle of a spintronic emitter. In (a) a femtosecond laser pump pulse photoexcites electrons in the ferromagnetic layer which then propagates along the horizontal axis. Adapted from [133]

How do they work? The basic operating mechanisms of a spintronic THz emitter are depicted schematically in Figure 3.4. The emitter consists of a ferromagnetic (FM) and a non ferromagnetic (NM) metal thin film, where an external magnet magnetises the FM layer anti parallel to the y axis. Rare earth neodymium magnets were used providing an effective $\vec{B}$ -field of around 20 mT at the centre of the emitter holder. Upon illumination with the 800 nm amplified femtosecond laser pulse, electrons are excited above the Fermi energy in both metals, generating hot carriers. A net current is launched along the z -axis, as the FM and NM layers differ in their transport properties. Using the example of iron, the photoexcited majority-spin electrons have mainly sp -like character, which is associated with a higher velocity in comparison to the d -type excited minority-spin electrons. Consequently, the current along the z -axis is spin-polarised and gives rise to the spin-current j_s . This means that on entering the NM layer, spin-orbit interactions between the electrons and the nuclei will give rise to the inverse Spin Hall effect which in turn will convert the spin current into an ultrashort transverse charge-current burst j_c . The rapid change in charge density in one direction upon deflection in the plane, will finally emit a THz electromagnetic pulse $E(t)$ into the far-field. [171–175]

A typical THz waveform and its spectrum of the spintronic emitter used on our system are shown in Figure 3.5. A 100 μm thick GaP crystal in a free-space EO sampling (description given in the next section) detection method was used. The signal was recorded under a high vacuum, $\approx 10^{-7}$ mbar. As a result, absorption due to water vapour was minimal and the spectrum was very smooth. The “dip” in the frequency spectrum at around 7.5 – 8 THz is due to the phonon mode of the GaP detection crystal. However, we can see a quick recovery in the spectrum immediately after and up to around 9.5 THz after which the spectrum hits the noise level. Kampfrath et al. reported a bandwidth of up to

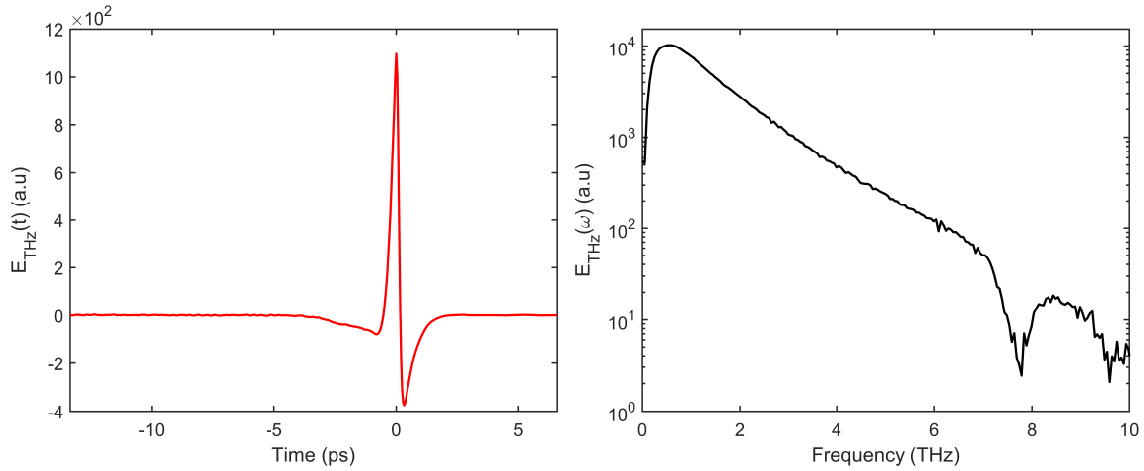


Figure 3.5: Spintronic Emitter THz pulse waveform and its spectrum in an ultra-high vacuum environment. Here we can clearly see a maximum bandwidth of around 10 THz before the noise level kicks in. The dip at ≈ 7.8 THz is due to the phonon absorption of the GaP detector crystal.

≈ 100 THz [133] which was not achieved in our case due to the detection crystal thickness and the longer pulse duration of our amplified femtosecond laser pulses (10 fs vs. 35 fs).

With optical rectification and spintronic emission, usually reflections at the boundaries of the substrate and metallic layers will reduce the efficiency of the emission due to a loss of energy and therefore causing a decrease the field strength at the sample position. Additionally, one would need to attenuate any residual 800 nm optical excitation pulses after the emitters. We therefore designed a novel emitter based on spintronic layers with added coatings: antireflective (AR) and highly reflective (HR). The former ensures that most of the optical pulse is transmitted through the substrate and hits the spintronic layer while the latter ensures that any residual beam is blocked and reabsorbed into the spintronic layer. The new design was done in collaboration with Simonas Kicas at the LTS-FTMC in Lithuania and the emitters were tested. The results are shown in Figure 3.6.

Overall, these newly-designed emitters, all sitting on *c*-sapphire substrates have shown great improvements in increasing the THz field amplitudes. This means better SNR and better data acquisition. The bandwidth has not significantly changed except for the emitters having the HR coating where a slight reduction was seen, possibly due to some absorption beyond 6 THz. On the other hand, the HR coating acts as a mirror at 800 nm with almost no light passing through it, thereby avoiding the need to filter out residual beams that would otherwise cause unnecessary reflections within the optical setup.

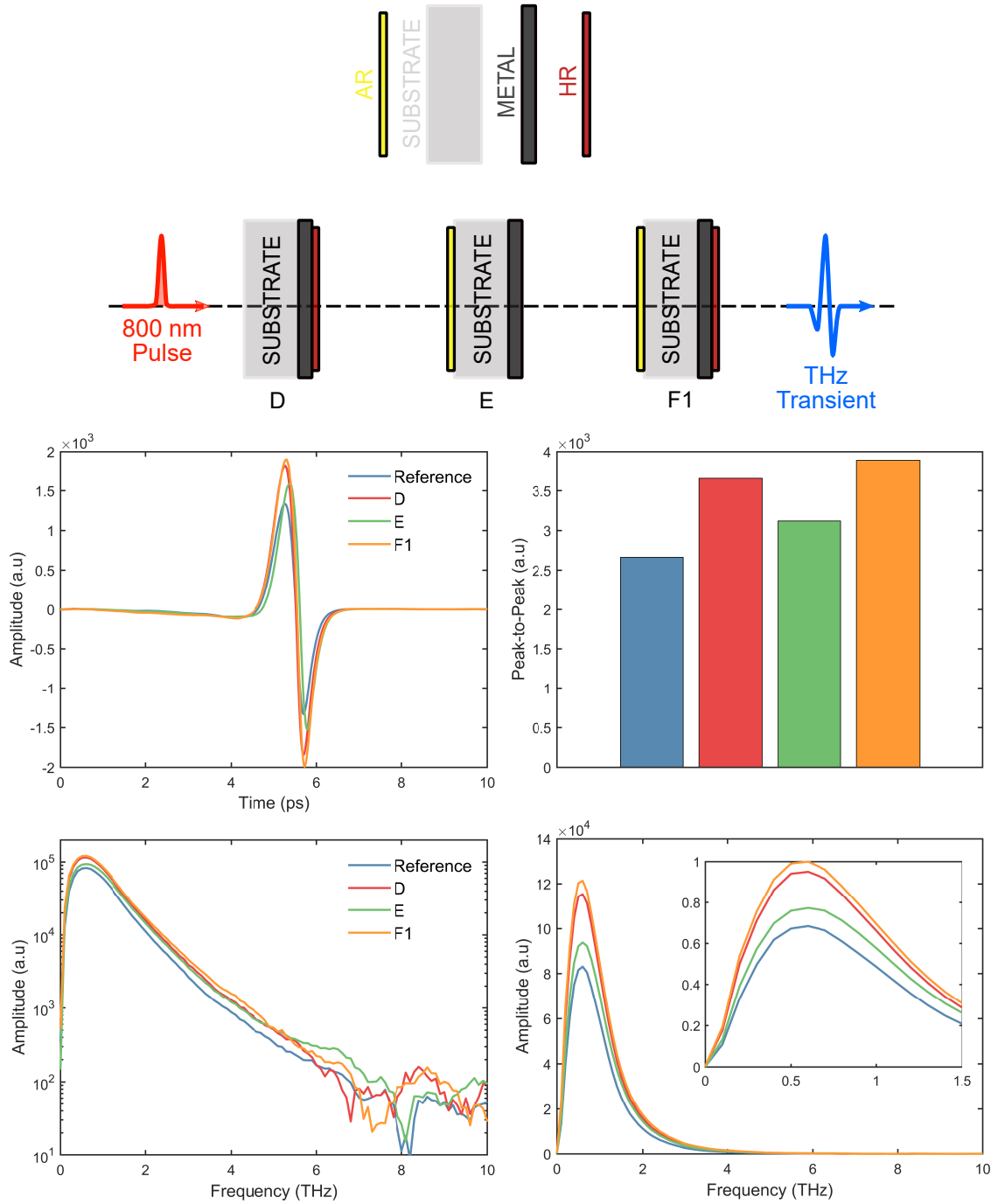


Figure 3.6: **Spintronic Coatings:** Plots depicting the effects of the various coatings onto the spintronic emitters. The reference emitter is the one we currently have on our system. It can be seen that all the coatings increased the peak-to-peak field amplitude of the emitted THz pulses with the double coating reaching twice as high. Unfortunately the HR coating may have some THz absorption beyond 6 THz which reduces the bandwidth. The metal in the top section is the spintronic layer.

Method	Reported THz field (MV/cm)	Photon Energy Conversion Efficiency	Central Frequency (THz)	Bandwidth (THz)
PA	< 1	10^{-6}	≈ 2	≈ 5
Dual-Color-Laser Excited Air Plasma	8	10^{-4}	≈ 2	≈ 50
Optical Rectification	83	10^{-2}	≈ 4	≈ 5
TW in LiNbO ₃	1	10^{-3}	≈ 0.8	≈ 2
SEBR	200	10^{-4}	-	> 10
Free Electron Laser	2	10^{-3}	3	≈ 10

Table 3.2: Table summarising the various methods for THz generation, their efficiencies, THz peak field strengths and their potential bandwidth range. PA: Photoconductive Antenna, TW: Tilted Wavefront, SEBR: Short Electron Bunch Radiation.

3.2.4 Air-Plasma Generation

The three abovementioned mechanisms have been tried and tested and so far have yielded good results. However, all of these methods necessitate the use of materials such as electro-optic crystals or metallic layers which all possess a damage threshold, severely limiting the possibilities for generating high THz field strengths to study non-linear dynamics in semiconductors. Moreover, phonon modes and phase-matching conditions can present some serious issues in both THz generation and detection. Recently, air-plasma filamentation has become the main method for generating ultra-wide bandwidth pulses that circumvent many issues presented before. The next Chapter focuses entirely on a system I built based on air-plasma photonics. For brevity, Table 3.2 below gives a summary of the various methods used to generate THz radiation and their efficiencies.

3.3 THz Detection

The generation of THz waves is pointless without an effective way of detection and over the years numerous methods have been developed and implemented for detecting THz waves with the two primary optoelectronic methods for detection being photoconductive antennas and free-space electro-optic sampling (FS-EOS). [160] With the recent advance in air-plasma photonics, detection via plasma formation is also possible and Chapter 4 goes into more details regarding this particular method. One of the advantages of FS-EOS is that it is a non-resonant method of detection, so the potential for damaging the detector crystal is much lower. [176] Electro-optic THz receivers have demonstrated exceptionally

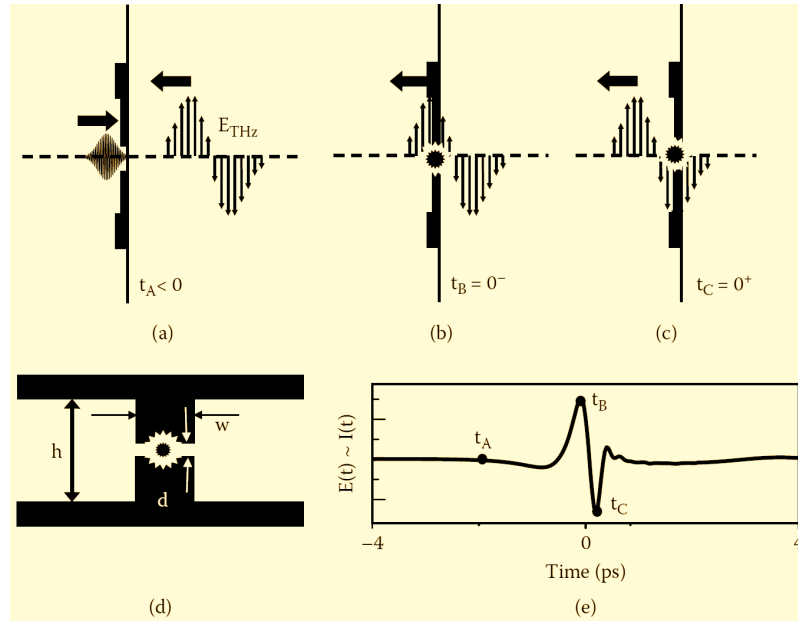


Figure 3.7: Principles of THz detection via a photoconductive antenna. The THz antenna of frame (d) is shown in cross section in frames (a-c). The electric field measurement is determined by the relative arrival times of the optical and THz pulse. In (a), the optical pulse arrives before the THz pulse. By delaying the arrival of the optical pulse to coincide with the THz pulse as shown in (b) and (c), the measured current (e) maps out the THz field in time. Adapted from [146]

high-frequency performance, but have not demonstrated the continuous spectral coverage of photoconductive antennas owing to several factors such as THz absorption and dispersion of the EO crystal, the frequency dependence of the EO susceptibility and phase mismatch between the interrogating pulse and the THz pulse. [177] Electro-optic detection is an easy setup which has become an increasingly popular way to measure the amplitude and phase of THz radiation. There are two reasons for this: first, unlike time-gated antennas, electro-optic materials are readily commercially available and second, electro-optic detection is suitable for signals with a large bandwidth depending on the crystal dimensions. [178]

3.3.1 Photoconductive Antenna

A PC antenna measures the electric field of a terahertz pulse as a function of space and time as shown in Fig. 3.7. [179–181] In contrast to bolometric detectors where only the amplitude of the signal is detected, PC receivers allow both the phase and amplitude of the electric field to be recorded, thereby retaining the full complex information encoded in the signal and bypasses the use of the complicated Kramers–Kronig relations. The simplest device design consists of two metal contacts evaporated onto a semiconductor substrate. Typically, these electrodes are connected to the current input of a lock-in

amplifier. To operate such a detector, a laser pulse (the gate pulse) is shone at the gap between the electrodes generating photocarriers and hence closing the circuit. Thereafter a terahertz pulse is focused onto the gap region where its electric field will act as a bias voltage and control the current. This THz-induced current depends on the type of PC detector (PCD). The two main modes of PCD operation are: (1) *direct sampling mode*, and (2) *integrating mode*.

Direct sampling detectors are fabricated from highly resistive semiconductor substrates that exhibit very short photocarrier lifetimes. Such materials are usually either grown at low temperature [182,183] or are ion-implanted [1,181,184,185] to create trapping centers in the crystal structure which reduce the carrier lifetime. In the limiting case, to maintain a closed circuit, there has to be charge carriers at all times, so the switch is only closed for as long as it is illuminated by the gate pulse. In this case the current in the circuit samples only the point of the terahertz transient that overlaps spatially and temporally with the laser pulse. Thus the measured photocurrent will be proportional to the strength of the terahertz electric field at that point. By varying the time delay of the gate pulse with respect to the terahertz transient, it is thus possible to measure the electric field E of the pulse as a function of time t . Thus the photocurrent is given by:

$$I(\tau) \propto E_{\text{THz}}(t = \tau), \quad (3.2)$$

assuming that the laser pulse generates a spike in conductivity in the semiconductor substrate that is of much shorter duration than any feature in the terahertz waveform (≈ 1 ps). The measured photocurrent intensity in the detector is directly proportional to the strength of the incident THz electric field. Therefore, there is no requirement to perform corrections to recover the THz waveform from the measured data.

Integrating detectors are made from materials that have charge-carrier lifetimes that are much longer than the duration of the terahertz transient. The detection method is similar to that for the direct detectors; however, the longer charge-carrier lifetime means that after the PCD is photoexcited, the circuit is closed for a period much longer than the duration of the terahertz transient. Therefore, the measured current will be proportional to the integral of the electric field of the terahertz transient. As shown schematically in Fig. 3.8, the lower limit of the integral is the time τ in the terahertz transient when the gate pulse overlaps with it. By delaying the laser pulse with respect to the terahertz transient by τ , the terahertz electric field, E_{THz} , can be recovered from $I(\tau)$ by differentiation with respect to τ . That is,

$$I(\tau) \propto \int_{\tau}^{\infty} E_{\text{THz}}(t) dt, \quad (3.3)$$

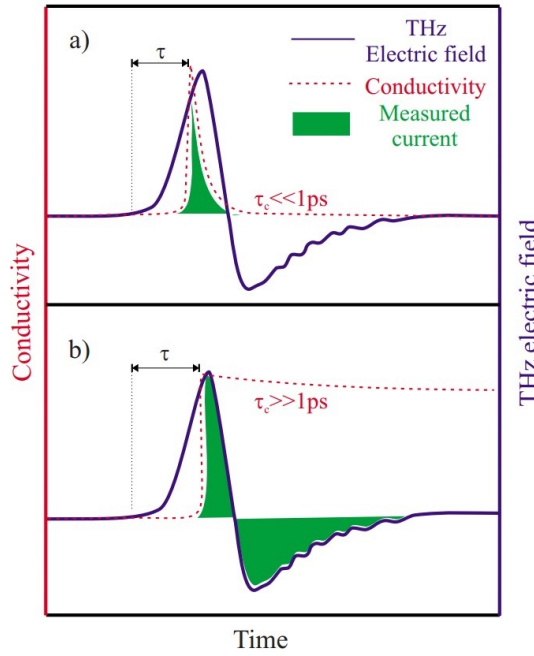


Figure 3.8: Schematic representation showing a terahertz pulse, the conductivity in a photoconductive receiver, and the current induced between the contacts, which is proportional to the integral of the product of the electric field and the conductivity. In the top and bottom panels, the cases of short ($\ll 1$ ps) and long ($\gg 1$ ps) carrier lifetimes in the semiconductor are illustrated. Reproduced with permission from [186]

where it is assumed that the conductivity of the semiconductor rises like a step function upon photoexcitation.

However, one might encounter a problem when the charge-carrier lifetime of the detection material is on the same scale as the measurement range. In this case, the approximation breaks down and $E_{\text{THz}}(t)$ can be obtained by deconvoluting $I(\tau)$, which is written as:

$$I(\tau) = \beta \int_{-\infty}^{+\infty} E_{\text{THz}}(t) \sigma(t - \tau) dt, \quad (3.4)$$

where σ is the normalized time-dependent conductivity of the material, β is a constant directly related to material's properties and optical excitation condition. Eq.(3.4) is a Fredholm integral equation that can be seen as a convolution of functions $E_{\text{THz}}(t)$ and σ (in the Fourier sense), whose solution is given by:

$$E_{\text{THz}} = \beta F^{-1} \left[\frac{F(I)}{F(\sigma)} \right], \quad (3.5)$$

where F is the Fourier transform operator. In fact, in most THz-TDS systems, the duration of the gate pulse is on the order of femtoseconds which is much shorter than the THz transient with a pulse width on the order of picoseconds. Therefore σ can be approximated further as:

$$\sigma \approx F_s(t) \exp^{-t/\tau_c}, \quad (3.6)$$

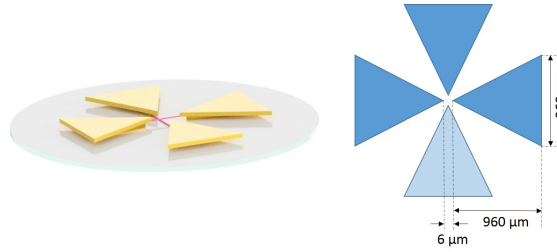


Figure 3.9: Schematic diagram of device design.

where F_s is the unit step function. Thus Eq. (3.6) may be simplified into the form:

$$E_{\text{THz}} = \beta F^{-1} \left[F(I) \left(\frac{1}{\tau_c} + i\omega \right) \right], \quad (3.7)$$

where ω is the angular frequency, τ_c is the photoconductivity lifetime of the detection materials. In this case, the detector is categorised as an “**intermediate**” photoconductive detector.

The ideal materials for PCD applications must therefore satisfy two conditions: have a short photogenerated charge-carrier lifetime to minimise the noise current and a high peak conductivity to maximise its responsivity. Of all the three regimes, the **intermediate** one is the most suitable this would mean that the integral (3.3) happens on a much longer time scale thereby carrying with it the noise levels as well. Semiconductor nanowires are the perfect contenders for this type of material and below is a project done on our group with collaborations from various members on implementing a novel design for PCD.

Polarisation-Resolved THz Detection. Theoretically speaking, in order to implement polarisation-resolved THz detection one **E**-field component would be measured and then the receiver rotated by 90° and subsequently measure the orthogonal **E**-field component. However, such a technique brings along two major disadvantages. First, by rotating the receiver slight misalignment of the laser pulse will significantly shift the relative phase of the **E**-field, and second the process will be time consuming as each component is recorded separately thereby having to break vacuum during each measurement (all experiments are performed under vacuum as THz radiation is highly absorbed by water vapour). In 2005, Castro-Camus *et al.* [179] showed a polarisation-sensitive THz detector from a multi-contact PC receiver bypassing the aforementioned issues. Although this was a step forward, the noise level was a drawback and there was very poor coupling of the antenna to the far-field. Hence, we look towards novel materials, III-V semiconducting nanowires, capable of encompassing all the needs for an efficient polarisation-sensitive THz detector.

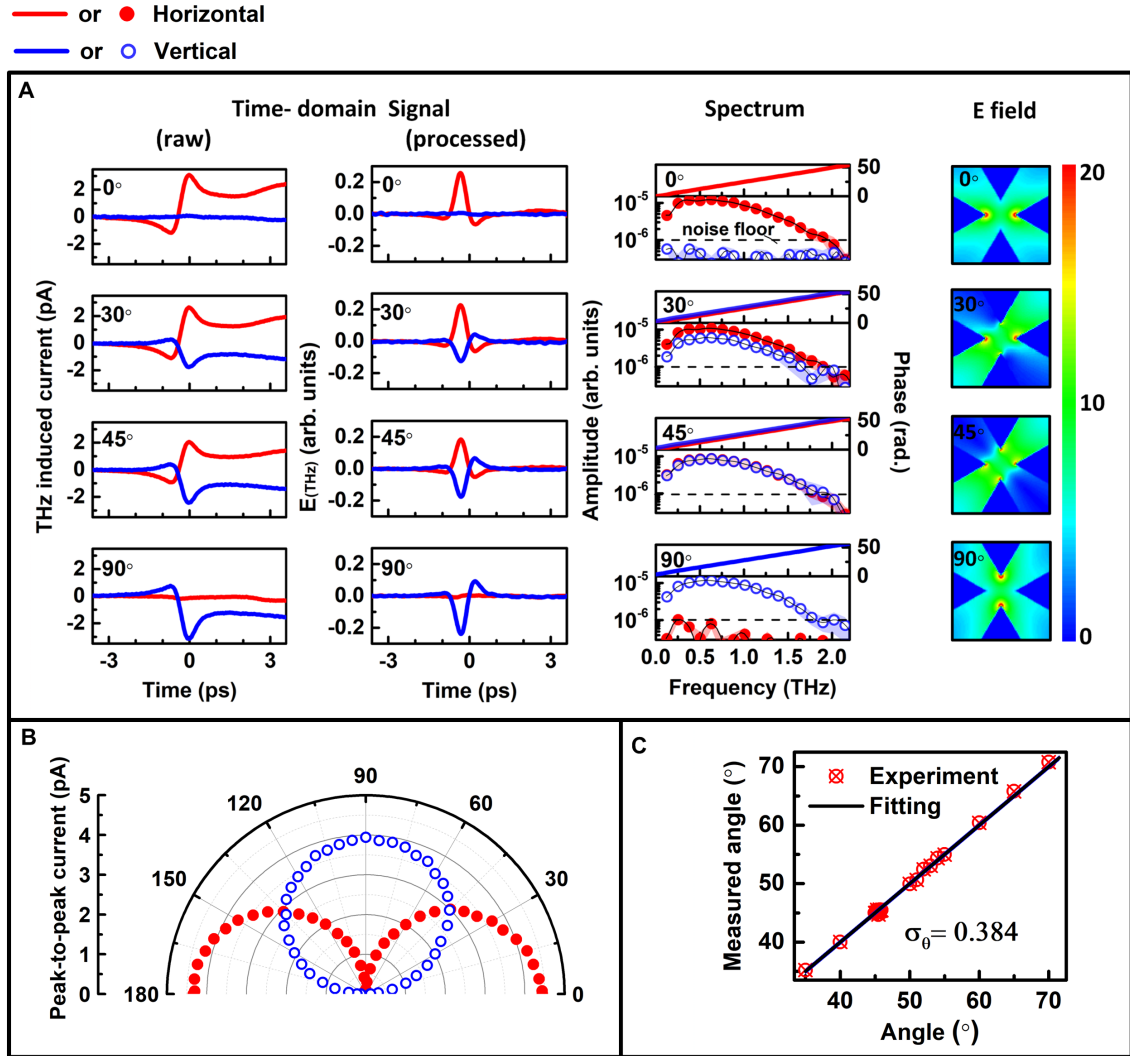


Figure 3.10: Double Bow-Tie Device Characterisation: In (A) we have the responses of the NW detector with the THz pulses incident at various angles. Both raw and processed data are shown and the corresponding spectra. Also shown are the FDTD simulations done depicting the enhancement of the field are the tips of the bow-tie design for the incident THz pulses. (B) shows the relationship between the two orthogonal detection channels with the red depicting the peak-to-peak value of the horizontal detection channel and the blue depicting the peak-to-peak of the current. (C) shows the dependence of the device angle with the rotation of the emitter for which a linear dependence is expected and seen.

In this project led by Dr. Kun Peng, a novel PC antenna capable of resolving THz polarisation was demonstrated. The device is based on a bow-tie structure, as previously shown by Peng *et al.* [81] However, as the latter device was based on a single nanowire, it was only possible to detect THz radiation polarised parallel to the nanowire axis. This new and improved device has two orthogonal bow-ties with orthogonal nanowires that will be able to detect both s - and p - polarised THz radiation. Figure 3.9 shows a schematic diagram of the design. It is worth noting that the two orthogonal nanowires do not touch each other at all times which would otherwise cause a charge leakage and short-circuit the device. Figure 3.10 shows the results obtained for the device. It has been possible to detect THz pulses incident on the detector at various angles. More information regarding the fabrication process, experimental setup and data extraction can be obtained from the paper due to be published.

3.3.2 Free-Space Electro-Optic Sampling

Free-space electro-optic sampling (FS-EOS) [187–189] emerged as a very powerful method to detect THz transients. The remarkable performance potentials of this particular technique in transient local field measurements result from its simplicity and yet ultra-broadband detection of the sensor crystal. It is a purely contact-free optical method since there are no conducting elements or wiring associated with the crystal detector. As such, the bandwidth should only be limited by the dielectric response of the crystal and the laser pulse duration.

FS-EOS is in essence the reverse process of optical rectification. It is based on the electric field of the THz pulse, Figure 3.11, which through a non-linearity of the first order (Pockels effect) induces a small birefringence in the electro-optic (EO) crystal (GaP, ZnTe or GaSe). FS-EOS consists of a few optics that help in generating the signal and the method of operation for this technique is described below. It is important to note that the polarisation of the optical gate must match with that of the THz pulse as the birefringence is sensitive to the direction of the electric field.

In the absence of an electric field (a), the EO crystal is inactive with no birefringence felt and the vertically polarised gate pulse passes unchanged. A quarter wave-plate is set to produce circularly polarised light from this gate pulse. The result of this effect is that the initially linearly polarised optical probe beam gains a small elliptical polarisation when propagating through the electro-optic crystal, where the ellipticity the probe beam experience is proportional to the electric field applied to the crystal. A Wollaston prism (WP) spatially separates the horizontal and vertical components of this light, which is detected by two photodiodes. In the absence of the THz field, no ellipticity is conferred

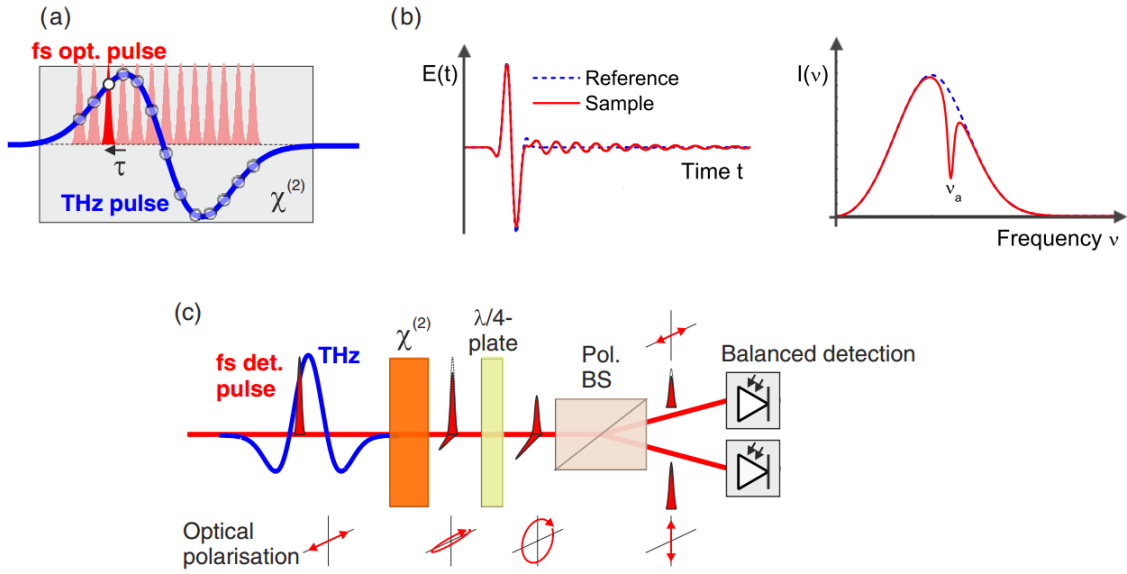


Figure 3.11: Principle of electro-optic sampling of a THz pulse using an optical gate pulse. Adapted from [187]

upon the gate pulse and the quarter wave-plate produces perfectly circular polarised light. In this particular case both orthogonal components are equal, thus both photodiodes measure the same intensity, and the potential difference between them is 0. If the optical delay is set such that the THz pulse and the gate beam overlap in time (b), here at $t = t_{max}$, the presence of a THz electric field modifies the birefringence of the crystal, changing the polarisation of the gate pulse, thus encoding the electric field into the polarisation of the gate. The quarter-waveplate now produces elliptically polarised light, yielding different intensities on each of the photodiodes the difference of which is proportional the the THz electric field, Figure 3.11. [187]

The mechanism described above may seem simple and straightforward, but EOS can be a very daunting method to extract a large signal with good SNR and optimum bandwidth as it is afflicted by the same issues as OR, such as:

- dispersion and absorption inside the crystal and at the air-crystal interface;
- Fabry-Perot reflections inside the detection crystal,
- finite pulse duration of the optical gate pulse,
- phase-mismatch between the optical gate and THz pulses due to their different group velocities and,
- the geometrical overlapping between the probe and THz beams (the optical gate beam must be much smaller than the THz beam).

From the above 5 issues, the phase-mismatch and the geometrical overlap are by far the most important ones when it comes to extracting maximum bandwidth and reasonable SNR. As for the phase-mismatch, it is nearly impossible to circumvent all the above-mentioned issues because the frequency extent of terahertz pulses is so broad. Finding an EO crystal that satisfies all the phase-matching properties is a difficult task. An effective way however is to use a thinner crystal. Wu et al. showed in 1997 [190] that the temporal displacement, $\tau(\Omega)$, between the optical gate pulse and the THz pulse, which is indicative of phase-mismatch, is directly proportional to the thickness of the EO crystal as shown by Equation (3.8). Hence, a decreasing thickness will reduce the phase-mismatch and give better bandwidth,

$$\tau(\Omega) = \frac{n_g(\lambda_0) - n(\Omega)}{c}d. \quad (3.8)$$

As for the geometrical overlap, this is due to the fact that all the frequencies within the THz pulse are distributed along the diameter of the focusing point as well as the gold mirror introducing achromatic aberrations. Finding the correct spot for optimum detection requires a lot of effort. Tomasino *et al.* goes into much more detail regarding optical rectification and electro-optic sampling in terahertz spectroscopy. [191] Despite all of these issues, EO crystals are still one of the better contenders for both THz generation and detection.

A word of caution, part I: FS-EOS has been the detection scheme of choice for most spectroscopic applications owing to its simplicity. Being non-resonant in nature, this method is capable of detecting substantially high bandwidth with a maximum range of ≈ 100 THz. [190] Both the THz emission strength of an electro-optic crystal and its bandwidth in detection are proportional to the crystal's thickness. Unfortunately these two quantities have a reciprocal relationship. A thicker crystal will have a much higher sensitivity but a lower bandwidth whereas a thin crystal will be the exact opposite. Therefore a compromise needs to be reached. Chapter 4 goes into much more detail regarding how the EO response can be corrected for by taking into account several factors.

$\langle 110 \rangle$ -oriented ZnTe is usually the material one would use in EO sampling. It is customary to have the crystal sat onto a very thin “inactive” $\langle 100 \rangle$ -oriented ZnTe substrate to prevent Fabry–Perot effects and perfect refractive index matching. The next chapter showcases the spectrum of a zinc telluride crystal where the bandwidth is limited to around 4 THz after which no reasonable signal can be extracted. This is because of the material's strong phonon mode. However, for ultra thin ZnTe acting as a detection crystal, there exists a nice trick to circumvent such an issue. By employing the correct method, it is possible to filter out the phonon mode and recover the signal thus allowing for higher frequencies to be detected. This will be touched upon in the next chapter on air-plasma photonics,

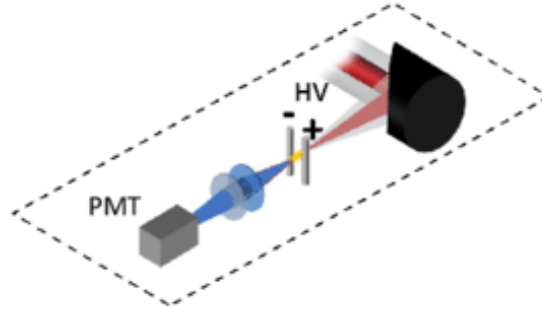


Figure 3.12: **ABCD:** Working principle of an Air-Biased Coherent Detection scheme. Both the THz pulse and the optical gate beam are overlap spatially. The latter produces a very weak plasma in the air and with the AC-bias at $\approx 5\text{ kV}$ and a delay stage, the second harmonic of the optical gate pulse is produced that is then detected by the photomultiplier tube (PMT). The intensity of the second-harmonic will depend on the intensity of the THz pulse while the phase will be recovered by varying the time delay. In this way heterodyne detection is achieved.

“A word of caution, part II,” where the issue of phase-mismatch is discussed in greater detail.

3.3.3 Air-Biased-Coherent-Detection

Air-Biased-Coherent-Detection or ABCD, similar to THz air-plasma generation, depends on the third-order non-linear susceptibilities of gases. It is yet another way to avoid the use of crystals or materials that are prone to damage in the presence of high-powered lasers as gases do not possess a damage threshold and can easily be replenished. ABCD is the reverse process of its counterpart, THz generation in a gas. Although this method used to be termed as air-breakdown coherent detection where the formation of a plasma was necessary, in ABCD this requirement is essentially dropped as only a very weak plasma is needed.

This method allows one to detect broad bandwidths, up to 100 THz without the presence of any phonon modes which would otherwise limit the bandwidth measurement. The only downside to this method is that the signal tends to be noisy and relies heavily on detecting very low amplitude signals using a photomultiplier tube. A simple setup is shown in Figure 3.12 and the detection method is described in greater detail in Chapter 4.

3.4 Terahertz Spectroscopy

The basics of THz generation and detection have been touched upon, and this section onwards looks at how to implement all of this in a spectroscopic setup. Terahertz spectroscopy in the recent decades has become a rapidly evolving field with interesting

Table 3.3: Comparison of key merits and drawbacks of THz generation methods. [24]

THz Radiation Properties	PCA	Optical Rectification	Air-Plasma
	Asymmetric quasi half-cycle THz pulses with peak field of few hundreds kV cm^{-1} Low THz frequencies of 0.1-3 THz Picosecond pulse duration Large spot size of $\geq 2.5 \text{ mm}$	Single to multi-cycle THz pulses with peak fields from several 100 kV cm^{-1} up to several MV cm^{-1} Broad bandwidth of from 0.1 to 6 THz depending on the nonlinear crystal used	Single cycle THz pulses up to MV cm^{-1} with conical emission profile Broad bandwidth of from 0.1 to 10 THz and over depending on the gaseous medium used
Advantages	Large pondermotive potential High stability Extraction and control of THz energy from bias voltage	High conversion efficiency Simple experimental configuration High stability	No damage as using air Whole THz region covered without gap High electric field
Disadvantages	Relatively low THz peak electric field Laser damage threshold of the antenna High EM noise THz radiation saturation at low optical fluence Short lifetime of the emitter	Laser damage threshold of the nonlinear medium Complicated phase matching conditions for some nonlinear crystals Thermal and multi-photon effects in the crystal when high pump laser intensities are used	Needs phase matching sensitivity and stability between 800 nm and 400 nm beams Low energy level Conical shape

applications in medical imaging, remote sensing, security, scientific imaging (chemistry, biochemistry, astronomy), communications, and manufacturing. [142, 192–226] Many molecules, especially biomolecules, [227] provide fingerprint spectroscopic lines in the terahertz region.

The next few sections describe in detail our THz systems including: THz time-domain spectroscopy (THz-TDS), optical-pump THz-probe spectroscopy (OPTPS). My DPhil revolved mainly around setting up the optical bench with the various optical components, laser aligning, and improvements.

3.4.1 Time-Domain Spectroscopy

An important class of terahertz sources relies on the frequency conversion of femtosecond lasers to deliver coherent few-cycle pulses, enabling terahertz time-domain spectroscopy (THz-TDS). Time-domain spectroscopy emerged as a powerful technique that measures the power of electromagnetic radiation as a function of time as opposed to normal spectroscopy which measures radiation as a function of frequency or wavelength. Time-domain spectroscopy usually requires the use of Fourier transforms with the unique ability to characterize the complete electric field of a terahertz pulse to yield full phase and amplitude information, an advantage over typical detectors that measure only intensity.

TDS: Why the Fuss? In conventional optical spectroscopy, the intensity of electromagnetic radiation is measured as a function of frequency. The intensity of an electromagnetic wave is given by the Poynting vector, $\bar{\mathbf{S}}$, the electric field vector, $\bar{\mathbf{E}}$, and the magnetic field vector, $\bar{\mathbf{B}}$ via the relation:

$$\bar{\mathbf{S}} = \bar{\mathbf{E}} \times \bar{\mathbf{B}}. \quad (3.9)$$

At optical frequencies, only the time-averaged Poynting vector can typically be measured. For a plane wave of the form

$$\mathbf{E}(t, z) = E_0 \exp^{i(kz - \omega t)}, \quad (3.10)$$

the time-averaged intensity is proportional to $|E_0|^2$, thus all the phase information is lost, and for instance the complex refractive index of the sample cannot be measured. This problem can be avoided by using the *Kramers-Kronig* relations, which utilise the relationship between the electric displacement $\mathbf{D}$ and the electric field $\bar{\mathbf{E}}$ to extract the full complex refractive index of the material from the intensity measurements. [228] However, this analysis can be complicated, and requires knowledge of either the real or the imaginary part of the refractive index over a large spectral range, which is not necessarily achievable.

Time-domain spectroscopy, such as THz-TDS, provides an alternative. By measuring the electric field of the radiation rather than just intensity, the phase of the wave is retained, allowing the complex refractive index or complex conductivity to be extracted directly. To measure and extract the spectral response of a target material, we would need a reference spectrum and the sample spectrum. There are two types of samples: (1) free-standing, and (2) sample on substrate. In the former case, the reference measurement would be the free-space vacuum whilst for the latter, it is the bare substrate without any deposited sample. This reference measurement allows us to eliminate any optical effects introduced by the substrate which would otherwise interfere with the data analysis. Using these two measurements, one can then extract the desired optoelectronic properties of the material in question. A brief explanation of the underlying principles as applied to nanowire materials used in this project is given in the next section, including data analysis and the various models one can use to fit the data.

3.4.2 Time-Resolved Optical-Pump Terahertz-Probe Spectroscopy

Time-resolved THz Spectroscopy (THz-TRS), or alternatively Optical-Pump Terahertz-Probe Spectroscopy (OPTPS), is an optical pump probe technique used primarily as a non-contact electrical probe for studying time-dependent charge carrier dynamics in semiconductors.

Why do time-resolved spectroscopy? TRS is different from TDS on a very fundamental level. While the latter provides information about the equilibrium dynamics and static properties of the sample under study, the former probes the temporal dynamics and time-changing properties of the sample which offer a greater insight into the optoelectronic properties of the material. Most of the samples studied have an enormous number of atoms so that the system possesses a very large number of degrees of freedom. It would be impossible to rely on a combination of time-independent measurements to infer the time evolution of a system. The dynamics become too complicated and the quantum effects more pronounced.

Furthermore, conventional measurement systems that are based on fast electronics, for example a photodiode signal read out by an oscilloscope, typically have response times exceeding tens of picoseconds. Using a pump-probe approach for time-resolved experiments eliminates this limitation given by detector timescales by utilising two ultrashort pulses to conduct a measurement.

What is the difference? In contrast to THz-TDS, an OPTPS has an extra beam path known as the *pump* pulse which will photoexcite or photodope the sample. This is

Experimental Dimension	Delay Stage Movement		Beam Path Length	
	(length)	(time)	(length)	(time)
Minimum Delay Stage Increment	1 μm	3.34 fs	2 μm	6.67 fs
Amplifier pulse duration	5.25 μm	17.5 fs	10.5 μm	35 ps
1 ps Pump-Probe delay	0.15 mm	0.5 ps	0.3 mm	1 ps
Typical Delay Stage Increment	1 mm	3.34 ps	2 mm	6.67 ps
1 ns Pump-Probe delay	150 mm	0.5 ns	300 mm	1 ns
Maximum Delay Stage Increment	200 mm	0.67 ns	400 mm	1.33 ns

Table 3.4: Summary of how movement of a delay stage affects the path length, shown in both length and time taken for light to travel the distance in air. For any delay stage movement, double this distance is added to the beam path, as the beam passes along the stage once and is then reflected back parallel to the initial direction of travel. [229]

achieved by using a beamsplitter before the THz emitter. Usually, the spintronic emitter has a maximum saturation pump power, and therefore this will help determine the beamsplitting ratio to generate the photoexcitation pump pulse energy. A typical time-resolved experiment will make use of delay stages to control the time delay between the pump and the probe pulses. First, the pump pulse is made to reach the sample before the THz-probe. This photoexcites the sample and triggers a transient change in its properties. The changes after excitation are then measured by a second pulse, the probe pulse. The temporal delay between the two pulses is typically set by a delay stage inserted into either the pump or the probe branch, and varying the delay between the two pulses allows to record a time trace of the evolution of the material properties accessible with the probe pulse. The delay stage will change the length of the beam path and therefore the time of flight for a pulse passing it. This is all done electronically through the use of motorised linear stages. Table 3.4 depicts the two main scans one can perform using a THz-TDS and THz-TRS: a spectral scan gives information about the various frequency-dependent mechanisms happening in a material such as phonon modes whereas a pump scan gives information about the temporal dynamics of charges upon illumination. Various information can be obtained from these two scans and this thesis uses both methods in the study of materials.

3.4.3 THz-TRS vs. Transient Absorption

It is often misunderstood that THz-TRS is exactly the same as Transient Absorption (TA) spectroscopy. This section deals with a brief comparison of these two popular methods. The basic operating procedure of a TA system is the same as in OPTP as they are both based on the principles of pump-probe measurements and the change in transmission caused by the photoexcitation pulse being monitored by a probe pulse. In THz, the probe is solely a picosecond THz transient with frequencies spanning between 0.1 THz – 10 THz,

while for TA the probe beam is produced by white light generation, spanning an ultra wide frequency range, in a media such as diamond, water or sapphire. Additionally, the pump beam in TA can either be a broadband or narrowband optical pulse.

The chief differences between TA and OPTP spectroscopy are that, in the former case, the signal is detected directly in the frequency domain, and that the sample is probed at optical wavelengths. As TA probes the absorption of a photoexcited sample in the visible range, it provides a wide range of information simultaneously in the spectrum such as charge-carrier cooling, refractive index changes, and charge-carrier recombination. [230–232] However, the sensitivity of TA to such a wide range of processes significantly complicates the interpretation of the TA spectrum, meaning great care must be taken to disentangle the various processes. As for OPTP, the equilibrium or photoexcited sample is probed in the THz regime, so is sensitive only to the total THz absorption of all of the photo-excited species, rather than their individual contributions. Since OPTP spectroscopy is not directly sensitive to the wide range of processes as measured by TA, the interpretation of photoconductive transients is significantly simplified. As it is only directly sensitive to the density and mobility of charge-carrier separation in a sample, OPTP is an exceptional contact-free method for probing the recombination dynamics in semiconductor nanowires and thin films. [229]

3.5 Experimental Details

Throughout the course of my DPhil, I have been highly involved in setting up and optimising multiple THz systems. This section goes briefly through those various systems with schematic diagrams of the beam paths and details of how experiments are carried out, and finally data analysis to extract meaningful information. For the rest of this thesis, all the results have been obtained using one of these systems. Any experimental sections in further chapters should be referred back to this one unless specified otherwise such as in the next chapter.

The spectroscopy experiment relies on ultrashort amplified laser pulses, which are provided by a laser amplifier. The mode-locked Ti:Sapphire laser amplifier generates 35 fs pulses with a centred wavelength of 800 nm at a repetition rate of 5 kHz. The average power of the laser at the output is 8 W (4 W in Rm146). This system has a nominal beam diameter of $1/e = 12$ mm, which is just short of an inch. Therefore, to accommodate this beam size, the beam-paths were fitted with 2 inch mirrors so as to avoid loss of power at the edges. From now on, we will describe how the systems operate and how the samples are measured.

3.5.1 THz-TDS

THz time-domain spectroscopy (THz-TDS) is a resourceful technique that has been employed to analyse various steady-state far-infrared response of a wide range of materials. In THz-TDS, the transmission function of a THz pulse through a sample medium is measured in the time-domain. In order to extract the transmission/reflection coefficients of the sample, one would need a reference signal. In this case, there exist two possibilities: first if the sample is free-standing, the reference would be the signal without any sample in position, and second if the sample is sitting on a substrate, the bare substrate would be the reference. By relating the reference signal to the sample signal in the frequency-domain via a Fourier transform, one can determine the transmission coefficient, the reflection coefficient or the dark conductivity of the sample as a function of frequency.

To achieve sub-picosecond resolution, it is necessary to use time-gated optical techniques wherein an ultra short NIR optical pulse ($\ll 100$ fs) is split using a beamsplitter along two paths: generation and detection the time-dependent THz field. Here, once the THz beam is generated through either a photoconductive antenna or optical rectification, the radiation is collected by a protected gold off-axis parabolic (OAP) mirror and collimated onto a second one which focuses the THz onto the sample. The transmitted THz is collected, collimated, and focused onto a detector using a second pair of OAPs. At the detector position, a gate pulse overlaps with the THz pulse and through the Pockels effect in the electro-optic crystal, a quarter wave-plate, a wollaston prism and a pair of balanced photodiodes, the THz signal can be recovered.

It is important to note that the detector is only “active” when both pulses overlap spatiotemporally. The optical pulse duration ($\tau_{\text{optical}} \approx \text{fs}$) is significantly shorter than the THz pulse ($\tau_{\text{THz}} \approx \text{ps}$) and this allows us to measure the THz electric field as a function of time. Additionally, the detector is sensitive to the sign of the electrical field and consequently we are measuring the THz time-dependent amplitude, $E(t)$, as opposed to other techniques which measure only the intensity, $|E(t)|^2$, of an electromagnetic signal and, therefore, do not capture the phase information. This significantly reduces the amount of computation one has to perform such as the Kramers-Kronig relationship, to obtain the full encoded information.

The measured signal corresponds to the THz field amplitude at a single point in time. In order to reconstruct the THz wave profile, the signal at all time delays has to be measured which can be achieved by controlling the optical gate pulse delay relative to the THz pulse using an electronically controlled delay line. The output of the laser is split into

two beams: one of the beams is used to generate THz radiation, and the other is the optical gate beam that will initiate the detection.

The temporal delay is achieved by increasing the path length of one of the beams, in our case the THz beam path. The travel time of a laser pulse is $t = s/c$, where s is the path length and c is the speed of light. This simplifies the problem of femtosecond time resolution to one of micrometer spatial resolution. Precise micro positioning is achieved with computer-controlled positioning stages. In THz-TDS (and ultrafast spectroscopy in general), these stages are usually referred to as delay lines. The round trip delay time changes 6.6 fs for each micrometer of delay line displacement. The moving speed of the delay line defines the sampling speed in the time domain. It is, therefore, common to state the speed of the delay line in ps/s. Table 3.4 gives a brief overview of delay times and resolution one can achieve through the use of motorised linear stages.

The resolution of the reconstructed THz waveform can be further improved by using an even more precise stage. The M-VP-25XL Metric Precision Compact Linear Stage from Newport provides high-precision positioning performance with an excellent minimum incremental motion of 0.01 μm and a travel range of 25 mm. For high bandwidth systems, such as the air-plasma system described in the next chapter, this stage is used for high accuracy THz waveform recovery. On the other THz systems, the M-ILS200CC DC Servo Linear Stage from Newport was used, and it is capable of 200 mm travel range with sub-micron resolution motion.

3.5.2 THz-TRS

An optical-pump terahertz-probe (OPTP) system (or THz time-resolved spectroscopy (THz-TRS)) is just an extension of the TDS system described above. This is achieved with the addition of an extra optical beam path: the pump beam. In contrast to the THz-TDS where the THz and gate beams were split from the pump pulse, the pump beam is directed along a separate beam line and directed onto the sample.

With this additional photoexcitation pulse, temporal dynamics of charge carriers in materials can be probed. This allows us to extract a lot of useful information as will be described in the data extraction section. It is customary that with materials possessing bandgap larger than the 800 nm wavelength pulse, the pump beam is frequency-doubled so that twice the energy can be used for photoexcitation of charges into the conduction band. This is done using a type-I β -Barium Borate (BBO) crystal with dimensions of $12 \times 12 \times 0.3$ mm, with an antireflective coating @800/400 nm cut at $\theta = 29.2^\circ$ and $\phi = 90^\circ$,

providing a 400 nm pump excitation which is above the 780 nm absorption onset of many materials.

A 100% conversion efficiency is not achieved and any remaining light at 800 nm is blocked using a bandpass filter from Thorlabs (FBH-400), which admits light only in the region 380 – 420 nm. To study the effect of fluence dependence on various samples, the energy of the pump pulse need to be attenuated and this is facilitated through the use of an automated variation of a neutral density (ND) filter wheel, allowing the pump fluence to be attenuated by several orders of magnitude (typically a full fluence dependence analysis will consist of 100%, 75%, 50%, 25%, 10%, 5%, and 1% of the total energy).

To obtain the temporal dynamics of charge carriers, it is necessary to be able to vary the time delay of the pump pulse. Like the THz beam, the time delay of the pump pulse is controlled using a delay stage, which provides a total time delay of 1250 ps while the beam is mechanically chopped at 1.25 kHz before entering the sample box. This is half the THz chopper frequency and needs to be taken into account when calculating fluences.

Due to space restriction, inside the sample box, the pump beam is focussed through a hole in the back of the second off-axis parabolic mirror. It should be noted that because the beam is going through a tiny hole, a lens with the correct focal length must be chosen such that the beam does not hit the sides of the pinhole. After passing through, the focal point beam then re-expands before illuminating the sample. The pump beam diameter should be much greater than the THz beam at the sample position to ensure uniform photoexcitation of the sample surface. Furthermore, the THz probe beam must sit in the centre of the pump beam and this can be checked by performing a series of measurements as depicted in Figure 3.13. Any remaining pump-beam light is blocked by a cellulose-nitrate filter, which is transparent to THz radiation, but block the pump beam and so protect the THz detection crystal.

Determining the beam waist size: The overlap of the THz pulse with the pump pulse is critical as otherwise this can cause irregular, non-reproducible results. This is due to the fact that the pump beam has an energy density distribution similar to a Gaussian function and for each fluence, a certain number of photoexcited charge carriers are pumped into the conduction band. If the THz pulse is not centred, the charge density across the probed area would be deficient and this will be reflected in the calculation of charge density and any parameters depending on the latter.

The Pump Stage: As with the THz pulse delay stage, the pump beam stage should be correctly aligned as this is critical in extracting carrier dynamics over the whole 1250 ps range. To check whether this has been done properly, we choose a material with a very

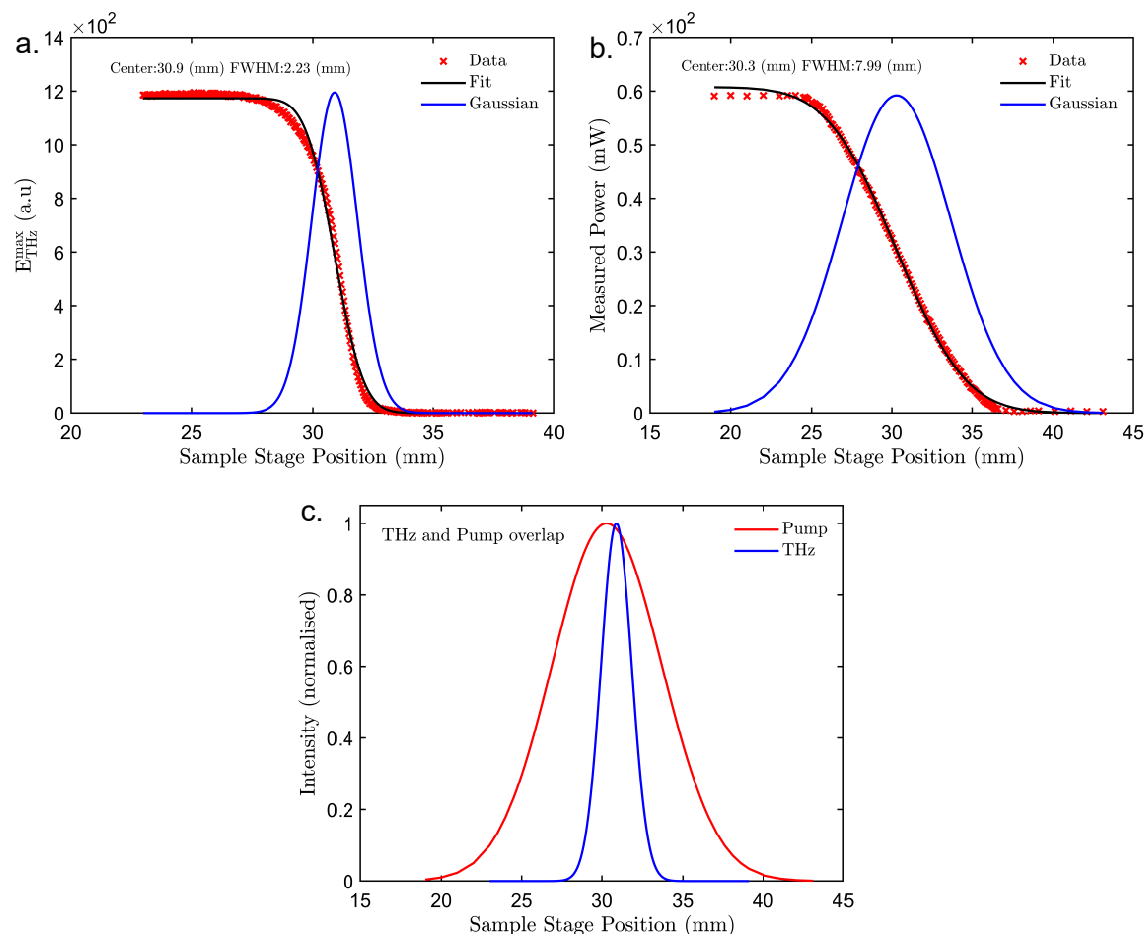


Figure 3.13: Beam Width Measurements: Beam alignment is critical in order to get good and reliable data. In time-resolved spectroscopy, the pump beam photoexcites the sample at various time delays, and the change in E_{THz} is measured as a function of time, τ . This means that the sample must be uniformly photodoped to ensure constant photoconductivity or charge carrier pumping across the sample surface at any particular instant. The pump beam must be at least the size of the sample area, while the THz must be as small as possible for the best overlap integral. In a. and b. the THz and the pump beam waists respectively are measured by scanning a razor blade across the sample stage Figure 3.14. The intensities are plotted against distance and an error function is fitted to obtain their centre and their corresponding FWHM. In c. both plotted Gaussian profiles are overlaid on top of each other to see whether the THz is in middle of the pump beam. It should be noted that the same razor blade and stage positions should be used when measuring beam widths such that this method is valid. In this situation, the THz and the pump beams were off by 0.6 mm, which should not cause significant issue when acquiring data.

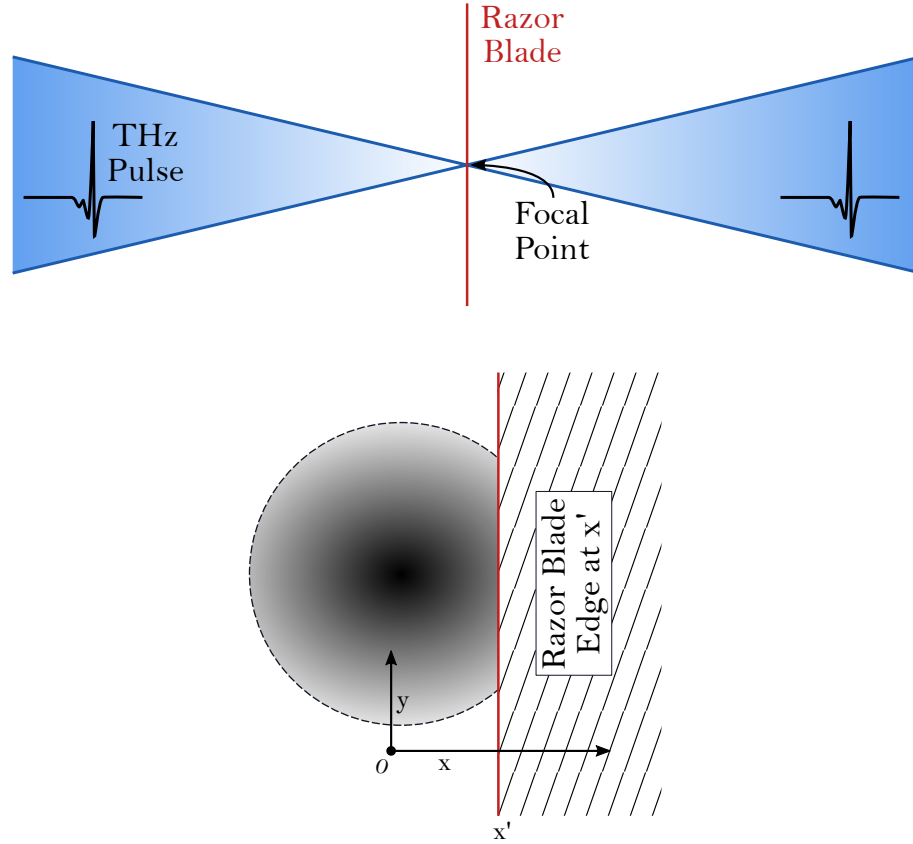


Figure 3.14: **Razor Blade Experiment:** Schematic diagram showing how to determine the FWHM or standard deviation of the THz and pump pulse from a razor blade.

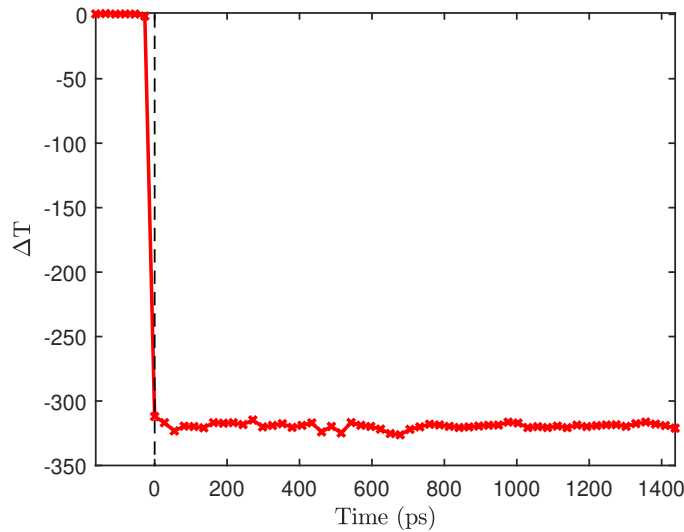


Figure 3.15: **Silicon Wafer Pump Scan:** Photoconductivity decay of Silicon wafer. Si has a very long carrier lifetime such that over the full range of the pump delay stage, it has not decayed at all. Using this to our advantage, it is then possible to check whether the pump stage has been aligned properly. A perfectly flat line is what we expect. Any misalignments or kinks in the motorised stage will result in either a decaying curve or humps.

long carrier lifetime and silicon is the ideal material for this. A typical pump scan is performed and the effective signal over the whole delay line should be as flat as possible. Any dents or misalignment would result in humps or increase/decrease of the signal after the onset. Figure 3.15 shows the pump scan for a perfectly aligned stage.

Here, it is helpful to know that care must be taken to keep the pump excitation fluence as low as possible (around 3-5% of the maximum value), as the THz refractive index of silicon changes upon photoexcitation. At too high fluences, the silicon wafer will exhibit changes in the refractive index and hence a change in the decay process. To avoid changing the time delay between the THz pulse and the gate beam, the excitation fluence must be kept as low as possible, otherwise the scan will not appear flat as the stage scans.

During experiments the sample box, including the sample, THz emitter and THz detector, are evacuated and held under a vacuum of 10^{-2} mbar. This is due to the fact that THz is strongly absorbed by water vapour in the air, resulting in dips in the frequency domain. For cryogenic measurements, i.e. temperature-dependent measurements, the whole box is evacuated to a high vacuum, typically on the order of 10^{-7} mbar to avoid air molecules condensing on the surface of the sample when it is brought down to very low temperatures.

3.6 THz Electric Field Strength

Earlier in this chapter, it was mentioned that an applied electric field, in this case the E-field being our THz pulse, to a non-centrosymmetric electro-optic crystal will change its index ellipsoid that will consequentially alter the polarisation state of an optical gate pulse. The magnitude of this polarisation change manifests itself in a voltage difference at the pair of photodiodes and is dependent on the strength of the electric field. By exploiting this change, one is able to gauge how strong the field is at the detector position and by means of suitable approximations, at the sample position. What follows is a method how one is able to quantify the THz E-field strength.

Consider Figure 3.18 depicting a THz pulse propagating along the z direction through an EO crystal. The electric field associated with the pulse will introduce some mixed terms in the index ellipsoid and the major axes of the ellipsoid are no longer parallel to the crystal axes shown in the figure. Let the new set of axes be x' , y' , and z' and that the THz electric field is in the x direction. The new principal refractive indices are then given

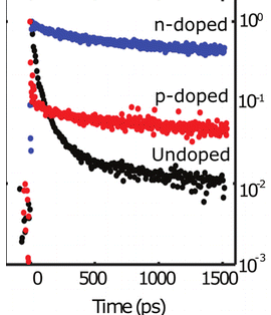
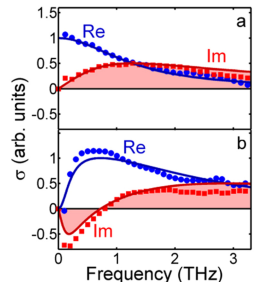
	Pump Scans	Spectral Scans
Fixed Stages	THz and Gate	Pump and Gate
Moving Stage	Pump Pulse	THz Pulse
Independent Variable	Pump Delay	THz Delay
Dependent Variable	$\Delta T/T(t)$	$T_{\text{THz}}(\omega)$
Plots		
Measurement	$\Delta T/T$	T_{THz}
Extracted Parameters	Carrier Lifetime, Scattering Rates, Saturation of Traps, Recombination Rates	Carrier Mobility, Carrier Density/Doping, Plasma Frequency, Dielectric Constant

Table 3.5: Table summarising the various experiments that can be carried out using a THz-TRS and the different parameters that can be extracted.

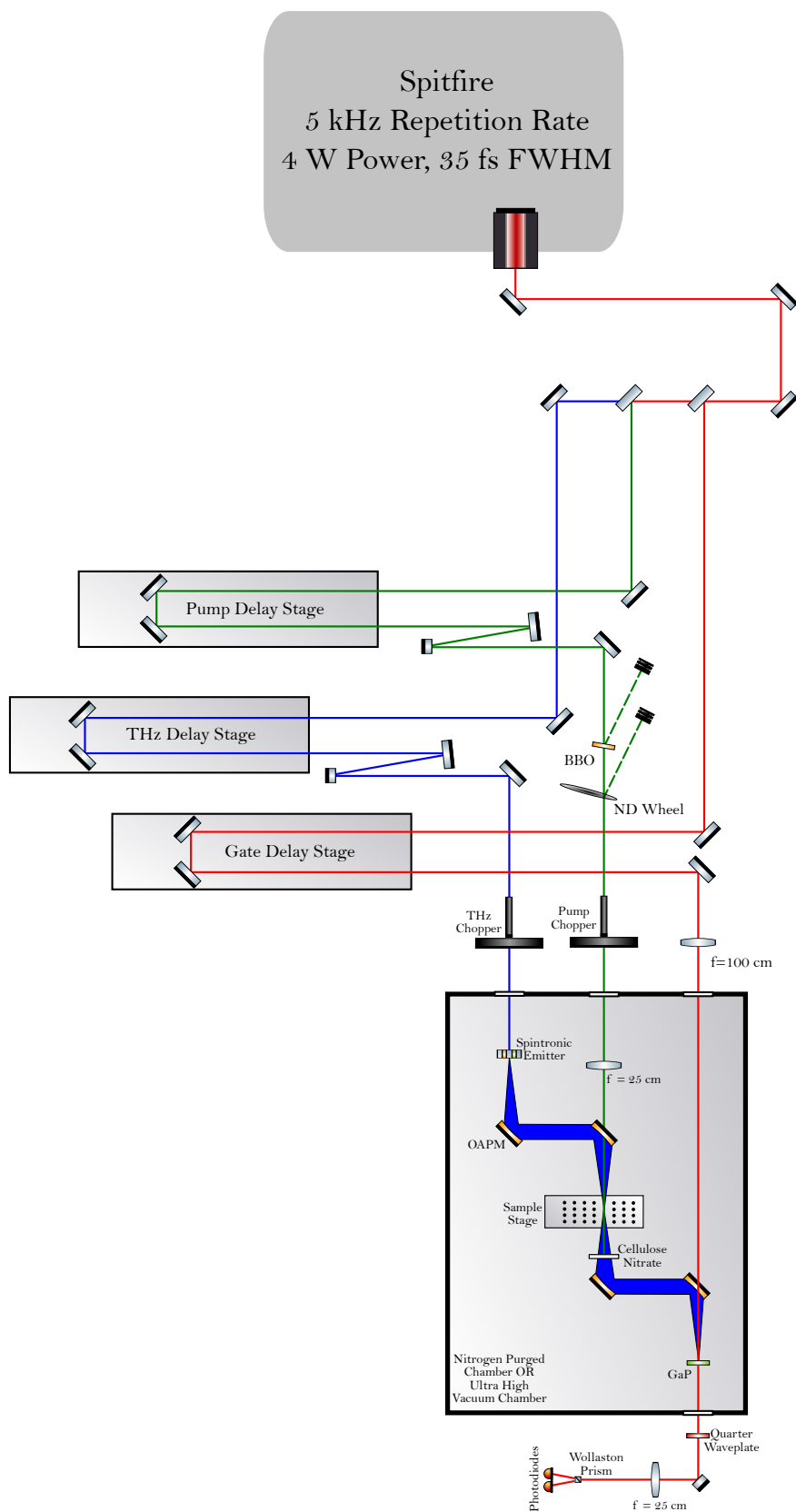


Figure 3.16: **THz-TRS I:** Schematic of the THz-TRS in Rm146.

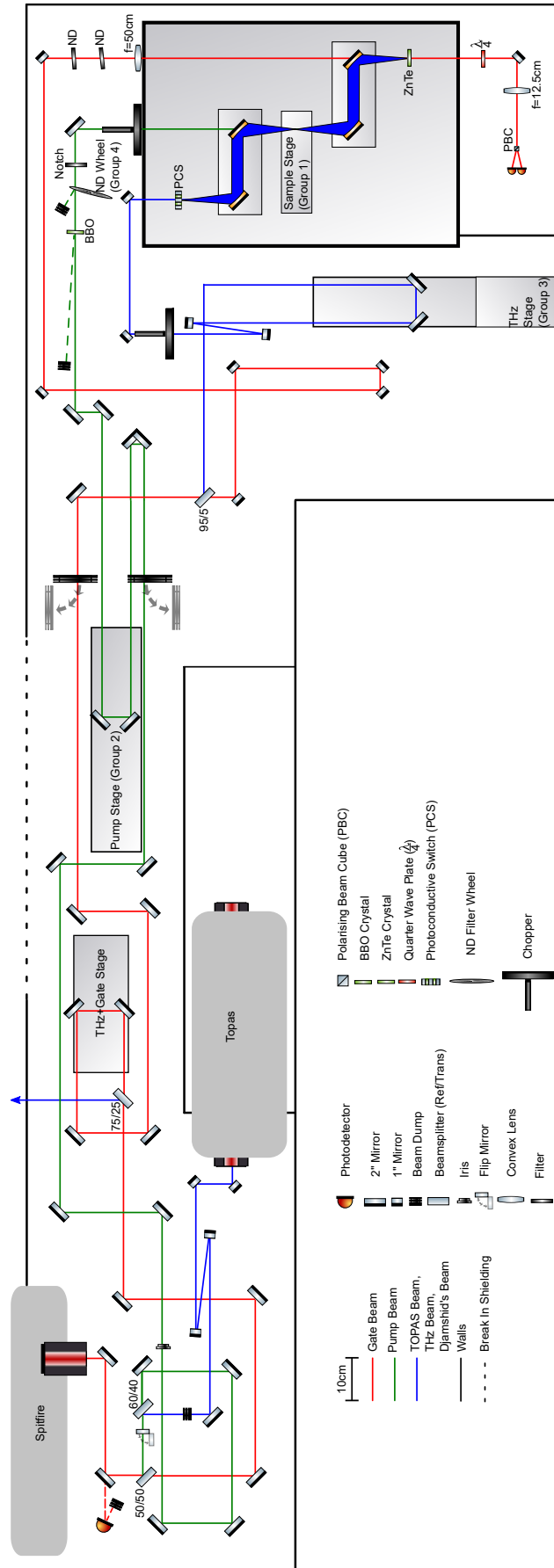


Figure 3.17: THz-TRS II: Schematic of the THz-TRS in Rm145.

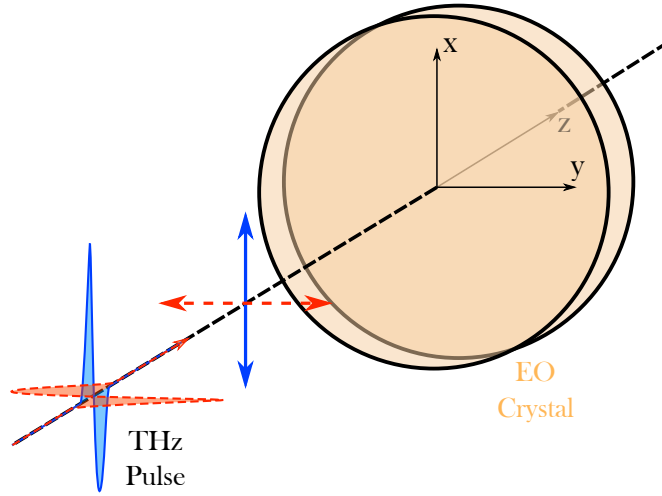


Figure 3.18: **Optic Axis:** The x , y , and z axes of an EO crystal. The THz pulses travel in the z -direction and be either be polarized parallel to the x or y axes. In our case, it is ensured that the polarisation is horizontal. This is achieved by the magnetic field direction in the spintronic emitter as explained earlier.

by: [170]

$$\begin{aligned} n_{x'} &= n_0 - \frac{1}{2}n_0^3r_{41}E_z, \\ n_{y'} &= n_0 + \frac{1}{2}n_0^3r_{41}E_z, \\ n_{z'} &= n_e. \end{aligned} \quad (3.11)$$

where r_{41} is the electro-optic coefficient of the crystal, and n_0 and n_e are the ordinary and extraordinary axis refractive index respectively. The birefringence felt by the crystal is then given by:

$$n_{y'} - n_{x'} = n_0^3r_{41}E_z. \quad (3.12)$$

If L is the thickness of the crystal, the phase retardation acquired is

$$\Gamma = \frac{\omega}{c}(n_{y'} - n_{x'})L = \frac{2\pi}{\lambda}n_0^3r_{41}V, \quad (3.13)$$

where V is the voltage generated while the electric field passes through. The phase retardation is proportional to the voltage applied. The electric field is then given by: [170]

$$E_{\text{THz}} = \frac{2\Delta V}{V_{\text{max}}} \cdot \frac{c}{\omega n_0^3r_{41}L}, \quad (3.14)$$

where V_{max} is the voltage when all the light goes to one photodiode only, i.e. when there is no THz passing through the crystal, ω is the angular frequency of the optical gate pulse, and L is the width of the crystal. ΔV is the voltage difference when a THz pulse passes through. For our system in both labs, the electric field strength is on the order of kV/m.

3.7 Data Extraction

The electrical resistance of metals and semiconductors, or its inverse, the conductivity, is a crucial parameter to gauge, especially when it comes to device applications. The conductivity of a material is dependent on many factors: grain boundaries in films, atom size, stoichiometry and the concentration/density of charge carriers (electrons, holes and quasiparticles) in the material and on how easily these can flow through the material. The carrier dynamics are affected by scattering processes such as collisions with other charge carriers and interactions within the crystal lattice that complicate the concept of conductivity. These processes typically result in a spectral signature in the lower THz range. The ability to generate THz radiation as freely propagating beam and detecting it, THz spectroscopy is therefore an ideal non-invasive tool to measure the conductivity and obtain knowledge about charge-carrier behaviour without the need for electrical contacts. Compared to electrical methods which introduce a lot of constraints and uncertainties and which may damage the material, THz spectroscopy offers a more decisive route to understanding the optoelectronic properties of semiconductors. The material properties can then be expressed either as a complex-valued conductivity or the fully equivalent complex-valued dielectric function.

The parameter extraction procedures described in the following sections are mainly applicable to semiconductor nanowires (NWs) as this thesis is concerned with such materials. In addition, it deals with the complex refractive index of *c*-sapphire and the method used in the data analysis is described in detail.

3.7.1 Frequency-Dependent Complex Conductivity

THz spectroscopy allows one to measure the response of charge carriers in a sample subjected to an applied electric field, which in this case is the THz electric field. As will be shown in the next few sections, this electrical response is directly proportional to the overall conductivity of the materials, which in turn is directly related to the optical properties of the probed material: complex refractive index and dielectric function. As such, in order to fully characterise and understand the fundamental physics of semiconductors, we would need to be able to extract these material properties. By measuring both the transmission and reflection functions, the complex conductivity, $\tilde{\sigma}(\omega)$, can be extracted. It is also worth noting that $\tilde{\sigma}(\omega)$ is directly related to the charge current density and therefore a material's full response can be probed. From there, it is easy to pull out fundamental parameters such as the plasma frequency, charge carrier lifetime, and charge carrier mobilities.

To extract nanowire conductivity from THz measurements, we need to consider the interaction of the pulse with the nanowires and the sample substrate (if it is not a free-standing). The nanowire geometry is also of great importance since we are looking at quasi-1D systems with dimensions much smaller than the diffraction-limited spot size of the THz probe pulse impinging on the sample. An effective medium theory (EMT) was developed to take all of this into consideration, an explanation of which is outlined below. Additionally, in order to fully understand how we can relate THz measurements to the extraction of NW conductivity, it is necessary to show that the dielectric function and the refractive index are related to the conductivity. What follows is a brief derivation of the required formulae that will be helpful later on.

Under the influence of a THz electric field, $E(\omega)$, a nanowire's electrical response is quantified by its conductivity, $\tilde{\sigma}(\omega)$, and its current density, $J(\omega)$, and they are related by the following equation:

$$J(\omega) = \sigma(\omega).E(\omega). \quad (3.15)$$

The complex conductivity is frequency-dependent and consists of both a real part and an imaginary part:

$$\tilde{\sigma}(\omega) = \sigma_{\text{real}}(\omega) + i\sigma_{\text{imaginary}}(\omega). \quad (3.16)$$

The physical significance of a real part and an imaginary is related to the electrical resistance and capacitance/inductance respectively of the NWs. At very low frequencies, the imaginary part of the conductivity is very small while at THz frequencies it is too significant to be ignored.

The dielectric function or permittivity, $\tilde{\epsilon}(\omega)$, is also complex and frequency-dependent and can be written as:

$$\tilde{\epsilon}(\omega) = \epsilon_{\text{real}}(\omega) + i\epsilon_{\text{imaginary}}(\omega). \quad (3.17)$$

$\tilde{\epsilon}(\omega)$ and $\tilde{\sigma}(\omega)$ are related by the following equation:

$$\tilde{\epsilon}(\omega) = \tilde{\epsilon}_L(\omega) + \frac{i\tilde{\sigma}(\omega)}{\omega\epsilon_0} \quad (3.18)$$

where ϵ_0 is the dielectric permittivity of free space and has a value of $8.854 \times 10^{-12} \text{ Fm}^{-1}$, and $\tilde{\epsilon}_L(\omega)$ is the frequency-dependent dielectric function of the lattice component of the nanowire. Semiconductor NWs exhibiting a single transverse-optical phonon mode (TO), $\tilde{\epsilon}_L(\omega)$ is given by:

$$\tilde{\epsilon}_L(\omega) = \epsilon_{\infty} + (\epsilon_{\text{st}} - \epsilon_{\infty}) \frac{\omega_{\text{TO}}^2}{\omega_{\text{TO}}^2 - \omega^2 - i\omega\gamma_{\text{TO}}} \quad (3.19)$$

where

1. ϵ_∞ is the high frequency optical dielectric constant of the NW,
2. ϵ_{st} is the low frequency static dielectric constant of the NW,
3. ω_{TO} is the angular frequency of the transverse-optical phonon mode,
4. γ_{TO} is the phonon damping constant.

For most of the frequency range, the values for these parameters have been documented and therefore $\tilde{\epsilon}_L(\omega)$ is easily calculated. However, at frequencies above and below the TO phonon mode, $\tilde{\epsilon}_L(\omega)$ can be approximated as follows:

$$\tilde{\epsilon}_L(\omega) = \begin{cases} \epsilon_{\text{st}}, & \text{if } \omega \ll \omega_{\text{TO}}. \\ \epsilon_\infty, & \text{if } \omega \gg \omega_{\text{TO}}. \end{cases} \quad (3.20)$$

The complex refractive index (a definition of which is given below) of the NWs is directly related to its complex dielectric function. By definition therefore, it is also connected to the complex conductivity. It is then fairly obvious that these parameters contain equivalent information. Knowing one would allow us to know the other and using THz-TDS, we are able to extract these information.

3.7.1.1 Equilibrium Conductivity

THz-TDS does not in general examine the photoexcited/photodoped samples. By measuring the transmission function as a function of frequency, it allows us to measure the equilibrium conductivity of the NWs (the reader should note that to avoid confusion, equilibrium conductivity is different from photoconductivity).

As mentioned briefly before, an effective medium theory (EMT) is necessary to model NW systems: the nanowires are considered to be embedded in its surrounding medium, and the whole thing is treated as single composite layer l . By extension, all the optical constants are considered for the composite layer:

1. $\epsilon_l(\omega)$ is the effective complex dielectric function,
2. $\tilde{n}_l(\omega)$ is the effective complex refractive index,
3. σ_l is the effective complex conductivity, and
4. d_l is the effective thickness.

The NW composite layer consists of an ensemble of individual nanowires and they all occupy a volume fraction f , which can be obtained via microscope images. The substrates we used throughout this thesis is standard z -cut quartz discs of thickness 2 mm and a diameter of 13 mm.

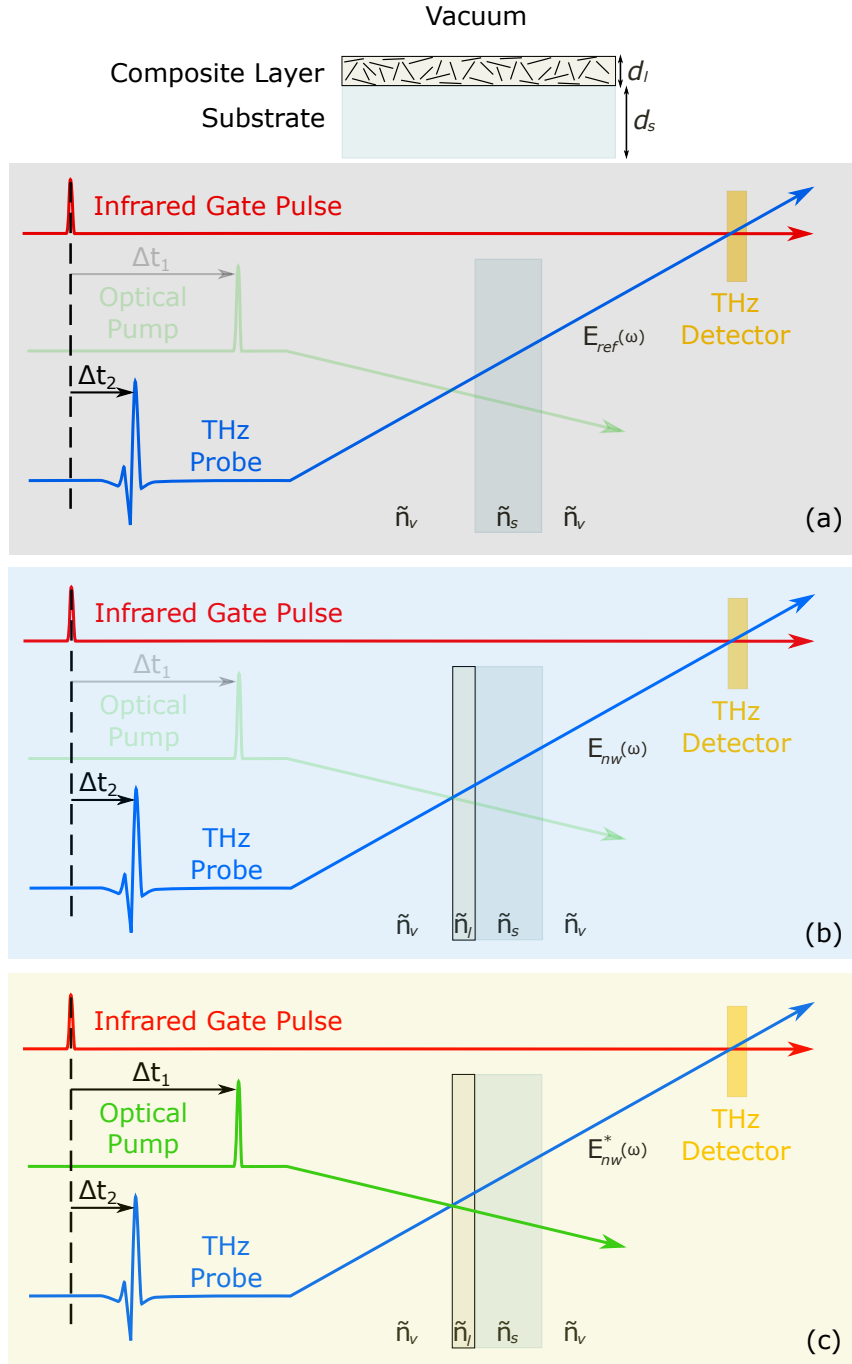


Figure 3.19: **Experimental Setup:** Schematic diagram of the models used to extract nanowire equilibrium conductivity and non-equilibrium conductivity. In the former (b), we only have the interaction of the THz pulse with the NW sample on a substrate which would be the equilibrium signal signal, $E_{nw}(\omega)$. In the latter (c), we have the interaction of the pump signal with the sample first followed by the THz probe pulse after a short delay. This gives the non-equilibrium signal, $E_{nw}^*(\omega)$. As our reference measurement, $E_{ref}(\omega)$, we used a bare substrate.

The theoretical complex transmission function, $\tilde{T}_{\text{theory}}(\omega)$, can be derived by considering the Fresnel expressions which take into account the transmission and reflection coefficients of a wave propagating through a medium. For such a configuration, we have [14]

$$\begin{aligned}\tilde{T}_{\text{theory}}(\omega) &= \frac{\tilde{E}_{\text{nw}}(\omega)}{\tilde{E}_{\text{ref}}(\omega)} \\ &= \frac{2\tilde{n}_l(\tilde{n}_v + \tilde{n}_s)}{(\tilde{n}_v + \tilde{n}_l)(\tilde{n}_s + \tilde{n}_l)} \exp\left(\frac{i\omega d_l}{c}(\tilde{n}_l - \tilde{n}_v)\text{FP}\right)\end{aligned}\quad (3.21)$$

where the subscripts l, v, s denote the composite layer, vacuum, and sample respectively. $\tilde{n}_i$ are the complex refractive indices of the respective medium, ω is the angular frequency, d_l is the thickness of the composite layer, c is the speed of light in free-space, and FP represents the Fabry-Perot terms accounting for multiple reflections within the composite layer at the interfaces.

The composite layer has a thickness that can be approximated by the nanowire diameter which is on the order of nanometres. This is very thin in comparison to the wavelength of THz radiation. In addition, the thickness of the substrate is much larger than the wavelength of the THz and together, through a series of approximations, [14] $\tilde{T}_{\text{theory}}(\omega)$ simplifies into the following expression

$$\tilde{T}_{\text{theory}}(\omega) = \frac{(1 + \tilde{n}_s)}{(1 + \tilde{n}_s) - \frac{i\omega d_l(\tilde{n}_l^2 + \tilde{n}_s)}{c}} \quad (3.22)$$

The complex dielectric function, $\tilde{\epsilon}(\omega)$, is related to the complex refractive index, $\tilde{n}(\omega)$, via the following relationship

$$\tilde{n}(\omega) = \sqrt{\tilde{\epsilon}(\omega)\mu} \quad (3.23)$$

By substituting this into Equation (3.22), and taking $\mu = 1$ due to the non-magnetic nature of the sample, $\tilde{T}_{\text{theory}}(\omega)$ can be re-arranged into

$$\tilde{\epsilon}_l = \frac{ic(1 + \tilde{n}_s)}{\omega} \left(\frac{1}{\tilde{T}(\omega)} - 1 \right) - \tilde{n}_s \quad (3.24)$$

Jumping back to Equation (3.18), once the dielectric function expression is found, it is possible to extract the effective complex conductivity of the composite layer

$$\tilde{\sigma}_l(\omega) = \frac{\epsilon_0 c(1 + \tilde{n}_s)}{d_l} \left(\frac{1}{\tilde{T}(\omega)} - 1 \right) + i\omega\epsilon_0(\tilde{n}_s + \epsilon_l(\omega)) \quad (3.25)$$

In the case of highly conductive samples, the second term in the above expression goes to zero, and the effective conductivity is approximated to

$$\tilde{\sigma}_l(\omega) = \frac{\epsilon_0 c(1 + \tilde{n}_s)}{d_l} \left(\frac{1}{\tilde{T}(\omega)} - 1 \right) \quad (3.26)$$

Once the transmission function is obtained via THz-TDS, it is then possible to extract the complex frequency-dependent conductivity of the composite layer. However, to obtain the conductivity of the nanowires alone, it is imperative to use the effective medium theory. This will be detailed shortly.

3.7.1.2 Conversion of THz Transmission to Photoconductivity

Photoconductivity is a well-known optical and electrical phenomenon featuring primarily in the physics of semiconductors. It is essentially an effect whereby the electrical conductivity increases due to the absorption of light radiation above the bandgap of the material. Several mechanisms (as have been described in the previous chapter), such as the absorption of the incident radiation, the generation of the electron-hole pairs, the carrier dynamics, photon reabsorption, and doping densities are involved in photoconductivity successively or simultaneously which make the whole process rather complicated. To induce excitation, the energy of incident photoexcitation pulse must be larger than the bandgap of the material so as to promote the electrons into the conduction band, or to excite the impurities within the bandgap, ultimately rendering the material conductive. The increase of the electrical conductivity depends on the number density of the photogenerated electron-hole pairs and the mobility of the carriers, while the duration of the increase is determined by many factors, such as the lifetime of the carriers or the time for the carriers to be decay/relax back into equilibrium state.

The photoconductivity of a sample, $\Delta\sigma$, is extracted from the OPTP measurements by taking the ratio of the change in THz transmission induced by a photoexcitation pulse to the THz transmission without any photoexcitation, $\frac{\Delta T}{T}$. The nanowires are considered to be embedded within a surrounding layer of thickness, d , which is the average diameter of the nanowire; and to have an effective areal fill factor obtained from optical microscope images. The transmitted terahertz fields with and without the optical pump are described as follows:

$$\begin{aligned} T_{\text{on}} &= f_w T_{w*} + (1 - f_w) T_v \\ T_{\text{off}} &= f_w T_w + (1 - f_w) T_v \end{aligned} \quad (3.27)$$

where T_w and T_v are the terahertz transmitted electric fields through the nanowires and surrounding vacuum respectively, with * denoting a photoexcited state. The pump beam does not change the complex refractive index of the vacuum, so the electric fields T_v , T_w and T_{w*} can be written as:

$$\begin{aligned}
T_v &= e^{in_v \omega d / c} T_i \\
T_w &= t_{vw} t_{wv} e^{in_w \omega d / c} F P_{vwv} T_i \quad . \\
T_{w*} &= t_{vw*} t_{w*v} e^{in_{w*} \omega d / c} F P_{vw*v} T_i
\end{aligned} \tag{3.28}$$

where t_{ij} are the Fresnel transmission coefficients, $F P_{ijk}$ the Fabry-Pérot terms, c is the speed of light in vacuum and n_{w*} , n_w the refractive indices for the nanowires with and without photoexcitation respectively. By combining Equations (3.27) and (3.28), the ratio of terahertz fields for the nanowires with and without photoexcitation is given in terms of the OPTP measurement of $\frac{\Delta T}{T}$:

$$\frac{T_{w*}}{T_w} = \frac{\Delta T}{T} \left[1 + \left(\frac{1}{f_w} - 1 \right) \frac{T_v}{T_w} \right] + 1. \tag{3.29}$$

where $\Delta T = T_{\text{on}} - T_{\text{off}}$, the photoinduced change in transmission and $T = T_{\text{off}}$, the THz transmission in the absence of photoexcitation. At THz frequencies, the thin film limit can be applied, as $\frac{n \omega \delta}{c} \ll 1$, so the approximation $\frac{T_v}{T_w} = 1$ can be made which greatly simplifies the calculation. Hence, a parameter A can be defined such that:

$$A = \frac{T_w}{T_{w*}} = \frac{1}{\frac{1}{f_w} \frac{\Delta T}{T} + 1}. \tag{3.30}$$

Substituting in the appropriate $F P_{ijk}$ and t_{ij} into Equation (3.29) and (3.30) and applying the thin film limit, the following equation is obtained:

$$\frac{T_{w*}}{T_w} = \frac{2 - \frac{i \omega d}{c} (1 + n_w^2)}{2 - \frac{i \omega d}{c} (1 + n_{w*}^2)}. \tag{3.31}$$

Substituting in the general relation $n^2 = \epsilon$ to the above equation:

$$\epsilon_{w*} = \left[-\frac{T_w}{T_{w*}} \left(2 \frac{c}{i \omega d} - (1 + \epsilon_w) \right) + 2 \frac{c}{i \omega d} - 1 \right], \tag{3.32}$$

where ϵ_{w*} and ϵ_w are the dielectric constants of the nanowires with and without photoexcitation respectively. The photoinduced conductivity, $\Delta \sigma$ is then given by:

$$\epsilon_{w*} = \epsilon_w + \frac{i\Delta\sigma}{\omega\epsilon_0}, \quad (3.33)$$

where ϵ_0 is the permittivity of free space. Substituting (3.35) into (3.36), the photoinduced conductivity can be extracted as follows:

$$\Delta\sigma = \epsilon_0 (A - 1) \left[\frac{2c}{d} - i\omega (1 + \epsilon_w) \right]. \quad (3.34)$$

Thus, using Equations 3.34 and (3.34), the photoinduced conductivity can be extracted from OPTP measurements using tabulated results from previous works for ϵ_w , with f_w and d taken from optical electron microscope measurements.

3.7.1.3 Effective Areal Overlap Integral

The photoinduced charge carrier density is proportional to the energy density (fluence) impinging onto a sample: a high fluence will photodope a large number of carriers into the conduction band and a low fluence will photodope a low number of carriers. When probing charge carrier dynamics, it is important to have the photoexcitation beam much larger than the probe beam, i.e. the THz beam. The beam waist size of the former must be such that the sample is photoexcited uniformly while the beam waist size of the latter must be as tightly focused as possible to induce intense THz electric field amplitudes.

The charge carrier mobility depends on the photoinduced sheet/sample conductivity which in turn depends on the number of photo-excited charge carriers. Ultimately therefore, one needs to calculate the absorbed intensity of the photoexcitation pulse which is directly proportional to the overlap of the THz pulse with the pump pulse given their Gaussian profiles. Presented below is a good estimate of how to determine the overlap, known as the effective areal overlap (A_{eff}).

The probed areal charge density, N/A_{eff} , is given by the following:

$$\frac{N}{A_{\text{eff}}} = \int_0^\infty \int_0^{2\pi} \hat{n}_{\text{pump}} f_{\text{THz}} r dr d\theta, \quad (3.35)$$

where $rdrd\theta$ is the integrated area, $\hat{n}_{\text{pump}}$ is the 2D areal charge density function, and f_{THz} is the normalised THz areal spread ($\int \int f_{\text{THz}} dA = 1$). Assuming both beams have a

2D Gaussian profiles,

$$\begin{aligned}
 f_{\text{THz}} &= \frac{1}{2\pi\delta_{\text{THz}}^2} \exp\left(\frac{-x^2}{2\delta_{\text{THz}}^2} + \frac{-y^2}{\delta_{\text{THz}}^2}\right) \\
 &= \frac{1}{2\pi\delta_{\text{THz}}^2} \exp\left(\frac{-r^2}{\delta_{\text{THz}}^2}\right) \\
 \hat{n}_{\text{pump}} &= \frac{N}{2\pi\delta_{\text{pump}}^2} \exp\left(\frac{-r^2}{\delta_{\text{pump}}^2}\right),
 \end{aligned} \tag{3.36}$$

therefore,

$$\frac{N}{A_{\text{eff}}} = \frac{N}{(2\pi)^2\delta_{\text{THz}}^2\delta_{\text{pump}}^2} \underbrace{\int_0^\infty \int_0^{2\pi} \exp\left(\frac{-r^2}{2}\left(\frac{1}{\delta_{\text{THz}}^2} + \frac{1}{\delta_{\text{pump}}^2}\right)\right) r dr d\theta}_{\frac{2\pi}{\frac{1}{\delta_{\text{THz}}^2} + \frac{1}{\delta_{\text{pump}}^2}}} \tag{3.37}$$

giving A_{eff} as:

$$A_{\text{eff}} = 2\pi(\delta_{\text{THz}}^2 + \delta_{\text{pump}}^2). \tag{3.38}$$

3.7.1.4 Effective Medium Theory

In a typical THz-TDS (or OPTP) experiment, one measures directly the conductivity and dielectric function of the composite layer. To extract the conductivity of the nanowire material, one has to consider the geometry of the nanowires and the nature of the electromagnetic pulse going through the sample. Characteristic dimensions of the nanowires are on the order of nanometres or microns. These are considerably smaller than the diffraction-limited spot size of the incident THz probe (≈ 1 mm) and present an issue when extracting nanowire parameters. It is therefore appropriate to use an effective medium theory (EMT) which treats the sample as a composite layer consisting of the nanowires embedded in its surrounding.

The EMT correlates the dielectric function of the composite layer, ϵ_l , to that of the nanowires, ϵ_{nw} , the surrounding medium (i.e. vacuum), ϵ_h , and the volume fraction occupied by the nanowires, f . This relationship allows one to use the EMT in reverse and thereby extracting the nanowire dielectric function and by extension its conductivity.

A few EMTs have been developed over time but the two most commonly presented ones are the Maxwell-Garnett and the Bruggeman models. [233] The Maxwell-Garnett formula is given by the following equation:

$$f \frac{\epsilon_{\text{nw}} - \epsilon_h}{\epsilon_{\text{nw}} + \kappa\epsilon_h} - \frac{\epsilon_l - \epsilon_h}{\epsilon_l + \kappa\epsilon_h} = 0, \tag{3.39}$$

which can be rearranged in either of two forms: one to solve for ϵ_{nw} :

$$\epsilon_{\text{nw}} = \epsilon_{\text{h}} \left(\frac{f(\epsilon_{\text{l}} + \kappa\epsilon_{\text{h}}) + \kappa(\epsilon_{\text{l}} - \epsilon_{\text{h}})}{f(\epsilon_{\text{l}} + \kappa\epsilon_{\text{h}}) - (\epsilon_{\text{l}} - \epsilon_{\text{h}})} \right), \quad (3.40)$$

or the other to solve for ϵ_{l} :

$$\epsilon_{\text{l}} = \epsilon_{\text{h}} \left(\frac{\kappa f(\epsilon_{\text{nw}} - \epsilon_{\text{h}}) + (\epsilon_{\text{nw}} + \kappa\epsilon_{\text{h}})}{-f(\epsilon_{\text{nw}} - \epsilon_{\text{h}}) + (\epsilon_{\text{nw}} + \kappa\epsilon_{\text{h}})} \right). \quad (3.41)$$

The Maxwell-Garnet EMT breaks down if percolation pathways exist for charge transport between NWs. This is particularly common in samples that have very long nanowires and one end of a nanowire sits on top of another thereby allowing inter-nanowire charge transport. However, most NW samples contain individual nanowires that are short enough such that they can be considered as well-isolated single-crystalline NWs. As a result, inter-NW percolative transport is usually not significant in these samples. This EMT theory also is not suitable when the volume fraction f the NWs occupy is too large. Therefore, in the case of large f , the Bruggeman approximation is more appropriate and can provide more accurate results for the NW conductivity:

$$f \frac{\epsilon_{\text{nw}} - \epsilon_{\text{l}}}{\epsilon_{\text{nw}} + \kappa\epsilon_{\text{l}}} + (1 - f) \frac{\epsilon_{\text{h}} - \epsilon_{\text{l}}}{\epsilon_{\text{h}} + \kappa\epsilon_{\text{l}}} = 0. \quad (3.42)$$

Just like the Maxwell-Garnet formula, this one can also be rearranged to solve for ϵ_{nw} in the following way:

$$\epsilon_{\text{nw}} = \epsilon_{\text{l}} \left(\frac{f(\epsilon_{\text{h}} + \kappa\epsilon_{\text{l}}) - (1 - f)\kappa(\epsilon_{\text{h}} - \epsilon_{\text{l}})}{f(\epsilon_{\text{h}} + \kappa\epsilon_{\text{l}}) + (1 - f)(\epsilon_{\text{h}} - \epsilon_{\text{l}})} \right). \quad (3.43)$$

The κ parameter is related to the depolarisation factor. The latter is essentially the extent to which the induced field inside the nanowire due to charge accumulation opposes the THz external electric field. Consequently, κ depends on the NW geometry and orientation relative to the electric field polarisation of the THz pulse: $\kappa = 2$ for spherical particles and $\kappa = 1$ for infinitely long cylinders oriented with their axes perpendicular to the THz electric field.

Although other EMTs exist, for analysis of the NW conductivity, both the Maxwell-Garnett and Bruggeman EMTs are the most appropriate, as they are derived considering the

local depolarisation fields arising in NWs under the applied electric field. This provides a link to the plasmon model, which is similarly based on the depolarisation fields in semiconductor NWs. This link can therefore be exploited by considering the Maxwell-Garnet approximation for conducting and non-conducting NWs. In the non-conducting case, $\epsilon_{\text{nw}} = \epsilon_{\text{L,nw}}$ and $\epsilon_{\text{l}} = \epsilon_{\text{L,l}}$, so becomes:

$$\epsilon_{\text{L,l}} = \epsilon_{\text{h}} \left(\frac{\kappa f(\epsilon_{\text{L,nw}} - \epsilon_{\text{h}}) + (\epsilon_{\text{L,nw}} + \kappa \epsilon_{\text{h}})}{-f(\epsilon_{\text{L,nw}} - \epsilon_{\text{h}}) + (\epsilon_{\text{L,nw}} + \kappa \epsilon_{\text{h}})} \right). \quad (3.44)$$

In the conducting case, $\epsilon_{\text{nw}} = \epsilon_{\text{L,nw}} + \frac{i\sigma}{\omega\epsilon_0}$ and $\epsilon_{\text{l}} = \epsilon_{\text{L,l}} + \frac{i\sigma_{\text{l}}}{\omega\epsilon_0}$ and becomes:

$$\epsilon_{\text{L,l}} + \frac{i\sigma_{\text{l}}}{\omega\epsilon_0} = \epsilon_{\text{h}} \left(\frac{\kappa f(\epsilon_{\text{L,nw}} + \frac{i\sigma}{\omega\epsilon_0} - \epsilon_{\text{h}}) + (\epsilon_{\text{L,nw}} + \frac{i\sigma}{\omega\epsilon_0} + \kappa \epsilon_{\text{h}})}{-f(\epsilon_{\text{L,nw}} + \frac{i\sigma}{\omega\epsilon_0} - \epsilon_{\text{h}}) + (\epsilon_{\text{L,nw}} + \frac{i\sigma}{\omega\epsilon_0} + \kappa \epsilon_{\text{h}})} \right). \quad (3.45)$$

Combining and solving for σ_{l} , gives:

$$\sigma_{\text{l}}(\omega) = \frac{\frac{A}{B}\sigma_{\text{nw}}}{B + (1-f)\frac{i\sigma_{\text{nw}}}{\omega\epsilon_0}}, \quad (3.46)$$

where the constants A and B are defined as:

$$\begin{aligned} A &= f\epsilon_{\text{h}}^2(\kappa + 1)^2 \\ B &= -f(\epsilon_{\text{L,nw}} - \epsilon_{\text{h}}) + (\epsilon_{\text{L,nw}} + \kappa \epsilon_{\text{h}}). \end{aligned} \quad (3.47)$$

Substituting in the Drude equation into gives:

$$\sigma_{\text{l}}(\omega) = \frac{A}{B^2} \frac{Ne^2}{m^*} \frac{i\omega}{\omega^2 - \omega_0^2 + i\omega\gamma}, \quad (3.48)$$

where the resonant frequency is given by:

$$\omega_0 = \sqrt{\frac{(1-f)}{B} \frac{Ne^2}{m^*\epsilon_0}}. \quad (3.49)$$

Thus, the conductivity takes the same functional form as the plasmon response described earlier and the resonant frequency displays the same dependence on the $\sqrt{N}$ as for the plasmon response. From the conductivity expression of the composite layer, the equilibrium NW conductivity can be extracted: [24]

$$\sigma_{\text{nw}}(\omega) = \frac{B\sigma_l}{\frac{A}{B} - (1-f)\frac{i\sigma_l}{\omega\epsilon_0}}. \quad (3.50)$$

Using the knowledge that $\Delta\sigma_{\text{nw}} = \sigma_{\text{nw}}^* - \sigma_{\text{nw}}$, the following expression for the NW conductivity can then be derived:

$$\begin{aligned} \Delta\sigma_{\text{nw}} &= \frac{B(\sigma_l + \Delta\sigma_l)}{\frac{A}{B} - (1-f)\frac{i(\sigma_l + \Delta\sigma_l)}{\omega\epsilon_0}} - \frac{B\sigma_l}{\frac{A}{B} - (1-f)\frac{i\sigma_l}{\omega\epsilon_0}} \\ \Delta\sigma_{\text{nw}} &= \frac{A\Delta\sigma_l}{\left(\frac{A}{B} - (1-f)\frac{i(\Delta\sigma_l + \sigma_l)}{\omega\epsilon_0}\right) \left(\frac{A}{B} - (1-f)\frac{i\sigma_l}{\omega\epsilon_0}\right)}. \end{aligned} \quad (3.51)$$

3.7.1.5 Extracting Nanowire Transport Parameters

Once an appropriate EMT has been applied and the data processed according to the abovementioned formulae, we obtain the nanowire complex conductivity, $\Delta\sigma_{\text{nw}}$. From the extracted photodoped NW conductivity (or alternatively, the photoconductivity), several material transport parameters can be extracted:

1. the charge-carrier density, n ,
2. the charge-carrier lifetime, τ ,
3. the surface recombination velocity, S ,
4. the charge-carrier mean free path, λ_{mfp} , and
5. the effective charge-carrier mobility, $\phi\mu$.

Firstly, the charge carrier density is directly related to the NW conductivity and can be obtained via the following equation:

$$n = \frac{2m^*}{\pi e^2} \int_0^\infty \sigma_l(\omega) d\omega, \quad (3.52)$$

where m^* is the effective mass of the charge carrier and e is the electronic charge. By probing how this carrier density changes with time after photoexcitation, the carrier lifetime can be determined by fitting the following carrier rate equation to the photoconductivity decay:

$$\frac{dn}{dt} = -\alpha n - \beta n^2 - \gamma n^3, \quad (3.53)$$

where α is the monomolecular recombination rate, β is the bimolecular radiative recombination rate and γ is the Auger recombination constant. For materials that are known to exhibit surface trapping, measurement of the photoconductivity decay for NWs of different diameters can determine the surface recombination velocity. The NW geometry is approximated as a cylinder of infinite length and a continuity equation describing the carrier concentration profile is given by,

$$\frac{\partial (\Delta n)}{\partial t} = D \frac{\partial^2 (\Delta n)}{\partial r^2} - \frac{\Delta n}{\tau_{\text{volume}}} = -S \Delta n, \quad (3.54)$$

where S is the surface recombination velocity, D is the diffusion constant and τ_{volume} is the electron lifetime of the bulk material. The solution of this continuity equation gives an exponential time decay of the carrier density with the following carrier lifetime:

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{volume}}} + \frac{4\beta^2 D}{d^2} = \frac{1}{\tau_{\text{volume}}} + \frac{4S}{d}, \quad (3.55)$$

where d is the NW diameter. This equation can then be fitted to plots of the photoconductivity decay to determine the carrier lifetime and surface recombination velocity of the material.

Furthermore, the effective carrier mobility, $\phi\mu$, can be extracted from the measured value of the photoconductivity and is given by:

$$\phi\mu = \frac{\Delta\sigma_{l,\max}(\omega) A_{\text{eff}}}{\phi} n_p e, \quad (3.56)$$

where μ is the mobility, A_{eff} is the effective area of the optical pump and THz pulse overlap, ϕ is the photon-to-carrier conversion rate and n_p is the photoexcited charge carrier density, which for a sample of thickness d equates to:

$$n_p = \frac{I}{Ed} \left(1 - e^{-d/\alpha}\right), \quad (3.57)$$

where I is the photoexcitation fluence, E is the photon energy and α is the absorption depth at the excitation wavelength for the material. By taking the peak value of the photoconductivity measured after photoexcitation and calculating the photoexcited carrier density, the effective carrier mobility can then be calculated. The effective carrier mobility is a sum of the carrier mobilities for both electrons and holes, as the two contributions cannot be separated. From this effective carrier mobility, the carrier scattering rate, mean free path, diffusion constant and length can then be obtained from the following equations respectively:

$$\begin{aligned} \mu &= \frac{e\tau}{m^*}, \\ \lambda_{\text{mfp}} &= v\tau = (\sigma n)^{-1}, \\ D &= \frac{k_b T \mu}{e}, \\ L &= (D\tau)^{1/2}, \end{aligned} \quad (3.58)$$

where τ is the carrier scattering rate, λ_{mfp} is the mean free path, D the diffusion constant, L the diffusion length, $k_b = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant and v is the average carrier velocity. Through this analysis, numerous key transport parameters can be determined and the data fitted to theoretical models.

3.7.1.6 Conductivity Models

I. Drude Model: when speaking about optoelectronic properties of semiconductors, the dielectric function is of great importance. One major contribution to the dielectric function is through the “free carriers”. The dynamics of these free carriers in semiconductors and metals can be understood in terms of a simple classical conductivity model, called the *Drude model*. This model, developed by Paul Drude in the 19th century, [234,235] is based on the classical equations of motion of an electron in an optical electric field, and gives the simplest theory of the optical constants. The postulates of the model are twofold: (1) electrons/carriers neither collide nor interact with each other, and (2) in between collisions, electrons/carriers do not interact with the scatterers. The collisions are instantaneous and randomise the electrons’/carriers’ momentum.

The classical equation for the drift velocity of the carrier is given by:

$$m \frac{d\mathbf{v}}{dt} + \frac{m\mathbf{v}}{\tau} = e\mathbf{E}_0 \exp(-i\omega t), \quad (3.59)$$

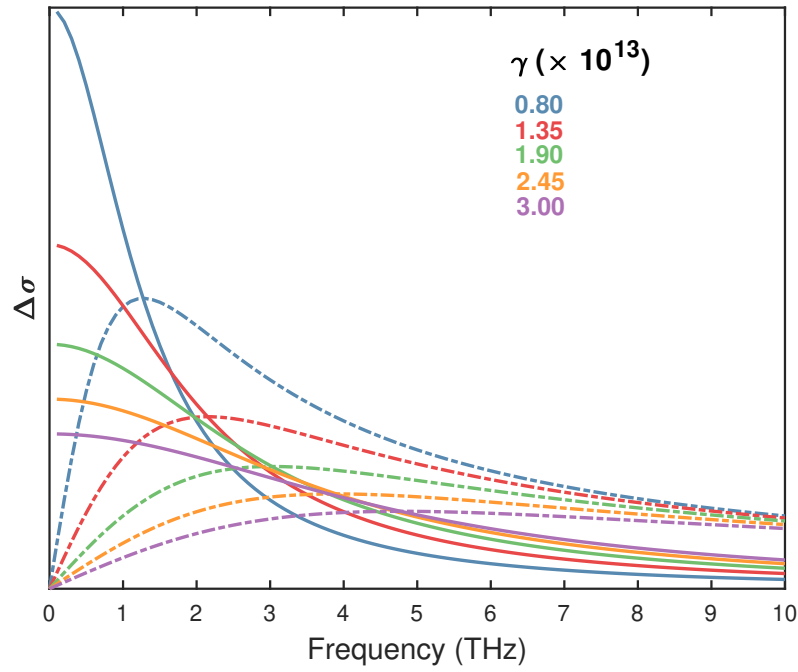


Figure 3.20: **Drude Model:** simulations of the Drude model with two different scattering rates, τ . On the left hand side, $\tau = 10^{13}$ and on the right hand side, $\tau = 10^{14}$. The real part has a peak conductivity of magnitude $Ne^2\tau/m_e$. The imaginary part starts at zero magnitude and peaks at $\omega\tau$ where it crosses the real part which has fallen to half of its initial value.

where τ is the relaxation time. The second term on the left hand side is known as the damping term due to the time-dependent electric field providing the driving force. Assuming the electrons undergo a sinusoidal motion described by:

$$\mathbf{v} = \mathbf{v}_0 \exp(-i\omega t), \quad (3.60)$$

then, Equation 3.59 becomes

$$\left(-mi\omega + \frac{m}{\tau}\right)\mathbf{v}_0 = e\mathbf{E}_0. \quad (3.61)$$

From EM theory, the current density, $\mathbf{j}$ is given by:

$$\mathbf{j} = ne\mathbf{v}_0 = \sigma\mathbf{E}_0, \quad (3.62)$$

where σ is the electrical conductivity. Substitution for the drift velocity then leads to:

$$\mathbf{v}_0 = \frac{e\mathbf{E}_0}{(m/\tau) - im\omega}. \quad (3.63)$$

Finally, combining the last two equations gives:

$$\sigma = \frac{ne^2\tau}{m(1 - i\omega\tau)}. \quad (3.64)$$

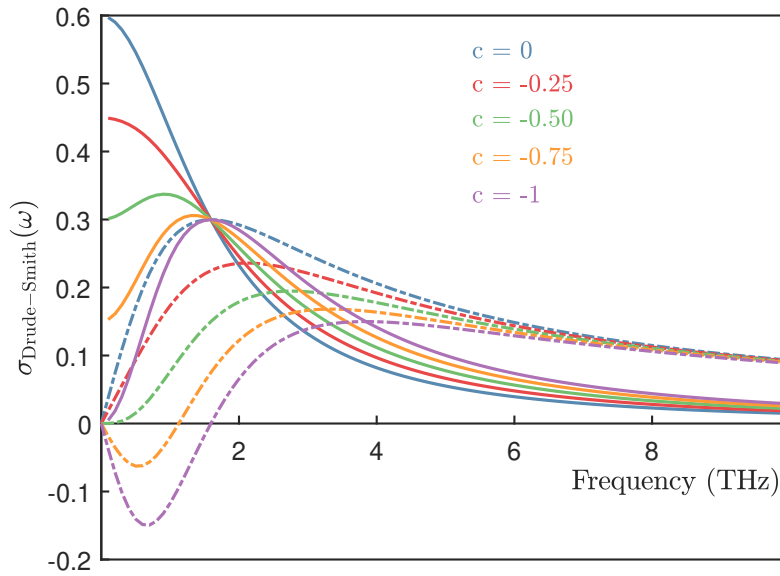


Figure 3.21: **Drude-Smith Model:** simulations of the Drude-Smith model with changing values of c between 0 and -1. Solid lines represent the real part of the conductivity and the colour-coordinated dashed lines represent its imaginary counterpart. For the case of $c = 0$, the DS equation is the same as the Drude model with no backscattering taken into account, and for the case of $c = -1$, the model includes complete backscattering from a single collision which resembles more the surface plasmon model. Increased backscattering, which corresponds to an increase in the magnitude of c reduces the real part of the conductivity at low frequencies while at the same time the restoring force due to the backscattering increases the imaginary part of the conductivity.

σ is the complex Drude conductivity for the case of a free carrier conduction. At low frequencies ($\omega\tau \ll 1$), semiconductors exhibit metal-like behaviour while at high frequencies ($\omega\tau \gg 1$) they act as insulators. This can be seen by considering the dielectric properties of the materials. A characteristic frequency at which the material changes from a metallic to an insulating behaviour is called the plasma frequency (ω_p). At this frequency, the dielectric function vanishes, and it is given by,

$$\omega_p = \sqrt{\frac{e^2 N}{\epsilon_0 m^*}}, \quad (3.65)$$

such that the Drude response now becomes,

$$\sigma_{\text{drude}}(\omega) = \frac{\omega_p^2 \epsilon_0 \tau}{1 - i\omega\tau}. \quad (3.66)$$

Thus by measuring the complex THz frequency resolved conductivity and fitting to Equation (3.66), these two parameters can be extracted directly. Further, if the effective mass is known, both the carrier mobility and the carrier density can be found. The complex conductivity predicted by the Drude model is shown in Figure 3.20.

II. Drude-Smith Model: the Drude model was successful in a lot of cases including studies performed on GaAs, [236, 237] ZnO, [238] and GaN [239, 240] amongst others.

The Drude-Smith model however is a modified Drude model that takes into account microscopic behaviours which were otherwise left out. As more materials were being studied, the Drude model showed poor agreement with experimental values. [110,114] The free electron assumption was too simple to account for interactions that govern charge carrier dynamics in semiconductors. In reality, free carriers will encounter and feel the force of other carriers around them thereby having their momentum and energy affected. This is termed as a memory effect and as a result each carrier will have their own scattering rate. This eventually led to new models being developed and the Drude-Smith has since been widely used to model carrier dynamics.

The Drude-Smith model was developed by Smith [241] and the equation includes an additional parameter, c_n , which relates the probability a charge carrier will maintain its velocity in a scattering event, n . Therefore, this change allows for the carrier's retention of some component of its velocity after a collision. Furthermore, it is assumed statistically that the collision probability of any carrier follows the Poisson distribution and that the collisions are randomly distributed in time. Following on from this, the generalized Drude-Smith model is given by the following:

$$\sigma = \frac{Ne^2\tau/m_e}{1 - i\omega\tau} \left[1 + \sum_{n=1}^{\infty} \frac{c_n}{(1 - i\omega\tau)^n} \right]. \quad (3.67)$$

Assuming that the persistence of velocity is retained only after the first scattering and subsequently randomised, the above expression can be further simplified by retaining only the first term. The conductivity then takes the form:

$$\sigma = \frac{Ne^2\tau/m_e}{1 - i\omega\tau} \left(1 + \frac{c}{1 - i\omega\tau} \right). \quad (3.68)$$

The Drude-Smith has been successful at explaining a great number of experimental measurements such as polymer samples, silicon nanocrystals, and InN nanorods. Figure 3.21 illustrates how changing c affects the conductivity.

III. Lorentzian Model: this model, also known as the *Surface Plasmon Model*, is an alternative physical model that closely resembles the Drude-Smith model. Nienhuys and Sundström [242] argued that the Drude-Smith model is inconsistent in its physical basis. In deriving the Drude-Smith, it was assumed that any carrier undergo only one backscattering process followed by the randomisation of its momentum afterwards. This is where the plasmon resonance model comes into play. Nienhuys and Sundstrom inferred from the studies done on various materials that conductivities were found to be more consistent with an oscillatory motion rather than the previously thought damped linear motion. This behaviour was then attributed to various processes such as charge-carrier

pairs bound in excitons, charge-carrier backscattering, and resonances with a Lorentzian line shape. [243–248] Hence, this model was developed.

In a THz experiment, one essentially applies an electric field to a sample and measures the resulting current. Since there are no electrical contacts, this current will lead to a surplus of positive charge at one side of the sample or the constituting particles, and a surplus of negative charge at the other side. This change in the charge distribution leads to an electrostatic force (otherwise known as the depolarisation field) that drives the charge carriers back to their original position, which results in a damped harmonic oscillation. The charge carriers experience strong localisation due to the one-dimensional geometry of the nanowire.

The equation for charge carriers as represented by a damped harmonic oscillator is of the form:

$$\ddot{x} + \frac{1}{\tau}\dot{x} + \omega_0^2 x = \frac{eE_0}{m} \exp(-i\omega t), \quad (3.69)$$

and from this, the derived conductivity equation is:

$$\sigma_{\text{plasmon}} = \frac{\tau e^2 N / m}{1 - i\omega\tau(1 - \omega_0^2/\omega^2)}, \quad (3.70)$$

where ω_0 is the frequency of the plasmon resonance. Figure 3.22 illustrates this behaviour. It can be seen that it resembles the Drude-Smith model for $c = -1$. For this particular model, the imaginary part of the conductivity is not solely positive but starts off as a negative quantity, crossing the x -axis at the plasma frequency and behaving the same way as the Drude model thereafter. The real part of the conductivity is positive just as for the Drude model, but starts at zero at zero frequency and peaks at the plasma frequency. One essential feature of the Lorentzian is the width of the function which determines the scattering rate and therefore the carrier mobility of the material. The smaller the width, the smaller is the scattering rate and the higher the mobility. Excellent agreement of experimental data with this model was found, for example extracting photocarrier mobility in isolated GaAs nanowires. [14, 75, 89, 249]

The g factor: The resonance frequency, ω_0 , in the above formula is related to the plasma frequency, ω_p , via the geometrical factor g which depends on the nanowire material, its geometrical shape, and the surrounding dielectric medium and has a value between 0 and 1 and is given by,

$$\omega_0^2 = g^2 \omega_p^2, \quad (3.71)$$

where the plasma frequency itself is given by

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m^*}}. \quad (3.72)$$

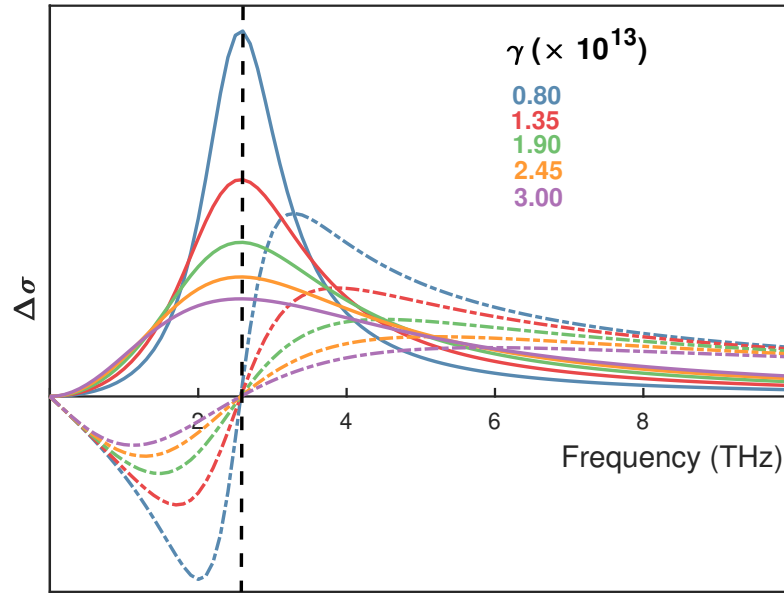


Figure 3.22: **Lorentzian Model:** simulations of the Lorentzian model with different scattering rates. The real part and the imaginary part are represented by the solid lines and dashed lines respectively. The plasmon frequency is the frequency at which the imaginary part of the conductivity crosses the frequency axis and the real part is at its maximum.

The plasma frequency scales as the square root of the charge carrier concentration which is a characteristic feature of plasmon modes. In order to determine the value for geometrical factor g , the NWs were approximated as cylinders. Pitarke *et al.* in 1997 derived the analytical solutions for the dispersion relations of the LSP modes in cylindrical geometries, [251] and it was also found that these LSP modes are quantized along the NW axis by taking into account the finite length L of the NWs. [252] We mentioned before that OPTP spectroscopy probes NWs in the far-field regime and the NWs lengths are much smaller than the THz wavelength ($L \ll \lambda_{\text{THz}}$), only the lowest-order modes are expected to be excited. By plotting the dispersion against the NW radius-to-length ratio, it is possible to extract the g factor for a range of NW geometries, Figure 3.24. [250] A typical value for our experimental data fit was found to be around 0.23 – 0.25 for a NW length of $2\mu\text{m}$ and diameter of 100 nm. [250]

The f factor: The fill factor (f_{fill}), or otherwise more precisely referred to as the *areal fill factor* of the nanowire samples can be obtained for each sample from images taken by an optical microscope in dark field mode as it is easier to see them scattering the light. A Matlab algorithm can easily be written to identify the nanowires on such an image and thereby obtaining the fraction f_a of the image covered with NWs. But, due to the diffraction limit of the optical microscope, NWs on the image appear thicker than they actually are. Then the real fill factor of NWs can be calculated using the following

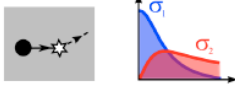
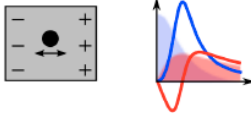
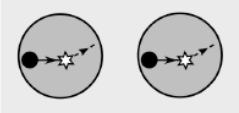
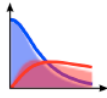
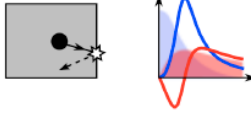
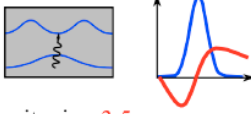
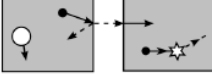
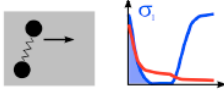
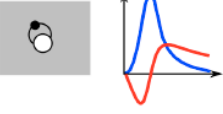
	Local conductivity models (homogeneous media)		Effective conductivity models (inhomogeneous media)
	Infinite media	Finite media	
Classical	Drude-Lorentz 3.1 <i>Mean scattering time τ</i> 	Plasmon 3.2 <i>Restoring force</i> <i>Polarisation field</i> 	Effective medium theory 3.6 <i>Composite media (e.g. metal in air)</i> <i>Simple sample shapes (e.g. spheres)</i> 
	Cole-Cole/Cole-Davidson 3.3 <i>Energy dependent τ</i> 	Smith 3.3 <i>Backscattering</i> 	
Quantum	Boltzmann 3.4 <i>Fermi-Dirac statistics</i> <i>Energy dependent τ</i> <i>Delocalised states</i> <i>Specific scatterers</i> 	Intersubband 3.5 <i>Quantum confinement</i> <i>Selection rules</i> 	Monte Carlo 3.6 <i>Non-equilibrium distributions</i> <i>Electrostatics & electrodynamics</i> <i>Quantum or classical particles</i> <i>Bandstructure, band bending etc.</i> <i>Arbitrary sample shapes</i> 
	Linear response theory 3.5 <i>Intraband</i> <i>Uses energy dispersion</i> Extended Drude 3.5 <i>Fermi liquids. Frequency dependent τ and m^*</i> Localisation modified 3.3 <i>Localised quantum states</i> Superconductors 3.5 <i>Gap in conductivity</i> 	Excitonic 3.5 <i>Intra-excitonic transitions</i> <i>[larger binding energy in quantum wells, but also in bulk]</i> 	

Figure 3.23: Conductivity Models: a visual summary of the various THz conductivity models. As can be seen, the local conductivity of a system can be divided into two main categories: (1) classical, and (2) quantum. This can be further subdivided into two main sections: one treating an infinite media where charges roam freely without any boundaries and the other treating finite media where charges are localised within the structure of the material. Photoconductivity spectra are shown with the x- and y- axes representing frequency and $\Delta\sigma(\omega)$ and the blue and red lines representing the real and imaginary part of the conductivity. The shaded background is a reference for the Drude-Lorentz model. The reader is encouraged to consult the paper cited for this diagram for an in-depth review of these models. Reproduced with permission from [4]

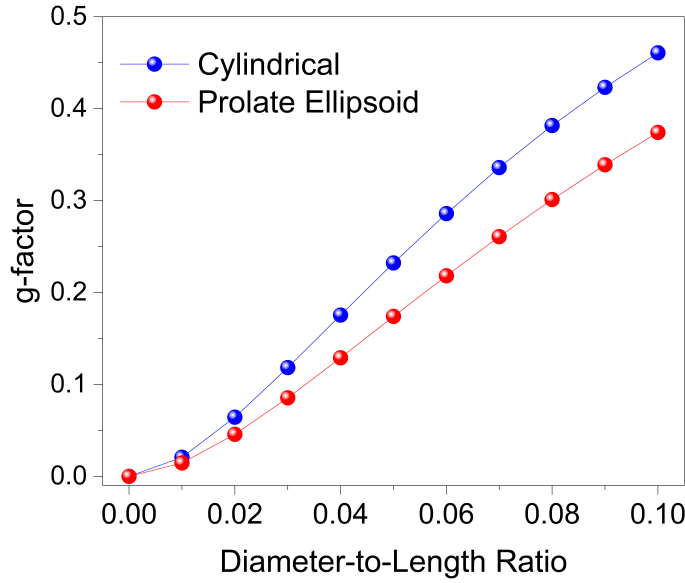


Figure 3.24: **g factor determination:** Geometrical factors for the fundamental longitudinal LSP mode in cylindrical (blue) and prolate ellipsoid (red) NW, as a function of diameter-to-length ratio. [250]

formula [250]

$$f_{\text{fill}} = f_a \cdot \frac{d}{d_a}, \quad (3.73)$$

where d_a is the apparent NW thickness and the real one d . Furthermore, since the NWs are randomly oriented, only some of them are oriented predominantly in the direction of the THz probe polarization and, therefore, contribute to the plasmonic response. Therefore, the effective fill factor f_w was finally obtained from

$$f_w = x_{\text{fill}} \cdot f_{\text{fill}}, \quad (3.74)$$

where x_{fill} stands for the fraction of the NWs which are effectively probed.

3.7.2 Frequency-Dependent Complex Refractive Index

This section details the methodology used to successfully extract the complex refractive index ($\tilde{n}$) of a sample under study using THz-TDS measurements.

So far we have seen that THz-TDS is a powerful technique for studying condensed matter systems over a large frequency range. Using ultrashort and ultrafast electromagnetic, it is possible to have access to a material's complex refractive index, $\tilde{n}(\omega)$. From there, it is straightforward to obtain the complex conductivity ($\tilde{\sigma}$) and together, both these parameters will give the frequency-dependent dielectric function ($\tilde{\epsilon}$). The extraction

method for $\tilde{n}(\omega)$ as outlined below was built upon what Duvillaret *et al.* proposed in which an error function is minimised to find the correct complex refractive index of the sample by comparing theoretical data and measured data. What follows is a detailed analysis of the problem under study and the various assumptions that have been made. This will lay the foundation for later in this chapter where we look at the temperature dependence of the complex refractive index of *c*-sapphire at terahertz frequencies.

3.7.2.1 Optical Coefficients

Understanding optical phenomena in laser spectroscopy is fundamental for parameter extraction. Therefore, one is tasked with being able to quantify them. Transmission, reflection, and refraction are but a few amongst the plethora of light-matter interactions that one can observe. The transmission through a sample and reflection at its surface are described by the coefficient of reflection or reflectivity (R) and transmission or transmissivity (T) respectively which is in essence a ratio of the transmitted/reflected power incident on the sample. Assuming an ideal system where there are no scattering or absorption, one would expect, through the laws of thermodynamics that

$$T + R = 1. \quad (3.75)$$

The propagation of electromagnetic radiation through a transparent medium is described through the complex refractive index, $\tilde{n}(\omega)$, given by

$$\tilde{n}(\omega) = n + i\kappa, \quad (3.76)$$

where n is the real part describing the phase lag of the radiation and κ is the imaginary part describing the absorption of the radiation as it passes through the material. For an ideal system, κ is zero and n is simply the ratio of the velocity of light in free space c to the velocity of light in the medium, v ,

$$n = \frac{c}{v}. \quad (3.77)$$

n depends on the frequency of the light wave and this effect of phase lag is known as *dispersion*. In a real system however, absorption of light as it passes through the material can be significant and as such is quantified through the coefficient of absorption, α , which is defined as the natural log of the fraction of the absorbed power per unit length of the medium. Assuming a propagation along the z -direction, the change in intensity, dI , in an incremental thickness dz of the medium thickness is given by

$$dI = -\alpha dz \times I(z), \quad (3.78)$$

where $I(z)$ is the intensity at position z . If we consider an infinitesimally small thickness, the above equation can be integrated to give the famous Beer's Law.

Going back to the complex refractive index, we no longer have $\kappa = 0$. This imaginary part as shall be seen, is directly connected to the absorption coefficient α of the medium. If we consider a plane wave of frequency f propagating through a medium at a velocity of v in the z -direction, the electric field $\mathbf{E}$ can be described by the following wave equation:

$$\mathbf{E} = E_0 \exp(i2\pi f[t - (z/v)]), \quad (3.79)$$

where E_0 is the incident electric field vector and the exponential term is the displacement of the wave at time t . Plugging the complex refractive index into (3.77) leads to

$$\frac{1}{v} = \frac{n}{c} + \frac{i\kappa}{c}. \quad (3.80)$$

Substituting this into (3.79) produces

$$\mathbf{E} = E_0 \exp(i2\pi ft) \exp\left(\frac{-i2\pi zn}{c}\right) \exp\left(\frac{-2\pi f\kappa z}{c}\right), \quad (3.81)$$

where the last term of the exponential is a measure of the damping factor or extinction. The fraction of the incident power that has propagated from position 1 (say $z = 0$) through a distance (z) in the material with conductivity, σ is given by:

$$\frac{P(z)}{P(0)} = \frac{\sigma \mathbf{E}^2(z)}{\sigma \mathbf{E}^2(0)} = \exp\left(\frac{-4\pi f\kappa z}{c}\right). \quad (3.82)$$

The exponential term is what gives the absorption coefficient in terms of the extinction coefficient

$$\alpha = \frac{4\pi\kappa}{\lambda}. \quad (3.83)$$

We can see from Equation (3.83) that the absorption coefficient is proportional to the extinction coefficient. From Maxwell's equations described earlier on in this chapter, it is possible to show that both the refractive index and the dielectric function are related to each other and as a result they are independent variables. Knowing either one of them will allow one to know both. Specific to this thesis, we shall look at the complex refractive index of substrates as most of our samples (nanowires) cannot be free-standing. We require a substrate such that we are able to conduct our experiments. Knowledge of the substrate's refractive index will dictate which material is best suited for THz spectroscopic measurements.

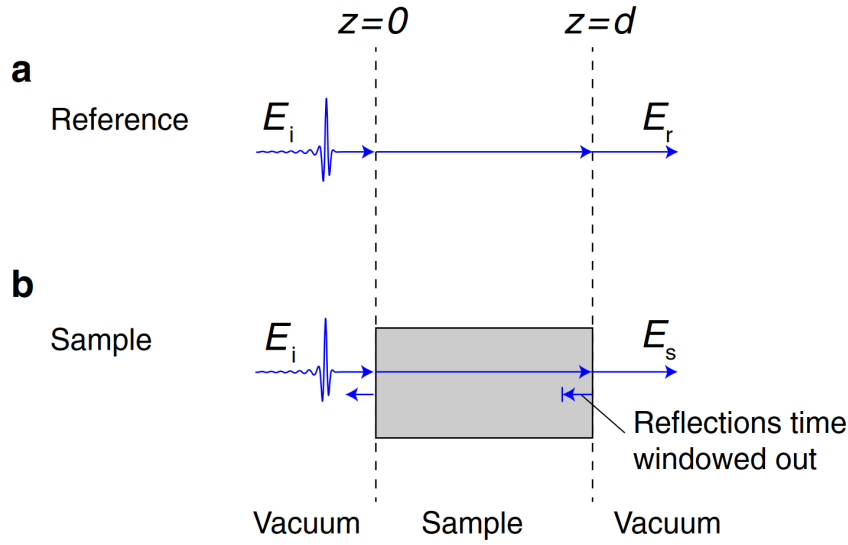


Figure 3.25: **THz-TDS:** (a) The reference measurement is done without any sample in position, i.e. vacuum in this case. This is the THz pulse propagating freely in air without any phase delay or attenuation. (b) The measurement with the sample in place. The THz pulse now interacts with the medium and both the phase and amplitude of the signal will be changed. The ratio of these two pulses will give the transmission function.

3.7.2.2 Experimental Method

THz-TDS experiments have been used multiple times to obtain the frequency-dependent complex refractive indices ($\tilde{n}(\omega)$) of many materials including dielectrics, semiconductors, liquids, and superconductors amongst others. [108, 130, 253, 254] In order to extract $\tilde{n}(\omega)$, the temporal profiles of the THz pulses are recorded in a time-domain setup, i.e. without any photoexcitation pulses in order to probe the equilibrium properties. Two traces are effectively recorded as shown schematically in Figure 3.25: one with the sample in place (E_{sample}), and the other with no sample which will serve as the reference (E_{ref}). These waveforms correspond to the temporal dependence of the electric fields associated with the pulses and therefore encode the phase delay and the absorption of the pulses as they pass through the material which are directly related to the refractive index and absorption coefficient respectively. The profiles are first converted from time domain to frequency domain via Fourier Transform, and then their ratio gives the complex frequency-dependent transmission function, $\tilde{T}(\omega)$, of the sample. $\tilde{T}(\omega)$ is related to the material's complex refractive index and by solving the corresponding equation, it is possible to extract $\tilde{n}(\omega)$.

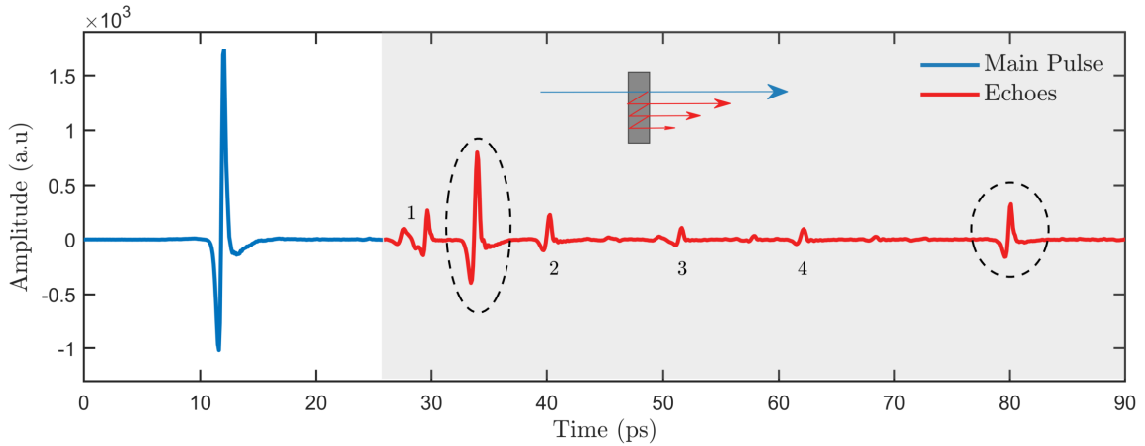


Figure 3.26: **Pulse Echoes:** (Top) Diagram representing the Fabry-Perot (FP) reflections at the interfaces. It is evident that for thick samples, these echoes can be time-windowed out while for a thin sample, they would overlap with the main THz pulse. (Bottom) The THz pulse is recorded in the time domain over a certain stage delay path length to avoid recording the echoes.

3.7.2.3 Description of the System and Assumptions

The reader should note that here we will only describe the extraction method for a thick, free-standing sample. The extraction procedure for thin samples, and samples on substrates is different and a more detailed study was given by Duvillaret. [255]

For this extraction method, three main assumptions are made: (1) the system/sample is treated as a homogeneous slab with a smooth and even interface, (2) the sample and the surrounding medium (vacuum in this case) are non-magnetic and therefore possess a magnetic susceptibility of unity, and finally (3) the sample and the surrounding medium respond linearly to the electromagnetic wave. With the sides of the sample being flat and parallel, we further assume that the impinging wave is at normal incidence with its polarization being linear and parallel to the optical axis. The experiment is carried out under high vacuum to prevent water vapour absorption of THz and formation of water droplets on the sample at cryogenic temperatures.

As the THz pulse impinges onto the surface of the sample, some of it is reflected back. The rest passes through the sample and undergoes multiple internal reflections at the interfaces. This is represented in Figure 3.26. The emerging and measured THz pulse is the first one that goes out whilst the reflected pulses appear as echoes in the time-domain. As the sample is thick enough, it is possible to remove these echoes by windowing them out, i.e. measure the THz pulse over a short distance. In contrast, if this was a thin sample, the echoes are too close to each other, and therefore overlap with the main THz pulse. In this case the THz waveform is recorded over a broad range until it has

decayed to zero on either side. The analysis for extracting the refractive index then takes a different form which has been outlined in reference. [255]

Following on from our assumptions, the sample spectral component at an angular frequency of ω of the electric field of the THz wave is written as: [255]

$$S_{\text{SAMPLE}} = \eta(\omega) \cdot T_{12}(\omega) \cdot P_2(\omega, L) \cdot T_{23}(\omega) \cdot \sum_{k=0}^{\infty} R_{23}(\omega) \cdot P_2^2(\omega, L) \cdot R_{21}(\omega)^k \cdot E(\omega), \quad (3.84)$$

where

1. $E(\omega)$ is the THz wave electric field incident on the sample,
2. $R_{ab}(\omega) = \frac{\tilde{n}_a - \tilde{n}_b}{\tilde{n}_a + \tilde{n}_b}$ is the reflection coefficient at the a/b interface,
3. $T_{ab}(\omega) = \frac{2\tilde{n}_a}{\tilde{n}_a + \tilde{n}_b}$ is the transmission coefficient from medium a to medium b,
4. $P_a(\omega, d) = \exp\left[-i\frac{\tilde{n}_a\omega d}{c}\right]$ is the propagation coefficient in medium through a distance d and $\tilde{n}_a = n_a + i\kappa$ being the complex refractive index of medium a which is a function of frequency.

The $\eta(\omega)$ terms contains all the reflection, transmission and propagation coefficients and the summation term accounts for all the Fabry-Perot reflections within the sample. For the vacuum reference, the spectral component of the electric field of the THz wave is given by

$$S_{\text{REFERENCE}}(\omega) = \eta(\omega) \cdot T_{13}(\omega) \cdot P_{\text{air}}(\omega, L) \cdot E(\omega). \quad (3.85)$$

The ratio of the sample to the reference spectral components then gives the complex transmission coefficient $\tilde{T}(\omega)$,

$$\begin{aligned} \tilde{T}(\omega) &= \frac{S_{\text{SAMPLE}}}{S_{\text{REFERENCE}}} \\ &= \frac{4\tilde{n}_s}{(1 + \tilde{n}_s)^2} e^{i((\tilde{n}_s - 1)d)\omega/c} \cdot \text{FP}(\omega), \end{aligned} \quad (3.86)$$

with

$$\text{FP}(\omega) = \frac{1}{1 - \left(\frac{\tilde{n}_2 - \tilde{n}_1}{\tilde{n}_2 + \tilde{n}_1}\right)\left(\frac{\tilde{n}_2 - \tilde{n}_3}{\tilde{n}_2 + \tilde{n}_3}\right) \cdot \exp(-2i\tilde{n}_2 \frac{\omega L}{c})}. \quad (3.87)$$

3.7.2.4 Optically Thick Samples

An optically thick sample is one for which the echoes of the terahertz pulses which is normally caused by multiple reflections within the samples and coming at defined time delays after the main pulse, are temporally separated such that it is possible to window them out. This can be performed by scanning the THz stage enough to allow the THz pulse to decay to zero whilst avoiding to measure the next THz pulse reflection. Thus, at

the expense of spectral resolution no information is lost and the Fabry-Perot term can be taken as 1.

It would require a significant computational time to solve Equation (3.86) analytically via conventional methods. The one developed by Duvillaret *et al.* is simpler and quicker. Their method requires only approximate starting values which is a huge advantage as other methods such as the Newton-Raphson which depends critically on the accuracy of starting guess values. Intuitively, it would make sense to search for a complex refractive index which will minimise an equation of the form $(\tilde{T}(\omega) - \tilde{T}_{\text{measured}}(\omega))$ where $\tilde{T}(\omega)$ and $\tilde{T}_{\text{measured}}(\omega)$ are the calculated and measured complex transmission coefficients. Owing to the complex exponent in Equation (3.87), $T(\omega)$ is oscillatory in n -space which would lead to convergence issues if a standard least squares fitting method is applied. To overcome this potential fitting difficulty, an alternate error function is used in the fitting algorithm, given by:

$$\delta(n, \kappa) = \delta_{\text{mod}}^2(n, \kappa) + \delta_{\text{arg}}^2(n, \kappa), \quad (3.88)$$

where n and κ are the real and imaginary parts of the complex refractive index. The functions δ_{mod} and δ_{arg} are defined by,

$$\delta_{\text{mod}}(\omega; n, \kappa) = \log(|T(\omega; n, \kappa)|) - \log(|T_{\text{meas}}(\omega)|) \quad (3.89)$$

$$\delta_{\text{arg}}(\omega; n, \kappa) = \arg(T(\omega; n, \kappa)) - \arg(T_{\text{meas}}(\omega)), \quad (3.90)$$

where T_{meas} is the measured value and T is the fitted value. The objective of the fitting algorithm is to minimise the error function, δ , a detailed explanation for which is given in reference. [255] The reader is highly encouraged to read through it.

Caveat I: When the sample is very thick, for example 10 mm, the THz pulse is shifted by a large amount compared to the reference signal. In this case, the phase has shifted by more than 2π and the extraction procedure will not work as one would expect. As an example, if we assume the phase of the sample THz pulse moves by $x + 2\pi$ radians, then the extraction procedure will generate a value for the complex refractive index which is closer to a thickness that would have moved the phase by x radians, which will be lower than the expected value. The way to circumvent this issue is to unwrap the phase properly. The Matlab function 'unwrap' will not do this correctly and the following piece of code has been added to the algorithm to make sure the correct phase is used:

```
1 function [PhiData] = PhaseUnwrap(PhiData, f)
2     freq = f/1e12;
3     freq = freq';
```

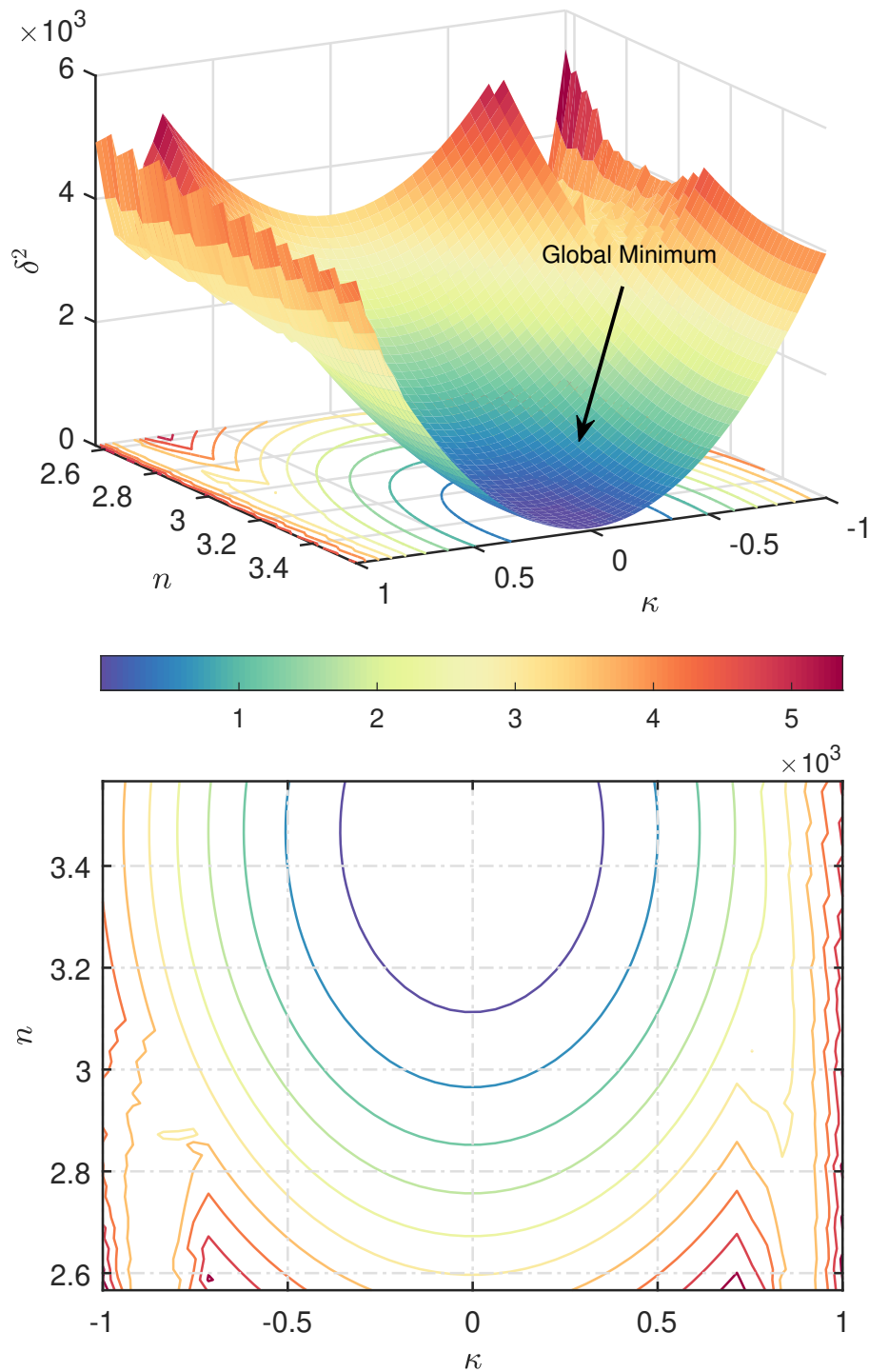


Figure 3.27: **Error Function:** (Top) The error function plotted against a range of values for n and κ . We can see that this error function is smooth and monotonous and has a paraboloid shape. Consequently it is easy to fit this surface with an appropriate equation and find the minimum point. (Bottom) A contour plot, or top view, of the paraboloid. By having a quick look at this plot, it is possible to have a very good guess of a range of values for n and κ to simulate the paraboloid.

```

4     p = polyfit(freq,PhiData,1);
5     while (p(2)>pi)
6         PhiData = PhiData-2*pi;
7         p = polyfit(freq,PhiData,1);
8     end
9     while (p(2)<-pi)
10        PhiData = PhiData+2*pi;
11        p = polyfit(freq,PhiData,1);
12    end
13    if (p(1)<0)
14        PhiData = -PhiData;
15    end
16 end

```

What this extra code does differently is the fact that when phase unwrapping, one should start at a frequency point where reasonable is obtained which is usually at around 1 THz and unwrap the phase on both sides. However, in doing so, the phase might not be zero at zero frequency and the code fits a polynomial of degree 1 to the phase and extrapolate the data such that the intercept is near zero at zero frequency.

Caveat II: Ideally when generating the theoretical values for the complex transmission function, one would want to restrict the window for the range of values for n and κ . This is because sometimes the surface generated for the δ error function will contain several local minima as shown in Figure 3.28. The minimisation process will converge to one point and if the starting value is nearer to a local minimum, then the extraction process will fail. To know which range of values is most likely to yield the answer, there is a quick way of determining a rough value for the real part of the refractive index. This is done by calculating the optical path difference, Δt_{pd} , between the reference and the sample, Figure 3.29. Δt_{pd} is related to the sample's refractive index via the following equation

$$\Delta t_{pd} = (n_{\text{sample}} - n_{\text{ref}}) \times d, \quad (3.91)$$

where d is the sample thickness and n_0 is the refractive index of air. Solving for n_{sample} gives

$$n_{\text{sample}} = \frac{c}{d} \Delta t_{pd} + 1. \quad (3.92)$$

This then gives a value which is much closer to the global minimum and the extraction will be much faster.

3.7.2.5 Temperature-Dependent Refractive Index of c-Sapphire

Earlier on, Davies *et al.* [256] presented a work on the temperature-dependence of the refractive index of z-cut quartz in the terahertz regime. This work was essential as z-cut quartz discs are highly used as substrates and windows in regards to optical-pump terahertz-probe (OPTP) spectroscopy. However, sapphire is another potential substrate

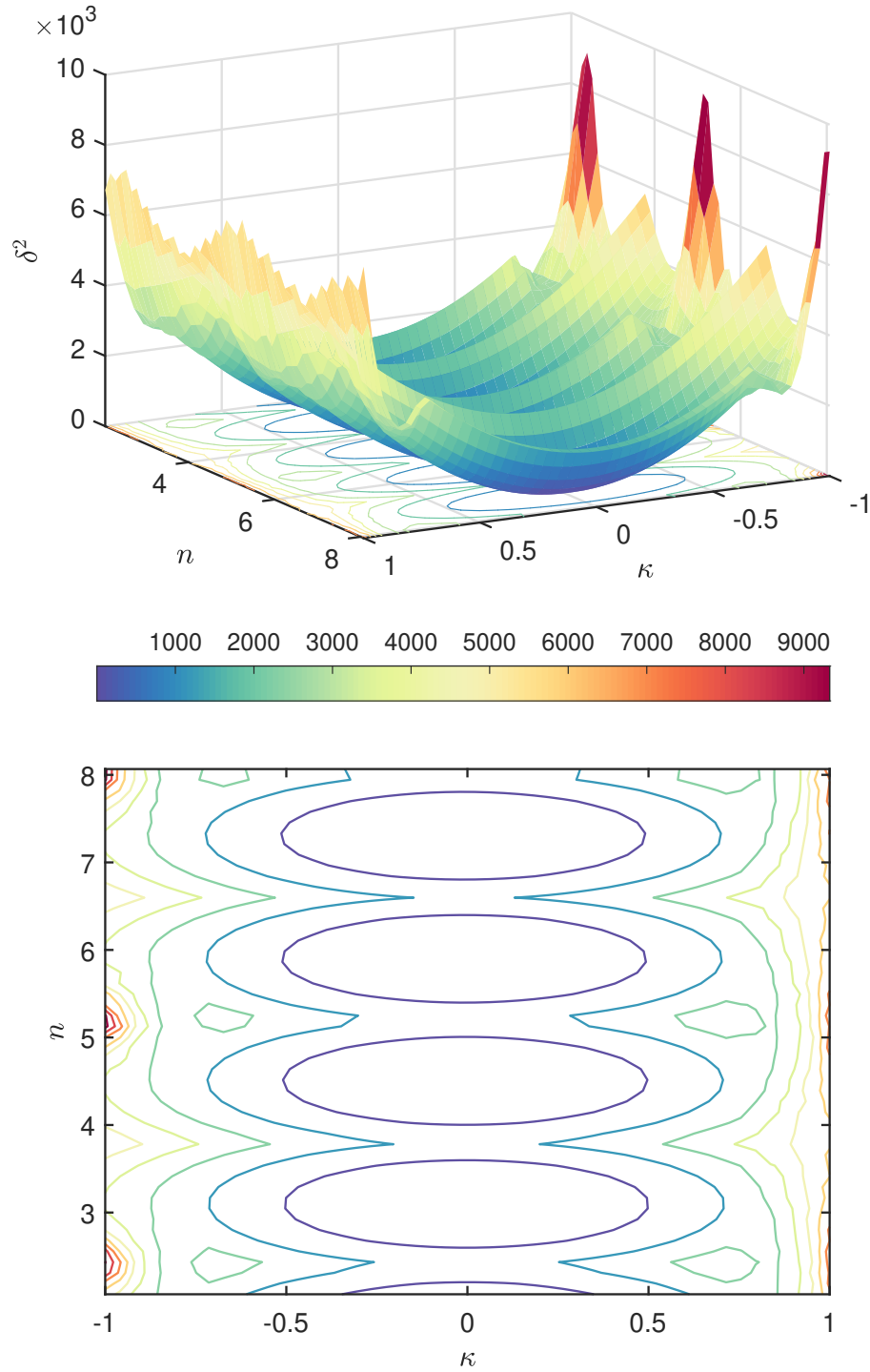


Figure 3.28: **Local Minima:** The generated surface contains multiple minimum points and to extract the correct value for the refractive index, the range of values simulated should be as close as possible to the actual value. Failure in doing so will give the wrong answer as the minimisation process will be sitting at the minimum closest to the starting value which may or may not be correct. Δt_{pd} may then be used to locate where the minimum is situated approximately.

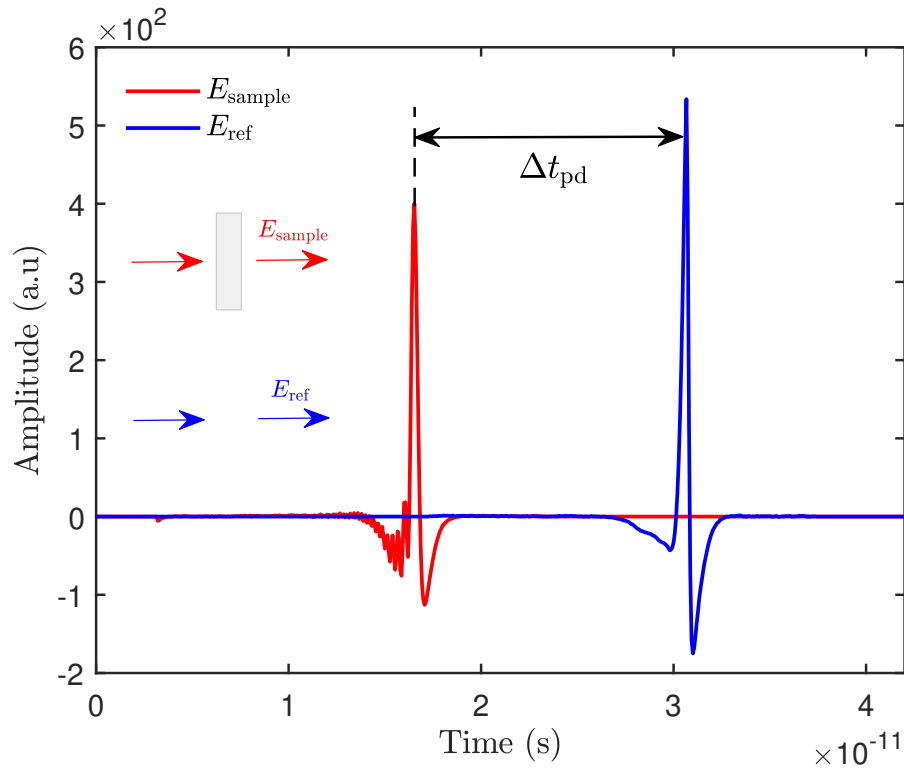


Figure 3.29: **Refractive Index Estimate:** A quick and accurate way of estimate the real part of the complex refractive index of the sample is to look at the time difference between the two peaks of the THz pulses. This is related to the optical path difference introduced by the sample, therefore slowing down the THz pulse compared to the reference vacuum signal. Using the formula mentioned, it is then straightforward to calculate this value.

which is more robust than quartz and scratch-resistant. In addition Sapphire is also a better thermal conductor which means heat is dissipated quicker during experiments keeping the sample deposited on them at a lower temperature. Therefore an optical characterisation of how the complex refractive index changes with temperature is important. Crothers *et al.* demonstrated that in order to extract the maximum information from an OPTP experiment, knowledge of the refractive indices of the substrate which dictate the internal Fabry-Perot reflections is required. Here, we go on to present how the complex refractive index of *c*-Sapphire change with temperature in a broadband regime between 0.5 THz and 7.0 THz taken at 6, 14, 46, 80, 120, 160, 200, 300, 350, and 420 K.

In the quest to characterise the optoelectronic properties of materials in any frequency regime, a free-standing sample is not always possible due to various reasons such as being too fragile or maybe too flexible, or even too thin to be held firmly in a sample holder. Usually a substrate is the solution onto which the sample sits (via spin coating, or evaporation or transfer from one substrate to another) which is then more convenient to place in a sample holder to be held under vacuum for subsequent measurements. *z*-cut quartz has been a material of choice typically for experiments done in the terahertz region of the electromagnetic spectrum. [256] This is due to its negligible dielectric response at THz frequencies and also being highly transparent to THz radiation. Furthermore, *z*-quartz has a near constant refractive index in the range of 0.1 – 4.0 THz. The addition of a substrate however complicates things. The sample-substrate entity mimics a multilayer structure, otherwise known as heterostructure, which introduces incoherent reflections within the substrate, absorption and therefore attenuation of the probe radiation, and two-photon excitation of the sample. Therefore, there is research being done on the ideal material of choice as substrate especially in the THz regime.

Sapphire, chemical formula $\alpha\text{-Al}_2\text{O}_3$, has been in the limelight for quite some time now. It is a non-polar compound playing an ever-increasingly important role as a material for high reliability electronics today due to its excellent mechanical properties, chemical stability and light transmission. Sapphire is also a very good thermal conductor which is highly sought in experiments dealing with high energy lasers in order to dissipate heat as fast as you can to prevent material damage. Additionally, sapphire is a material possessing a unique combination of physical, chemical and optical properties, which make it resistant to high temperature, thermal shock, water and sand erosion, and scratching. It is a superior window material for many IR applications from 3 μm to 5 μm . *C*-plane sapphire substrates are widely used to grow III-V and II-VI compounds such as GaN for blue LED and laser diodes, while *R*-plane sapphire substrates are used for the hetero-epitaxial deposition of silicon for microelectronic IC applications.

Grischkowsky *et al.* in 1990 [108] performed a series of THz-TDS on various dielectrics and semiconductors, albeit at room temperature. The absorption and the dispersion of single-crystal sapphire was performed for both the ordinary and extraordinary rays. A refractive index of around 3.07 and a power absorption of 1.5 cm^{-1} were obtained which matched with values obtained from previous works. [257,258] Later in 2003, Shan *et al.* [259] went on to assess the frequency-dependent complex conductivity in sapphire at various temperatures. A Drude-type response was observed and charge scattering was mainly attributed to interactions with acoustical and optical phonon modes at low and high temperatures respectively. In this paper, we add to Grischkowsky data analysis by looking at the temperature-dependence of the complex refractive index of sapphire at terahertz frequencies beyond 2.0 THz. This will give a better idea about the optical properties of this material which is widely used as substrates for THz experiments.

Experimental Methods Terahertz time-domain spectroscopy was performed in order to extract the complex refractive index of the sapphire substrate. Although the system setup has described elsewhere, [256] we will give a brief description of the system: the output of an amplified Ti:Sapphire laser system with 30 fs pulses at a repetition rate of 5 kHz with a central wavelength of 800 nm and an average power of 4 W is split into three beam paths: a probe beam, a photoexcitation beam, and a gate beam. As only THz-TDS is performed, the photoexcitation beam was blocked and not needed. Picosecond terahertz pulses were generated using a Spintronic emitter made of a 1.8 nm thick non-ferromagnetic material, $\text{Co}_{20}\text{Fe}_{40}\text{B}_{20}$, sandwiched between two 2 nm thick ferromagnetic materials, W and Pt, all sitting on a fused silica substrate. [133,260] Terahertz pulses were detected via electro-optic sampling using a 0.2 mm thick GaP $\langle 110 \rangle$ crystal sitting on a 1 mm thick GaP inactive substrate, Wollaston prism and a pair of balanced photodiodes. Temperature-dependent TDS measurements of sapphire were performed using a cold-finger cryostat from Oxford Instruments. The THz transmission in the time domain is measured for the sample in place and as a reference without the sample. The data was subsequently Fourier transformed into the frequency domain and thereafter the ratio taken.

Results

Time-domain spectroscopy, as detailed in this chapter, was used to measure the amplitude and phase of the transmission through *c*-cut sapphire with an average diameter of 13 mm and thickness of 2.05 mm (all measured with a micrometer gauge at various azimuthal angles with averaging) of a broadband terahertz pulse in the time-domain. The experiment was done under a high vacuum (10^{-7} bar) using a turbo pump in order to eliminate any absorption of THz due to water vapour and preventing the condensation of water molecules onto the sample at cryogenic temperatures. The terahertz transmission

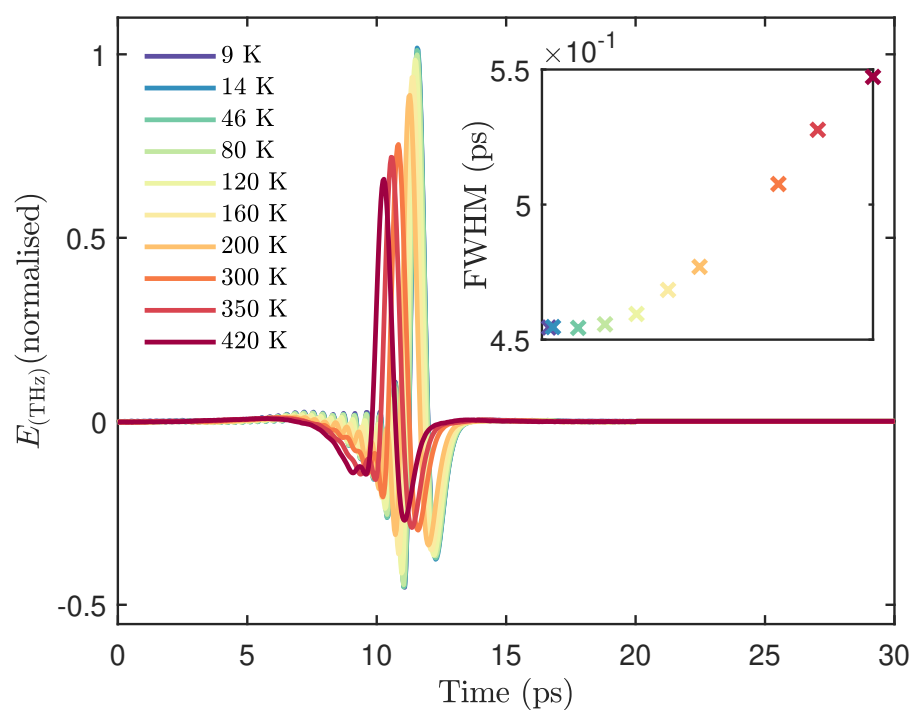


Figure 3.30: **THz Pulse Phase Shift:** Plots illustrating the effect of temperature on the transmitted THz waveforms. As the temperature decreases, the pulse width decreases, as shown in the inset, and Sapphire becomes more transmissive at higher bandwidth. At 4 K, *c*-Sapphire becomes transparent in the THz range while at temperatures above 300 K, the transmitted bandwidth drops below 3 THz.

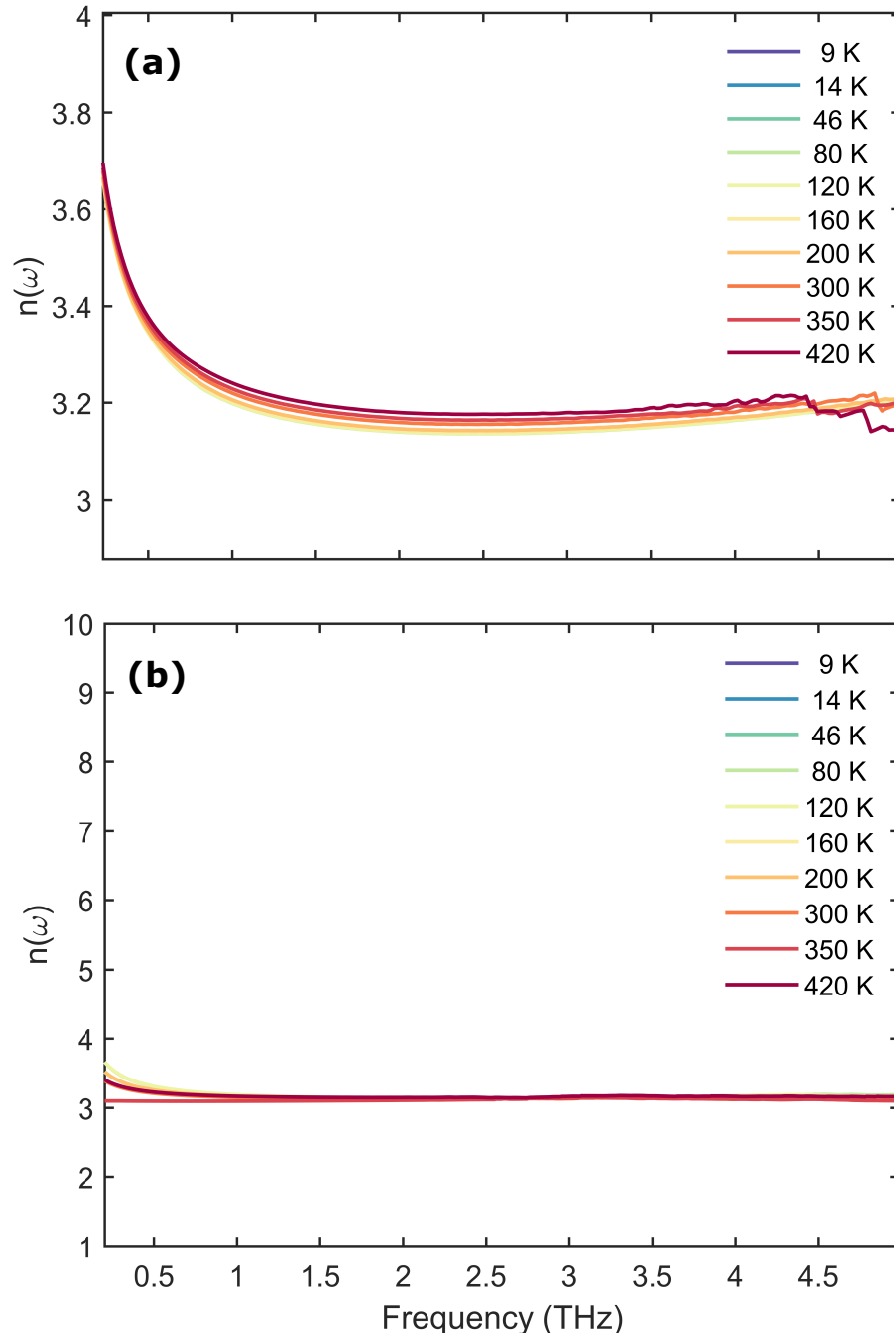


Figure 3.31: **Temperature Dependence of n :** Real part of the refractive index extracted via the downhill-simplex method for *c*-sapphire at various temperatures. Plot (a) is for a 2 mm thick crystal and plot (b) is for a 10 mm thick crystal. They both have a value of around 3.2 which is consistent with previous literature values.

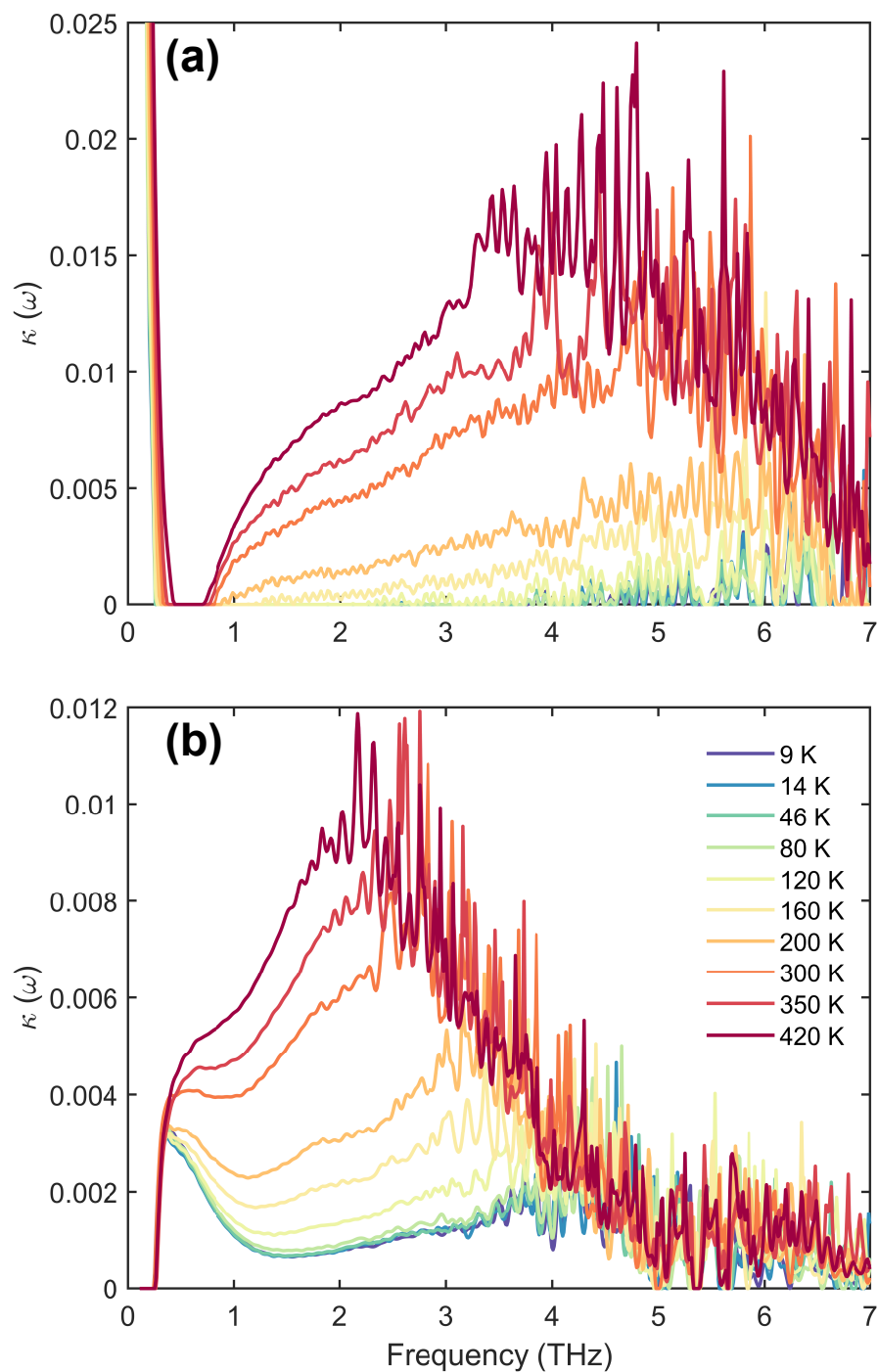


Figure 3.32: **Temperature Dependence of κ :** Imaginary part of the refractive index for c-sapphire for both a 2 mm thick (a) and 10 mm thick (b) crystal. Plot (a) have a very low value at very low temperatures and therefore extraction of the parameter was very hard. We therefore turned to a thicker crystal yielding higher values for the absorption coefficient which is much easier to extract.

in the frequency-domain is obtained by measuring the signal response of the sapphire disc and vacuum in the time-domain and dividing the Fourier transformed signal of the sapphire by that of vacuum. For each measurement, 3 scans were recorded and the signal averaged for better signal-to-noise ratio. The method for obtaining the complex refractive index from TDS has been described earlier. Tables 3.6 and 3.7 tabulate the refractive indices of sapphire at the various frequencies and temperatures. Unlike z-cut quartz, sapphire does not possess a phonon mode in the frequency range we measured at thereby eliminating the complex analysis of harmonic oscillators. This is particularly useful in choosing a substrate for sample analysis as any phonon modes will interfere in the results and render any information above the phonon mode frequency unreliable. Thereafter, the extraction procedure follows the same method that has been outlined as mentioned above.

Figure 3.30 displays the pulse shift and shape of the THz transmission waveforms with temperature while Figures 3.31 and 3.32 illustrate the refractive index, $n(\omega)$, and the absorption coefficient, $\kappa(\omega)$ as a function of frequency and temperature. The inset in Figure 3.30 is a plot of the full width half maximum (FWHM) of the different THz pulses showing an increase in the width with increasing temperature indicating that higher terahertz frequencies are not transmitted at high temperatures. This is particularly important when choosing a substrate for samples which would be unfavourable for ultra broadband systems. This is reflected in the plots for the complex refractive index components where at 420 K, the plots become unreliable above 2.5 THz. The absorption coefficient is also highest at 420 K. However, at cryogenic temperatures, *c*-sapphire is almost transparent to all frequencies in the terahertz regime with minimal absorption coefficient and retaining the FWHM of the reference pulse. For experiments at very low temperatures therefore, sapphire would be an ideal substrate owing to its unique mechanical properties as well as optical properties.

3.7.2.6 Summary

In summary, we have demonstrated that *c*-sapphire has a constant refractive index at terahertz frequencies. However, temperature plays a major role in selecting this material as potential substrates for sample analysis. Some samples require very high temperatures during the fabrication process and given its high thermal strength, *c*-sapphire would be the material of choice. However, for room temperature measurements at terahertz frequencies, one would probably opt for z-cut quartz. For very low temperature measurements, *c*-sapphire would be the ideal candidate due to the very low loss, low absorption

and the absence of phonon modes while z-cut quartz will present some difficulties due to the phonon mode, which highly restricts the information beyond 4 THz.

3.8 Errors & Uncertainties

THz spectroscopy, although being a very powerful non-contact method to determine semiconductor properties, is nevertheless not free from any deficiencies. Any experimentally determined quantity will contain both systematic and random errors introduced mainly due to approximations, methods, and modelling. Random errors are cumulative and therefore from the very first step such as aligning optics to the very end in data analysis the errors present are significant.

Building and troubleshooting THz systems has helped in recognising where some of these mistakes might come from, and how to deal with them, although it is near impossible to remove them. This section is devoted to these types of errors that have come up several times, which would otherwise, if avoided, make any experimental procedure and results very reproducible.

THz Pulse Amplitude: The first error is from pulse energy fluctuations due to the laser amplifier. As is the case with all equipments, they have a lifetime and sometimes drift with time. Jitter in delay stages coupled with electronic noise will undoubtedly introduce uncertainties in one's measurements. The way to reduce this is by taking several scans and averaging. Error bars are necessary to show the full picture.

Unwanted Reflections: Reflections in the optical beam path are often overlooked and this is one cause of issue especially when carrying out photoconductivity decay scans. For instance the pump pulse for the THz emission should be properly attenuated (using a cellulose-nitrate layer immediately after) once it has gone through the spintronic emitter or electro-optic crystal as any residual beam will photoexcite the sample resulting in an offset in the scans. Other sources of reflections will potentially come from the amplifier itself due to the Pockels cell inside. Unfortunately this cannot be avoided but can certainly be time-windowed out from a THz scan.

Sample Geometry: When extracting parameters from a data set, it is often assumed the samples are homogenous, and have smooth surfaces with flat sides. In reality, this is not the case and other methods should be employed to determine certain parameters. For example, sample thicknesses could be determined using an SEM image or a surface profilometer such as Dektak. Substrates with high quality polished surfaces should be employed when fabricating samples.

Beam Alignment: We have seen throughout this chapter that beam alignment is key to a time domain spectroscopy system. Most of the time, issues with alignment result in experiments being delayed. The best way to avoid this is to ensure that when a system is aligned, it should be done in a way such that any changes in the system will result in minimal re-aligning. One of the common mistakes is to not use alignment aids when aligning the optical gate pulse because this beam line is kept fixed. However, if it needs moving or someone by accident moves a mirror on that line, it would take a long time before the beam alignment is corrected. Another common mistake is to overlook how the beam spreads in the sample box. The user should make sure the beams are going in straight lines as otherwise this will result in astigmatism at the sample position or even at the detector position. This tend to decrease the spectral range of the system.

Table 3.6: Refractive index of *c*-cut sapphire.

f (THz)	9 K	14 K	46 K	80 K	120 K	160 K	200 K	300 K	350 K	420 K
0.204	3.659	3.659	3.659	3.66	3.661	3.517	3.521	3.386	3.099	3.403
0.257	3.536	3.536	3.537	3.537	3.539	3.425	3.429	3.325	3.099	3.341
0.311	3.454	3.454	3.455	3.455	3.457	3.363	3.367	3.283	3.098	3.3
0.364	3.396	3.396	3.396	3.397	3.398	3.319	3.323	3.254	3.097	3.271
0.418	3.352	3.353	3.353	3.353	3.355	3.287	3.29	3.232	3.096	3.249
0.471	3.319	3.319	3.319	3.32	3.322	3.262	3.265	3.215	3.096	3.232
0.525	3.293	3.293	3.293	3.294	3.295	3.242	3.245	3.202	3.095	3.219
0.578	3.271	3.271	3.271	3.272	3.274	3.225	3.229	3.191	3.095	3.208
0.632	3.254	3.254	3.254	3.254	3.256	3.212	3.216	3.182	3.095	3.199
0.686	3.239	3.239	3.239	3.239	3.241	3.201	3.205	3.174	3.094	3.191
0.739	3.226	3.226	3.226	3.227	3.229	3.191	3.195	3.168	3.094	3.185
0.793	3.215	3.215	3.215	3.216	3.218	3.183	3.187	3.163	3.094	3.18
0.846	3.206	3.206	3.206	3.206	3.208	3.176	3.18	3.158	3.095	3.175
0.9	3.198	3.198	3.198	3.198	3.2	3.17	3.174	3.154	3.095	3.171
0.953	3.19	3.19	3.191	3.191	3.193	3.165	3.169	3.15	3.095	3.167
1.01	3.184	3.184	3.184	3.185	3.187	3.16	3.164	3.147	3.095	3.164
1.06	3.178	3.179	3.179	3.179	3.181	3.156	3.16	3.145	3.096	3.162
1.11	3.174	3.174	3.174	3.174	3.176	3.153	3.156	3.143	3.096	3.159
1.17	3.169	3.169	3.169	3.17	3.172	3.149	3.153	3.141	3.097	3.157
1.22	3.165	3.165	3.165	3.166	3.168	3.147	3.15	3.139	3.097	3.156
1.27	3.162	3.162	3.162	3.162	3.164	3.144	3.148	3.137	3.098	3.154
1.33	3.158	3.158	3.159	3.159	3.161	3.142	3.145	3.136	3.098	3.153
1.38	3.156	3.156	3.156	3.156	3.158	3.14	3.143	3.135	3.099	3.152
1.44	3.153	3.153	3.153	3.154	3.155	3.138	3.141	3.134	3.099	3.151
1.49	3.151	3.151	3.151	3.151	3.153	3.136	3.14	3.133	3.1	3.15
1.54	3.149	3.149	3.149	3.149	3.151	3.135	3.139	3.132	3.101	3.149
1.6	3.147	3.147	3.147	3.147	3.149	3.134	3.137	3.132	3.101	3.148
1.65	3.145	3.145	3.145	3.146	3.148	3.133	3.136	3.131	3.102	3.148
1.7	3.144	3.144	3.144	3.144	3.146	3.132	3.135	3.131	3.103	3.147
1.76	3.142	3.142	3.143	3.143	3.145	3.131	3.134	3.13	3.103	3.147
1.81	3.141	3.141	3.141	3.142	3.144	3.13	3.134	3.13	3.104	3.146
1.86	3.14	3.14	3.14	3.141	3.143	3.13	3.133	3.13	3.105	3.147
1.92	3.139	3.139	3.14	3.14	3.142	3.129	3.133	3.13	3.106	3.147
1.97	3.139	3.139	3.139	3.139	3.141	3.129	3.132	3.13	3.107	3.147
2.02	3.138	3.138	3.138	3.139	3.14	3.129	3.132	3.13	3.108	3.147
2.08	3.138	3.138	3.138	3.138	3.14	3.129	3.132	3.13	3.109	3.147
2.13	3.137	3.137	3.137	3.138	3.139	3.129	3.132	3.131	3.11	3.147
2.19	3.137	3.137	3.137	3.138	3.139	3.129	3.132	3.131	3.111	3.147
2.24	3.137	3.137	3.137	3.137	3.139	3.129	3.132	3.132	3.112	3.148
2.29	3.137	3.137	3.137	3.137	3.139	3.129	3.133	3.132	3.113	3.15
2.35	3.137	3.137	3.137	3.137	3.139	3.129	3.133	3.133	3.115	3.149
2.4	3.137	3.137	3.137	3.137	3.139	3.13	3.133	3.133	3.116	3.15
2.45	3.137	3.137	3.137	3.138	3.139	3.13	3.134	3.134	3.117	3.149
2.51	3.137	3.137	3.137	3.138	3.14	3.131	3.134	3.136	3.118	3.144
2.56	3.138	3.138	3.138	3.138	3.14	3.132	3.135	3.136	3.123	3.146

Table 3.7: Refractive index of *c*-cut sapphire continued.

f (THz)	9 K	14 K	46 K	80 K	120 K	160 K	200 K	300 K	350 K	420 K
2.61	3.138	3.138	3.138	3.139	3.14	3.132	3.136	3.138	3.128	3.144
2.67	3.138	3.138	3.139	3.139	3.141	3.133	3.136	3.136	3.124	3.144
2.72	3.139	3.139	3.139	3.14	3.141	3.133	3.137	3.138	3.125	3.142
2.77	3.14	3.14	3.14	3.14	3.142	3.134	3.138	3.133	3.132	3.147
2.83	3.14	3.14	3.14	3.141	3.143	3.136	3.139	3.13	3.134	3.15
2.88	3.141	3.141	3.141	3.142	3.143	3.136	3.14	3.132	3.131	3.152
2.93	3.142	3.142	3.142	3.142	3.144	3.137	3.14	3.128	3.134	3.156
2.99	3.143	3.143	3.143	3.143	3.145	3.138	3.141	3.13	3.135	3.162
3.04	3.144	3.144	3.144	3.144	3.146	3.139	3.143	3.134	3.136	3.164
3.1	3.144	3.145	3.145	3.145	3.147	3.141	3.144	3.139	3.142	3.169
3.15	3.146	3.146	3.146	3.146	3.148	3.142	3.145	3.14	3.141	3.169
3.2	3.147	3.147	3.147	3.147	3.149	3.143	3.147	3.139	3.142	3.169
3.26	3.148	3.148	3.148	3.148	3.15	3.144	3.147	3.142	3.139	3.171
3.31	3.149	3.149	3.149	3.15	3.151	3.145	3.149	3.138	3.14	3.174
3.36	3.15	3.151	3.151	3.151	3.153	3.147	3.152	3.14	3.136	3.172
3.42	3.152	3.152	3.152	3.152	3.154	3.149	3.153	3.135	3.132	3.173
3.47	3.153	3.153	3.153	3.154	3.156	3.149	3.151	3.134	3.135	3.169
3.52	3.155	3.155	3.155	3.155	3.157	3.154	3.154	3.14	3.134	3.168
3.58	3.156	3.156	3.156	3.157	3.159	3.154	3.156	3.14	3.131	3.165
3.63	3.158	3.158	3.158	3.159	3.16	3.152	3.159	3.139	3.129	3.161
3.68	3.16	3.159	3.159	3.16	3.161	3.149	3.161	3.141	3.131	3.164
3.74	3.161	3.161	3.161	3.162	3.164	3.149	3.157	3.138	3.128	3.165
3.79	3.163	3.163	3.162	3.163	3.164	3.153	3.154	3.134	3.128	3.163
3.85	3.164	3.165	3.165	3.165	3.167	3.153	3.156	3.129	3.126	3.163
3.9	3.166	3.166	3.166	3.167	3.168	3.15	3.159	3.124	3.125	3.167
3.95	3.168	3.168	3.169	3.169	3.171	3.15	3.16	3.123	3.126	3.166
4.01	3.17	3.17	3.17	3.171	3.173	3.147	3.156	3.121	3.122	3.163
4.06	3.172	3.173	3.173	3.173	3.175	3.147	3.155	3.126	3.122	3.16
4.11	3.174	3.173	3.174	3.175	3.179	3.15	3.155	3.126	3.12	3.162
4.17	3.177	3.177	3.176	3.179	3.18	3.152	3.159	3.131	3.122	3.163
4.22	3.178	3.176	3.178	3.178	3.182	3.155	3.159	3.133	3.119	3.163
4.27	3.181	3.181	3.178	3.181	3.184	3.156	3.156	3.135	3.116	3.164
4.33	3.181	3.18	3.176	3.182	3.186	3.153	3.158	3.137	3.117	3.167
4.38	3.178	3.177	3.178	3.185	3.187	3.155	3.154	3.137	3.12	3.163
4.43	3.181	3.176	3.176	3.186	3.184	3.158	3.152	3.138	3.122	3.164
4.49	3.18	3.179	3.174	3.189	3.178	3.16	3.155	3.141	3.121	3.161
4.54	3.178	3.178	3.173	3.19	3.174	3.16	3.155	3.143	3.118	3.159
4.6	3.178	3.178	3.17	3.186	3.172	3.162	3.155	3.144	3.116	3.16
4.65	3.178	3.178	3.168	3.188	3.17	3.163	3.152	3.147	3.113	3.159
4.7	3.179	3.175	3.167	3.189	3.169	3.163	3.149	3.146	3.108	3.161
4.76	3.177	3.177	3.164	3.185	3.169	3.16	3.151	3.145	3.105	3.158
4.81	3.177	3.179	3.167	3.182	3.167	3.161	3.152	3.144	3.103	3.16
4.86	3.174	3.181	3.164	3.181	3.164	3.161	3.153	3.142	3.102	3.161
4.92	3.171	3.182	3.162	3.182	3.163	3.164	3.149	3.141	3.101	3.159
4.97	3.168	3.184	3.162	3.185	3.162	3.164	3.147	3.139	3.099	3.159

AIR-PLASMA THz PHOTONICS

IN the previous chapter, it was established the need for THz radiation since its inception. Although countless uses have been enumerated, for the purpose of this thesis we focus chiefly on the use of THz waves in a spectroscopic setup: Optical-Pump Terahertz-Probe Spectroscopy (OPTP). The advantage of such a system is that one can easily switch between time-domain spectroscopy and time-resolved spectroscopy through the use of optical delay lines as will be discussed later on.

Over the past decades, there has been a huge outpouring in the field of THz wave generation and detection. Indeed, the use of a femtosecond laser amplifier means that the power incident on a material automatically raises the issue of a damage threshold. This is particularly important in the case non-linear optical rectification using electro-optic (EO) crystals such as gallium phosphide (GaP), zinc telluride (ZnTe) or gallium selenide (GaSe) to generate and detect terahertz waves. Figure 4.1 is a visual demonstration that increasing power impinging on the EO crystals will generate higher THz amplitude fields. However, this comes with one caveat: the crystal can only take so much power until it is damaged. We therefore need to look towards alternative avenues for generating THz. This has opened up a new field termed as THz Wave Photonics where the radiation in question is produced via higher order non-linear processes occurring in a plasma or magnetized plasma. Unfortunately what this also means is that electrons and ions produced in the plasma are subjected to very high power and very fast motions which will necessitate the need for a relativistic approach to fully explain the mechanisms behind this process albeit beyond the scope of this thesis.

This chapter will look at how the air-plasma generation and detection setup was built and the theory behind, together with a set of independent parameter space and how each of these parameters affect the THz field amplitude. The first section is an introduction to the history and advances in the field of THz air photonics. We then proceed to give a detailed explanation of the physics of plasma formation and how they emit radiation.

Thereafter, we provide a schematic diagram of how the system looks like and the different optical components. A study of how various parameters affect the THz field strength and bandwidth is done. We finish this chapter with a series of experiments that the system will accommodate for this thesis.

4.1 Introduction

As discussed above, EO crystals present some serious limitations to the exploitation of terahertz radiation. An air-plasma is one such nonlinear medium that effectively bypasses these impediments for three main reasons: (1) it is already broken down, (2) a continuous flow of gas ensures it is replenished continuously, and (3) gases have very low dispersion and absorption. Consequently, there is no concern about material damage which allows the system to handle extremely high laser power.

The earliest work on THz wave generation from an intense laser air-plasma interaction was reported by Hamster *et al.* in 1993. Sub-picosecond (10^{-13} s) laser pulses centred around 800 nm with an average power of 10^{12} W were focused into a gas tube resulting in a breakdown of the electric field of the air. A strong emission of radiation at terahertz frequencies were detected and the effect was attributed to the ponderomotive force mechanism. Their experiment was based on ponderomotive forces from the intense electric fields of the light pulses causing the acceleration of the charged electrons and ions. Immediately afterwards, Löffler *et al.* demonstrated that the emission process can be enhanced and steered to the forward direction by applying a static bias field to the plasma. [261]

7 years later in 2000, Cook *et al.* demonstrated that a higher intensity THz radiation, around 200 times stronger, could be emitted from laser-induced gas-plasma excited from a combination of both the fundamental pulse (800 nm) and its second harmonic (400 nm). [262] This time, the emission mechanism was attributed to the four-wave mixing (FWM) nonlinear optical process. Research within this particular field sprouted and rapid progress was made to understand the underlying physics governing this emission process. [134, 136–138, 143–145, 261–264] Among them, Bartel *et al.* reported THz wave

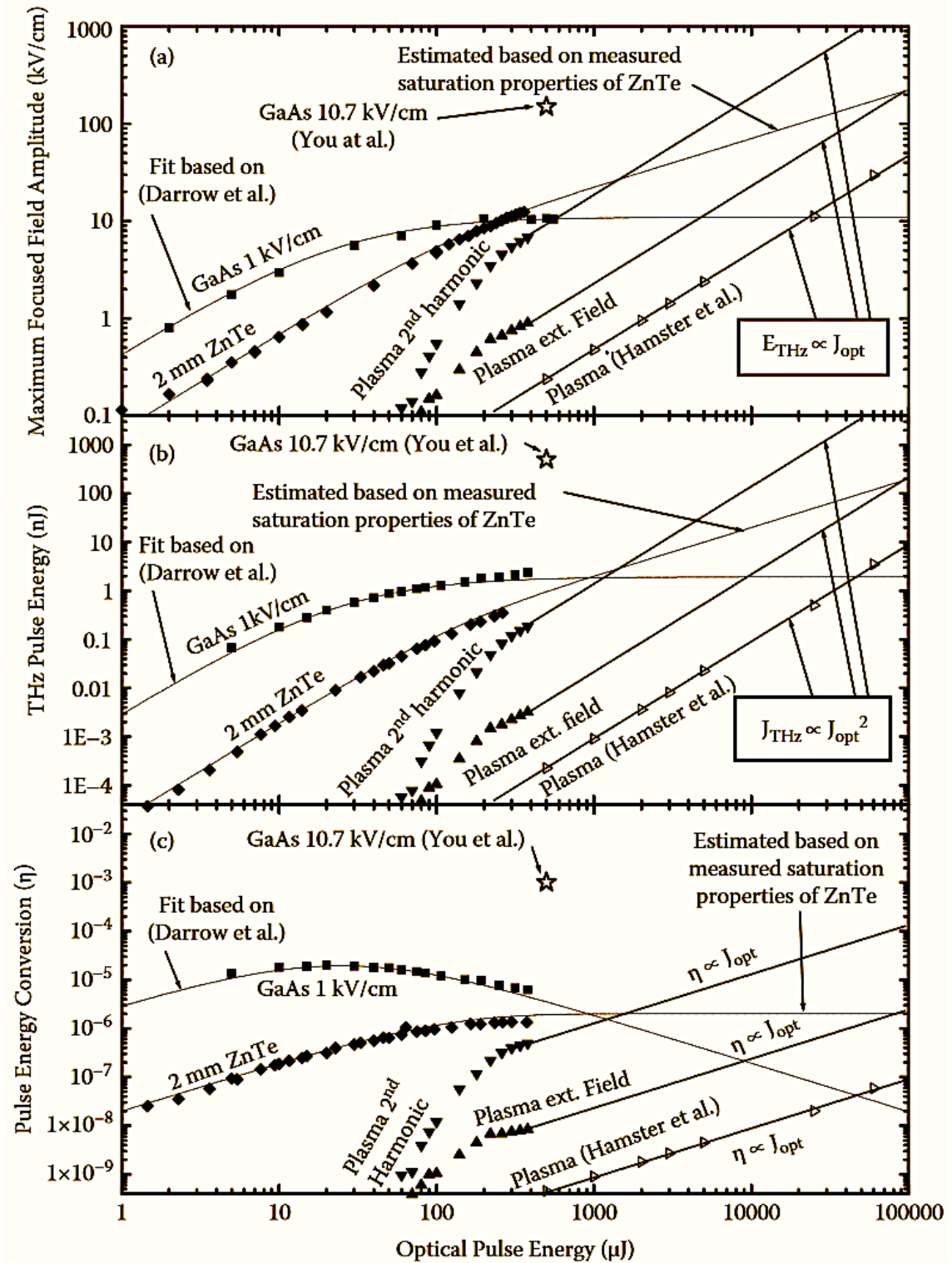


Figure 4.1: **THz Comparison:** Table comparing the various methods of THz generation and their efficacy. (a) the focused peak electric field, (b) the THz pulse energy, and (c) the energy conversion efficacy are displayed as a function of the energy per pulse of the femto-second near infrared pump laser. [146]

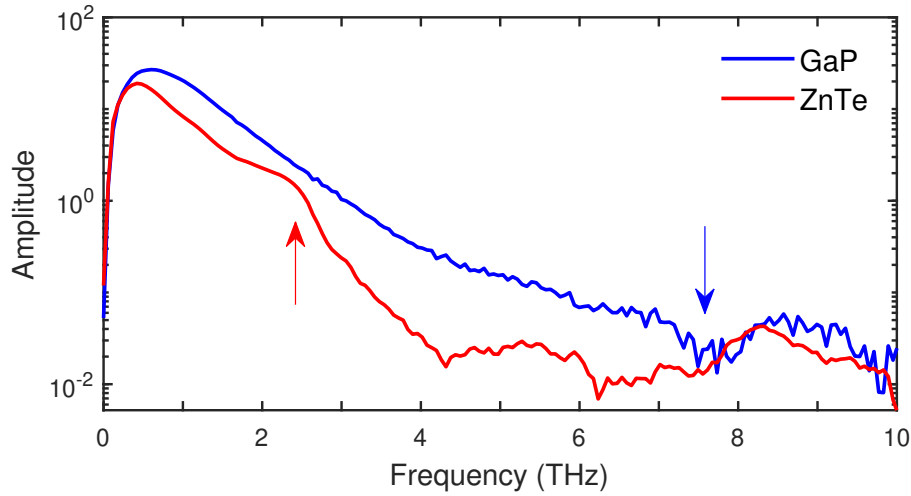


Figure 4.2: **Bandwidth & Phonon Modes:** Plots illustrating the effects of EO crystals possessing phonon modes. For GaP, the mode sits at around 7.5 THz while for ZnTe, it sits at around 4 THz. The spectral amplitude decreases sharply at these frequencies and any signal beyond are unrecoverable.

generation from gas-plasma with peak electric fields higher than 100 kV/cm, indicating promising applications of the gas-plasma THz wave source.

4.1.1 Motivation

Terahertz pulse generation and detection through non-linear interactions with EO crystals strongly restrains the bandwidth of any system due to longitudinal and transverse phonon modes. Figure 4.2 illustrates two THz pulses from our setup showcasing the effect of two detection crystals, GaP and ZnTe. The THz radiation was generated via a spintronic emitter, the operation of which has been explained in the previous chapter. Theoretically, this ensures that we have a large bandwidth of more than 10 THz. However, we can clearly see that in both cases, there is a cut-off frequency: 8 THz for the GaP (200 μm thick) and 4 THz for the ZnTe (200 μm thick). Ultimately this means any dynamics happening beyond these frequencies are veiled due to the very low signal-to-noise ratio.

Furthermore, when using these EO crystals, a collinear geometry can be used to satisfy the phase matching condition ensuring that the near-infrared excitation pulse (800 nm) propagates parallel to the THz radiation. However, the nonlinear susceptibility of these materials is not particularly high, and only THz pulse energies on the order of hundreds of picojoules (with field strengths of ≈ 1 kV/cm) can be achieved. We therefore look to significantly improve our experimental output by exploiting the photonics of air.

Non-linear interactions, namely second and third orders, of two-colour femtosecond laser field within laser-induced air plasmas is a recently developed technique. It is simple,

yet powerful enough to obtain ultrafast single-cycle broadband THz wave at extremely high field strengths, enabling the study of non-linear dynamics in condensed matter physics. Briefly, a fundamental laser beam at 800 nm and its second harmonic at 400 nm are focused to a point source by a lens into a pressurized gas cell creating a plasma filamentation that will then generate coherent THz radiation in a conical shape. This then allows us to extend our studies of charge dynamics in nanowires, perovskite solar cells and hexagonal boron nitride to high terahertz frequencies, a part of the spectrum which was not available to us. The following sections give an overview of the theory behind plasma creation in a gas and how THz is generated.

4.2 Theory

In order to be able to understand the physics of THz gas photonics, we will need to begin with the fundamental equations governing electromagnetic (EM) radiation, *i.e.* Maxwell's equations in differential form: [265]

$$\text{Gauss' Law:} \quad \nabla \cdot \mathbf{E}(\mathbf{r}, t) = \frac{\rho}{\epsilon_0}, \quad (4.1a)$$

$$\text{Gauss' Law (B Field):} \quad \nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0, \quad (4.1b)$$

$$\text{Faraday's Law:} \quad \nabla \times \mathbf{E}(\mathbf{r}, t) = -\frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t}, \quad (4.1c)$$

$$\text{Ampere's Law:} \quad \nabla \times \mathbf{B}(\mathbf{r}, t) = \mu_0 \mathbf{J} + \mu_0 \epsilon_0 \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t} \quad (4.1d)$$

where ρ and $\mathbf{J}$ are the free charge density and current density respectively. ϵ_0 and μ_0 are two constants known as the *electric constant (permittivity of free space)* and the *magnetic constant (permeability of free space)* which have the following values:

$$\epsilon_0 = 8.854187817 \times 10^{-12} \text{ m}^{-3} \text{ Kg}^{-1} \text{ s}^2 \text{ C}^2$$

$$\mu_0 = 4\pi \times 10^{-7} \text{ m Kg C}^{-2}$$

To fully describe EM theory, we need one final equation: the *Lorentz Force* law which governs the motion of charged particles in a magnetic field:

$$\text{Lorentz Force:} \quad \mathbf{F}(\mathbf{r}, t) = q(\mathbf{E}(\mathbf{r}, t) + \mathbf{v}(\mathbf{r}, t) \times \mathbf{B}(\mathbf{r}, t)) \quad (4.2)$$

Equations (4.1c) and (4.1d) tell us that the electric field and the magnetic field are intertwined - if the electric field “*shakes*”, it causes the magnetic field to “*shake*” and vice-versa. The two equations describing the motion of these quantities ($\mathbf{E}$ and $\mathbf{B}$) can be derived through the computation of the second time derivative of the respective variable. For brevity, the final equations are as follows:

$$\frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} - \nabla^2 \mathbf{E} = 0 \quad \text{and} \quad \frac{1}{c^2} \frac{\partial^2 \mathbf{B}}{\partial t^2} - \nabla^2 \mathbf{B} = 0, \quad (4.3)$$

where c is the speed of the waves given by

$$c = \sqrt{\frac{1}{\mu_0 \epsilon_0}}. \quad (4.4)$$

This dictates that the waves of the magnetic field travel at the same speed c as those of the electric field. Plugging in the values of ϵ_0 and μ_0 , the speed of the waves is $c = 299792458 \text{ ms}^{-1}$, which is unsurprisingly the speed of light.

It is noteworthy, at this stage, to mention that the above Maxwell's equations are for waves propagating in vacuum only. To describe the effect of the field in matter, it is incumbent to introduce another set of vectors namely the electric current density ($\mathbf{j}$), the electric displacement ($\mathbf{D}$), and the magnetic vector ($\mathbf{H}$). In general, the full set of equations are rather complicated and leave this for anyone who wants to consult advanced textbooks on the subject.

4.2.1 The Wave Equation

The two equations in (4.3) are known as the wave equations, one for $\mathbf{E}$ and $\mathbf{B}$. These can be solved independently whilst maintaining conformity with Maxwell's equations to yield a set of equations which encompasses the relationship between both quantities. We begin by assuming that the waves propagate in vacuum in the positive x -direction and that they do not depend on the y and z coordinates. These are known as *plane waves* because the fields $\mathbf{E}$ and $\mathbf{B}$ are constant in the (y, z) plane for fixed x and t .

In vacuum, Maxwell's equation (4.1a) reduces to $\nabla \cdot \mathbf{E} = 0$ which implies that we must have E_x constant. We look for solutions of the form

$$\mathbf{E} = (0, E(x, t), 0)$$

where E satisfies the wave equation (3) which is now

$$\frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} - \nabla^2 \mathbf{E} = 0$$

A general solution to the wave equation is of the form

$$E(x, t) = f(x - ct) + g(x + ct)$$

Here $f(x - ct)$ describes the phase of the wave moving to the right ('minus' sign) while $g(x + ct)$ describes the wave moving to the left ('plus' sign) with speed c . We further consider a wave oscillating at a single frequency, otherwise known as being *monochromatic*, and has the profile of a sine function. We therefore have

$$E = E_0 \sin \left[\omega \left(\frac{x}{c} - t \right) \right],$$

which is more commonly written in the form

$$E = E_0 \sin(kx - \omega t), \quad (4.5)$$

where k , the *wavenumber*, is related to the frequency by

$$\omega^2 = c^2 k^2. \quad (4.6)$$

Equation (4.6) is a very important relationship known as the **dispersion relation**. It relates the *angular frequency*, ω , to the *wavenumber*, k . This will come in handy when describing surface plasmons in nanowires in later chapters of this thesis.

The PDE for the electric field has been solved. To determine the magnetic field, we now use equation (4.1b) which states that the x -component of B is constant. B_y and B_z must obey the wave equation (4.3). However, their behaviour is dependent on the electric field through Faraday's Law, equation (4.1c). Setting B_y zero, we have

$$\mathbf{B} = (0, 0, B)$$

where

$$\frac{\partial B}{\partial t} = -\frac{\partial E}{\partial x} = -kE_0 \cos(kx - \omega t).$$

Solving this yields

$$B = \frac{E_0}{c} \sin(kx - \omega t) \quad (4.7)$$

From this, we conclude that both $\mathbf{E}$ and $\mathbf{B}$ propagate in phase and in the same direction but orthogonal to each other.

Maxwell's equations are linear and this implies that the sum of any number of solutions of the form (4.5) and (4.7) is still a solution. This becomes crucial in an important concept called the *principle of superposition* which will become apparent when discussing *velocity phase matching* when we speak of frequency doubling in non-linear crystals. It is also important to note that the equations governing both the electric and magnetic fields can be written in complex notations

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{x} - \omega t)} \quad , \quad \mathbf{B} = \mathbf{B}_0 e^{i(\mathbf{k} \cdot \mathbf{x} - \omega t)} \quad (4.8)$$

where $\mathbf{E}_0$ and $\mathbf{B}_0$ are complex-valued vectors. The physical quantities, E_0, B_0, k can be obtained by taking their corresponding magnitudes. From Maxwell's equations, one can easily go about proving that both the electric and magnetic fields are perpendicular to the direction of propagation, *i.e.*

$$\begin{aligned} \nabla \cdot \mathbf{E} = 0 &\Rightarrow i\mathbf{k} \cdot \mathbf{E}_0 = 0 \\ \nabla \cdot \mathbf{B} = 0 &\Rightarrow i\mathbf{k} \cdot \mathbf{B}_0 = 0 \\ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} &\Rightarrow i\mathbf{k} \times \mathbf{E}_0 = i\omega \mathbf{B}_0 \end{aligned}$$

4.2.2 Polarization of Light

Most sources of illumination, such as a light bulb or the sun, transmit light waves with their electric field vectors (the polarization of light is, by consensus, defined with respect to the electric field vector) oscillating in all the planes that are perpendicular to the direction of propagation. If looked sideways, the electric field vectors would be seen to form a cylindrical structure with an isotropic distribution. However, when the electric field vectors are restricted to a single plane by filtration through a waveplate or polariser, the light is said to be polarized with respect to the direction of propagation and the electric field vibrates in only one plane while the rest are cut off.

Any surface has some reflectivity properties and when light impinges on a boundary surface, some of it will be reflected. Unpolarized incident light such as sunlight, or a bulb is polarized to a certain degree when it is reflected from an insulating surface like water or a highway. In this case, light waves that have the electric field vectors parallel to the surface are reflected to a greater degree than those with different orientations. The optical properties of the insulating surface determine the exact amount of reflected light that is polarized. Mirrors are not good polarizers, although many transparent materials will be very good polarizers, but only if the incident light angle is within certain limits. In this case, the particular angle inducing maximum polarization is known as the **Brewster** angle given by the expression:

$$n = \frac{\sin \theta_i}{\sin \theta_r} = \frac{\sin \theta_i}{\sin(90 - \theta_i)} = \tan \theta_i \quad (4.10)$$

where n is the refractive index of the medium, θ_i is the angle of incidence, and θ_r is the angle of refraction. The Brewster angle will be highly useful in our setup when it comes to blocking off residual radiations (fundamental + second harmonic) from the plasma emission to allow only p -polarised terahertz radiation through without any loss due to reflection at the interface. The transmission and reflection coefficients of the polarised radiation is depicted in the plot in Figure 4.3. Although the p -polarized component of the impinging THz wave is fully transmitted, there is a small portion of the s -polarized wave that will go through, inducing a partial polarization of the light. The advantage of using silicon as a residual beam block is that there are no stray reflections at the air-silicon and silicon-air interfaces. This results in zero Fabry-Perot etalons at that particular angle.

4.3 Nonlinear Effects

Nonlinear effects in optics are usually small and insignificant when it comes to low energy sources. However, when dealing with high energy, femtosecond-amplified laser

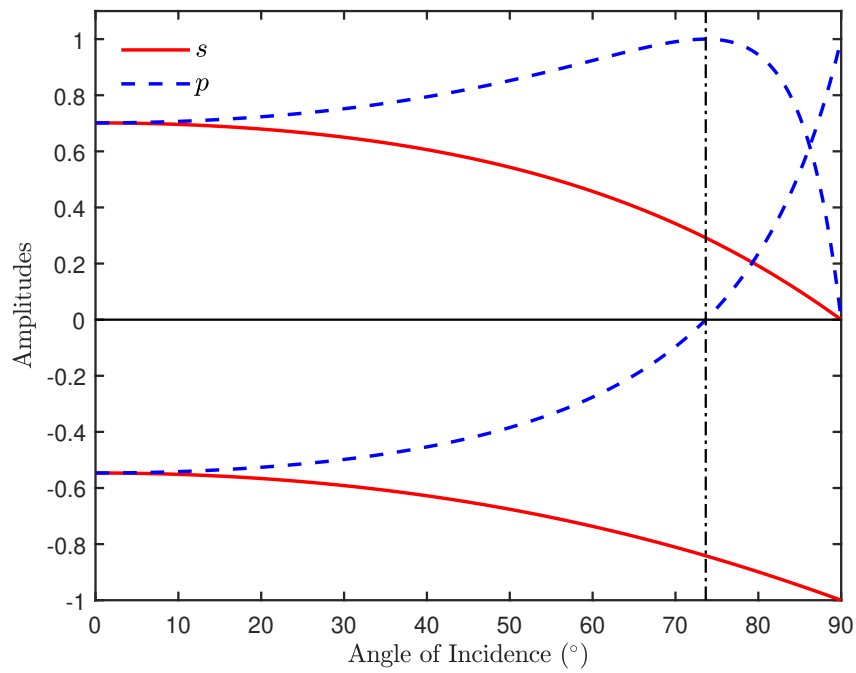


Figure 4.3: **Brewster's Angle:** Simulations of the Fresnel transmission and reflection coefficients at an air/silicon interface for both s - and p - polarized radiation. Silicon has a near constant refractive index of 3.41 in the THz regime, and at Brewster's angle, θ_B , given by $\theta_B = \arctan(n) = 73.66^\circ$, all p -polarized radiation is transmitted as well as a small portion of s -polarized radiation. This is indicated by the dashed line on the plot. Transmission coefficients are positive and reflection coefficients are negative.

pulses these effects introduce notable perturbations and are responsible for a whole new level of physics. In our case, we are looking at the occurrence of air-plasma filamentation to generate terahertz radiation and second-harmonic generation in a beta-barium borate (BBO) crystal from an 800 nm fundamental femtosecond laser pulse.

4.3.1 Basics of Nonlinear Optics

Although the field of nonlinear optics is vast, this section will attempt to explain a few basic concepts. More materials can be found in most standard/specialized textbooks. Most of the explanation from this section however can be read in detail from 'Laser Physics: Hooker & Webb'. [266] All atoms possess electron clouds orbiting around their nuclei. When an electric field $\mathbf{E}$ is applied to a dielectric material, a polarization density $\mathbf{P}$ is induced in that dielectric due to the response of the electron movement. In the simplest case, the polarization always occurs in the same direction as the electric field. Let's take a sample of liquid argon, for example. The electric field won't affect the motion of the argon atoms much unless it is extremely strong, but each atom's electron cloud will be perturbed so that electrons are more likely to be found on the side of the atom where the electric potential due to the external field is higher; the result is an induced dipole, and averaging then gives some polarization density in the bulk liquid. Increase the electric field strength, and the separation increases in magnitude and consequently so does the polarization density.

The polarization produced in a medium by an intense applied electric field is then of the form: [266]

$$\mathbf{P} = \epsilon_0 \left[\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}^2 + \chi^{(3)} \mathbf{E}^3 + \dots \right] \quad (4.11)$$

where the first term inside the square brackets, $\chi^{(1)}$ termed as electric susceptibility, relates to ordinary linear optics, the second term involving $\chi^{(2)}$ relates to second-order nonlinear effects responsible for second-harmonic generation, the third term involving $\chi^{(3)}$ describes third-order nonlinear effects responsible for terahertz generation from an air-plasma filament, and so on. In short, $\mathbf{P}$ can be expressed in a more concise equation,

$$\mathbf{P} = \epsilon_0 \chi^{(1)} \mathbf{E} + \mathbf{P}^{\text{NL}}, \quad (4.12)$$

where $\mathbf{P}^{\text{NL}}$ represent the higher-order nonlinear terms.

4.3.2 Phase Matching

The previous chapter touched briefly upon the importance of phase-matching in non-centrosymmetric crystals when it comes to THz generation and detection. Unfortunately, this is possibly the most crucial point in the physics of THz air photonics. Most of the optical nonlinear frequency-mixing processes are phase-sensitive, and as such, they require phase-matching in order to be efficient. This practically means that there is a certain phase relation between the interacting waves that needs to be maintained along the volume where the interaction takes place.

From a mathematical point of view and in order to appreciate this concept better, we shall look at some equations that will quantify this relationship. For the air-plasma setup, SHG is most important when it comes to generating the two-colour plasma filament to radiate the THz. So we will consider phase-matching for the case of a BBO crystal, converting the fundamental laser pulse (800 nm) to the second harmonic (400 nm). Assuming the laser $\vec{E}$ -field from the Ti:Sapphire amplifier is a plane wave propagating in the z -direction, we have:

$$E_{800\text{ nm}} = A_{800\text{ nm}} \cos \omega t - k_{800\text{ nm}} z, \quad (4.13)$$

where $k_{800\text{ nm}}$ is the angular wavenumber of the fundamental beam and is dictated by $k_{800\text{ nm}} = \frac{n_{800\text{ nm}} \omega}{c}$, and $n_{800\text{ nm}}$ is the corresponding refractive index in as it goes through the BBO. The second harmonic plane wave equation is then simply:

$$E_{400\text{ nm}} = A_{400\text{ nm}} \cos 2\omega t - k_{400\text{ nm}} z. \quad (4.14)$$

The cosine terms in Equations 4.13 and 4.14 are necessarily different unless the wavevectors of the two beams are the same, i.e. $\Delta k = 0$, which would hold true only if $n_{800\text{ nm}} = n_{400\text{ nm}}$. However, it is well known that they are different due to the dispersion inside the crystal. [267, 268] As a result, both waves will have different phase velocities inside the crystal and the second harmonic will be delayed with respect to the fundamental. The severity of this phase-mismatch is expressed in terms of the coherence length, l_c , given by: [269]

$$l_c = \frac{\pi}{|k_{800\text{ nm}} - k_{400\text{ nm}}|} = \frac{\lambda}{4|n_{800\text{ nm}} - n_{400\text{ nm}}|} \quad (4.15)$$

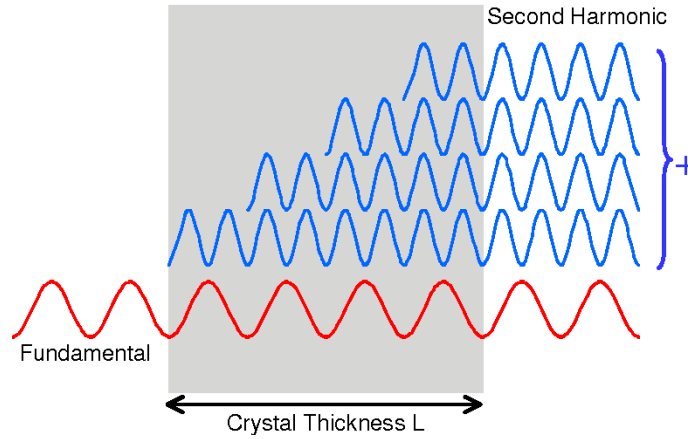


Figure 4.4: Schematic description of the concept of phase matching. Here, we consider the case of second harmonic generation (SHG) 400 nm from an 800 nm amplified femtosecond laser pulse. The fundamental wave at frequency ω has a well defined phase, polarization and amplitude everywhere in the β -Barium Borate (BBO) crystal. Second order nonlinear effects in the crystal will induce dipoles which will all radiate at a frequency 2ω with a phase dictated by the fundamental wave. As the SHG exits the crystal, all the dipoles radiate in phase in the forward direction such that constructive interference is achieved. [270]

The conversion efficiency is given by:

$$\begin{aligned}
 \eta &= \frac{1}{L^2} \left| \int_0^L \exp(i2k_\omega z) \exp(-i2k(\omega)z) dz \right|^2 \\
 &= \frac{1}{L^2} \left| \int_0^L \exp(i\Delta k z) dz \right|^2 \\
 &= \left(\frac{\sin(\Delta k L/2)}{\Delta k L/2} \right)^2
 \end{aligned} \tag{4.16}$$

which should be optimized for maximum conversion efficiency of the nonlinear process. If this relation is fulfilled, then all the amplitude contributions to the generated wave from different locations of the nonlinear medium are all in phase at the end of the medium. Otherwise, these contributions are out of phase, and essentially cancel each other out. This is depicted in Figure 4.4, which shows how the different contributions of the second-order nonlinearities accumulate.

4.4 Plasma Physics

A plasma, in the simplest definition, is a state of matter similar to a gas in which a certain portion of the particles is ionized. It is also referred to as “the 4th state of matter.” In a more standard definition, a plasma is defined as a quasi-neutral ionized gas that exhibits collective behaviour. Before moving on to plasma formation, let us define what we mean

by ‘quasi-neutral’ and ‘collective behaviour’ as this will enable us to grasp better the concept of plasma filamentation and how various physical models have been developed to understand their behaviour.

Plasmas tend to be neutral, *i.e.* having no effective charge. Let us imagine a plasma with all the electrons and positive ions floating around. If we were to count the number of positive and negative charges within a given volume, we will find

$$-en_e + Zen_i \approx 0 \quad (4.17)$$

where n_e and n_i are the number densities of electrons and ions respectively, and e and Z are the electronic charge and ionic charge respectively.

Why are plasmas neutral? If we could create a situation where Zn_i were $> n_e$, the resulting distribution would create a strong electric field. Consequently, the electrons from the surrounding plasma would rush in to neutralise this electric field and no plasma would exist.

What is meant by quasi-neutral? At temperatures suitable for plasma creation, random/thermal motion means that n_e and n_i will fluctuate (when considering a unit volume). Hence $-en_e + Zen_i \neq 0$ exactly (out say by 1 part per billion). This is why Eq. (4.17) has a $\approx$ sign.

What is meant by collective behaviour? In a gas, particles interact via short-range forces (and sometimes long-range depending on the type of gas used). In a plasma however, due to the strong electric fields existing between charged particles, the latter interact via long range electromagnetic forces which give rise to this ‘collective behaviour.’ From the laws of electromagnetism, collective charge flows/currents will result in the production of magnetic fields. In addition, collective charge imbalance (small but not zero) will produce electric fields. These $\mathbf{E}$ and $\mathbf{B}$ fields will give rise to bulk plasma motion. Therefore, plasmas can support many more types of waves and instabilities than a mere gas.

Now that we have painted the canvas about what a plasma is, let us dive into the occurrence of plasma filamentation.

4.4.1 Plasma Filamentation

When a high intensity amplified femtosecond laser pulse is strongly focused in a gas cell, the gas atoms/molecules at the focal volume will dielectrically collapse under the high electric field intensity. The electron clouds of the atoms/molecules will be stripped off the nuclear force and they will be subsequently ionized. As such, a plasma is created. [264,271] This process is usually accompanied by a fine bright white light

in a filament shape and a noise, at the same frequency as the laser repetition rate is heard. If an optical chopper is used, then it will be at the frequency of the chopper. The laser-induced plasma might seem similar to dielectric breakdown by an electric discharge, however its characteristics differ in size, temperature, carrier density and lifetime. Depending on the laser beam intensity, which governs the ionization regime, plasma generation is a result of two major mechanisms: multi-photon ionization (MPI) and/or tunnel ionization (TI). A parameter that helps to distinguish the transition from one ionization regime to the other, is the Keldysh parameter: [272]

$$\gamma = \sqrt{\frac{U_I}{2U_P}}, \quad (4.18)$$

where U_I is the ionization potential of the gas atoms/molecules and U_P is the average kinetic energy of a free oscillating electron under the influence of the laser electric field strength, E_{laser} , at a frequency of ω . This energy is also referred to as the ponderomotive force. U_P is given by the following expression:

$$U_P = \frac{e^2 E_{\text{laser}}^2}{4m_e \omega^2} \quad (4.19)$$

Significance of γ : This parameter reflects the characteristic time scale of tunnelling under the binding potential barrier of an atom over the optical period of the laser, and $\gamma \approx 1$ corresponds to the transition between MPI and tunnelling ionization. For the case of our experimental setup $\gamma \ll 1$, meaning that tunnel ionization is the dominant mechanism. This tunnel ionization is depicted in Figure 4.5.

4.4.2 THz Generation via Plasma Formation

Terahertz emission from a two-colour laser-induced plasma filament in a gas is a rather complicated process, as it involves a number of physical phenomena, such as strong-field ionization and interaction, plasma dynamics, relativistic mechanics and nonlinear frequency conversion phenomena. Due to this complex interplay of several processes, the physics of THz-air-plasma generation is still subjected to debates. Many physical models sprouted from various research groups across the world that attempted to predict and describe the behaviour of the plasma as THz pulses are emitted from it. In this section, we shall discuss briefly the two basic models that exist in literature: (1) the *Four-Wave Mixing model*, which was also the first ever theoretical attempt to explain the phenomenon, and (2) the *Microscopic Photocurrents model*. Whilst both methods are technically correct and do explain some parts of the THz generation, they both fail to give a full picture of this rather elusive phenomena.

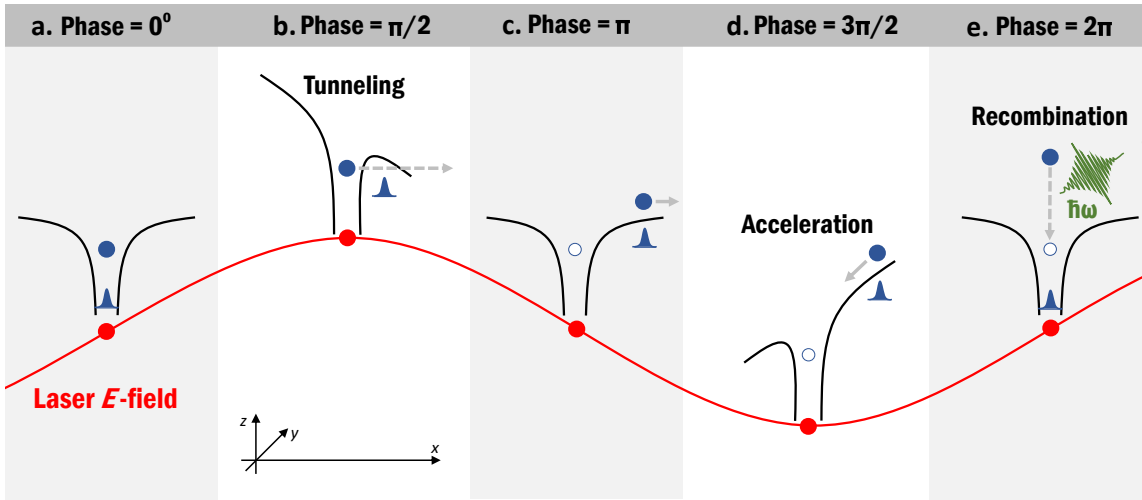


Figure 4.5: Schematic description of tunnel ionization under an intense laser field. As the laser beam is focused tightly, its E-field becomes too strong such that it will drastically distort the binding field of an atom. The electron clouds around the nuclei will feel a strong opposing force and be stripped off. While previously the probability for an electron to escape the barrier through tunnelling was practically zero due to a lack of activation energy, the applied laser field distorts the barrier and its length can easily be surpassed by the bound electrons. Once the atom is ionized, the loose electrons can either recombine with the parent atom, emitting the kinetic energy it got as high harmonic light generation, or further ionize other atoms through collisions.

4.4.2.1 Four Wave Mixing Model

The first ever observation of the emission of THz radiation was done in 1993 by H. Hamster and his colleagues. [273] At the heart of this experiment was an intense laser-plasma interaction where they focused the pulsed laser beam of 100 fs pulse duration and 800 nm wavelength to breakdown the voltage limit of the air forming a gas plasma. The source of the observed THz wave was attributed to ponderomotive forces inside the plasma, that drove it to oscillate coherently. The origin of the ponderomotive forces results from the motion of charged particles within an oscillating electric field. When a particle moves from a region of high field intensity to a low intensity region, a force is felt and this is the ponderomotive force described by the following equation: [273]

$$\mathbf{F}_{\text{ponderomotive}} = -\nabla \frac{q^2 I_{\text{optical}}}{2\epsilon_0 c_0 m_q \omega_{\text{optical}}^2}, \quad (4.20)$$

where q and m_q are the charge and mass of the charged particles. I_{optical} and ω_{optical} are the intensity and angular frequency of the light. The tight focus of the laser pulses create a gigantic ponderomotive force capable of modifying the spatial distributions of the particles within the plasma. Due to the difference in masses between the electrons and the ions formed, the electrons move much faster thus creating a net dipole moment inducing THz emission. However, the generation efficiency is very low and only small field amplitudes of the THz waves are obtained.

Later in 2000, D.J. Cook and R.M. Hochstrasser demonstrated that THz radiation of much higher field strengths can be generated ($\approx \times 100$). [262] The key to this success was to merge the fundamental beam with its second harmonic within the gas plasma. In this case, the THz wave generation mechanism was assumed to be a four-wave mixing process (FWMM). FWMM is a general case for nonlinear optical effects associated with the higher order susceptibilities (namely the 3rd). The effect arises when two waves of differing angular frequencies propagate in a Kerr medium producing two additional frequencies, hence the name 'four-wave'.

Despite its initial success, this model was used by several other groups for a while. [140,263,274] until it eventually failed to give an accurate description of the THz emission. For instance, for a FWM process, the intensity of the radiation emitted from the plasma was notably high in ambient air while the threshold for the ionization of the gas was strongly correlated with that of the THz generation which meant that a plasma is needed for the emission to take place which is not a requirement in the theory. [275] The model however remains at the forefront of theoretical models as it gives an intuitive picture of the phenomenon, and can help to better understand the underlying mechanisms for the ABCD detection scheme, which is the mechanism for THz detection.

4.4.2.2 Photocurrent Model

The photocurrent model was initially proposed by K.Y. Kim in response to the failure of the FWMM. [276–278] It is a sophisticated semi-classical model that combines strong-field ionization and classical electron dynamics in an effort to describe as accurately as possible what happens during the formation of a plasma and the subsequent generation of THz. As mentioned previously, the bound electrons of the gas atoms or molecules are subjected to fast tunnel ionization, since the combined laser field of the intense fundamental and second harmonic beams suppress the Coulomb barrier of the gas species. In the presence of the intense laser electric fields, the freed electrons are forced to oscillate about an equilibrium position which depending on the relative phase between the fundamental beam and its second harmonic can result in a directional transverse current. Since this current surge occurs on the time scales of photo-ionization, this mechanism can produce electromagnetic radiation at terahertz frequencies. What follows is a brief explanation of this process.

If an intense single frequency laser beam interacts with the atoms or molecules of a gas, there is high probability that a number of electrons will be liberated from their parent species. After they are released, these electrons are subjected to the electric field of the laser and oscillate along the direction of the laser field polarization. The drift velocity is

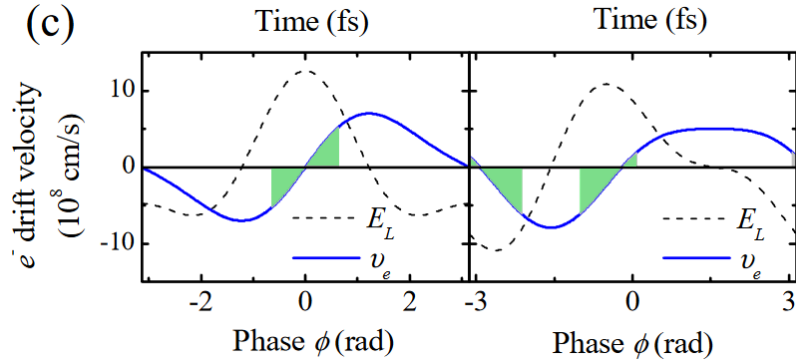


Figure 4.6: (c) Drift electron velocity versus ϕ (solid line), overlaid with the laser field (dashed line). Adapted from [276]

determined by the moment of their ionization and the magnitude of the laser electric field at the time. However, since the waveform of a single frequency laser field is symmetric, there cannot be a directional current of freed electrons. A directional electron current can arise if an additional laser field, oscillating at the second harmonic is combined with the fundamental. The combined laser field is given by the relation:

$$E_{\text{laser}} = E_{\omega} \cos(\omega t) + E_{2\omega} \cos(2\omega t + \theta), \quad (4.21)$$

where E_{ω} and $E_{2\omega}$ are the electric field amplitudes of the fundamental and the second harmonic respectively, and θ is the relative phase between them. Assuming tunnel ionization occurs at time $t = t'$, the freed electron velocity $v(t)$ driven by the external laser field at time t is given by the following expression:

$$v(t) = -\frac{e}{m_e} \int_{t'}^t E_{\text{laser}}(t) dt, \quad (4.22)$$

where e and m_e are the electronic charge and mass. The freed electrons then acquires a drift velocity of

$$v_{\text{drift}}(t) = \frac{eE_{\omega} \sin(\omega t')}{m_e \omega} + \frac{eE_{2\omega} \sin(2\omega t' + \theta)}{2m_e \omega} \quad (4.23)$$

Equation 4.23 dictates that the relative phase θ will affect the drift velocity of the freed electrons. Figure 4.6(c) illustrates this clearly: on the left, when $\theta = 0$, the combined electric fields of the waves (ω and 2ω) is totally symmetric. The drift velocity function, represented by the blue line, is then also symmetric. As a result, the total velocity of all the free electrons around the laser slopes cancels out (shown by the shadowed area in the same figure). However, when the relative phase of the fields is $\pi/2$, due to the asymmetric shape of the combined field waveform, there is a remaining drift velocity towards one direction. This non-vanishing electron density produces then a current surge $\bar{J}(t)$ given by the following equation,

$$\bar{J}(t) = e \int_{-\text{inf}}^t v(t') d\rho_e(t'), \quad (4.24)$$

where $d\rho_e(t')$ is the number density of electrons as ionized by the intense laser electric field in a time interval $\delta t'$.

4.4.3 THz Detection via Gas Photonics

The current most established heterodyne ultra-broadband THz detection in gaseous media is called ABCD (Air-Biased Coherent Detection). As discussed in the previous chapter, FS-EOS requires a non-centrosymmetric materials in order for the Pockel's effect to be detected. For a centrosymmetric crystal or isotopic medium such as a gas, direct second-harmonic generation is forbidden in the dipole-transition approximation. However, in the presence of a low-frequency external electric field, the second harmonic wave of the incident optical frequency can be obtained through a four wave mixing process described by the third order nonlinear polarization vector:

$$P(\omega' = 2\omega + \Omega) = \epsilon_0 \chi^{(3)}(\omega, \omega, \Omega) E(\omega) E(\omega) E(\Omega), \quad (4.25)$$

where $\chi^{(3)}(\omega, \omega, \Omega)$ is the corresponding third-order nonlinear susceptibility of the medium, ω is the frequency of the incident optical pulse, Ω is the frequency of the applied external AC bias, and ω' is the frequency of the generated wave.

Dai et al. have successfully demonstrated that terahertz field-induced second harmonic generation (TFISH), [135] a FWM process where a THz photon mixes with two photons of the probe beam in order to generate one second-harmonic photon of the probe beam, can be exploited to quasi-coherently detect a THz pulse using air as the sensor. According to Equation 4.25, the TFISH signal intensity, $I_{2\omega}^{\text{THz}}$, will be given by: [160]

$$I_{2\omega}^{\text{THz}} \propto |E_{2\omega}^{\text{THz}}|^2 \propto |\chi^{(3)} E(\omega) E(\omega) E(\Omega)|^2 \propto (\chi^{(3)} I_\omega)^2 I_\omega. \quad (4.26)$$

Equation 4.26 suggests that the detected second harmonic signal intensity is proportional to the intensity of both the incident optical beam and the THz wave. The phase information is therefore lost rendering the technique incoherent. However, as a first approach, they improved on this technique via a self-phase modulation mechanism through the introduction of a probe laser beam-induced plasma. The white-light supercontinuum acts as local oscillator and the detected SH signal is then modified to:

$$\begin{aligned} I_{2\omega} \propto \langle E_{2\omega}^2 \rangle &= \langle (E_{2\omega}^{\text{THz}} + E_{2\omega}^{\text{loc}})^2 \rangle \\ &= \langle (E_{2\omega}^{\text{THz}})^2 \rangle + 2\langle E_{2\omega}^{\text{THz}} E_{2\omega}^{\text{loc}} \rangle + \langle (E_{2\omega}^{\text{loc}})^2 \rangle \end{aligned} \quad (4.27)$$

The cross term in the above equation provides the basis for coherently detecting THz waves, preserving both the amplitude and phase information, crucial in reconstructing the THz waveform. The last term stems from the contribution of the local SH signal and

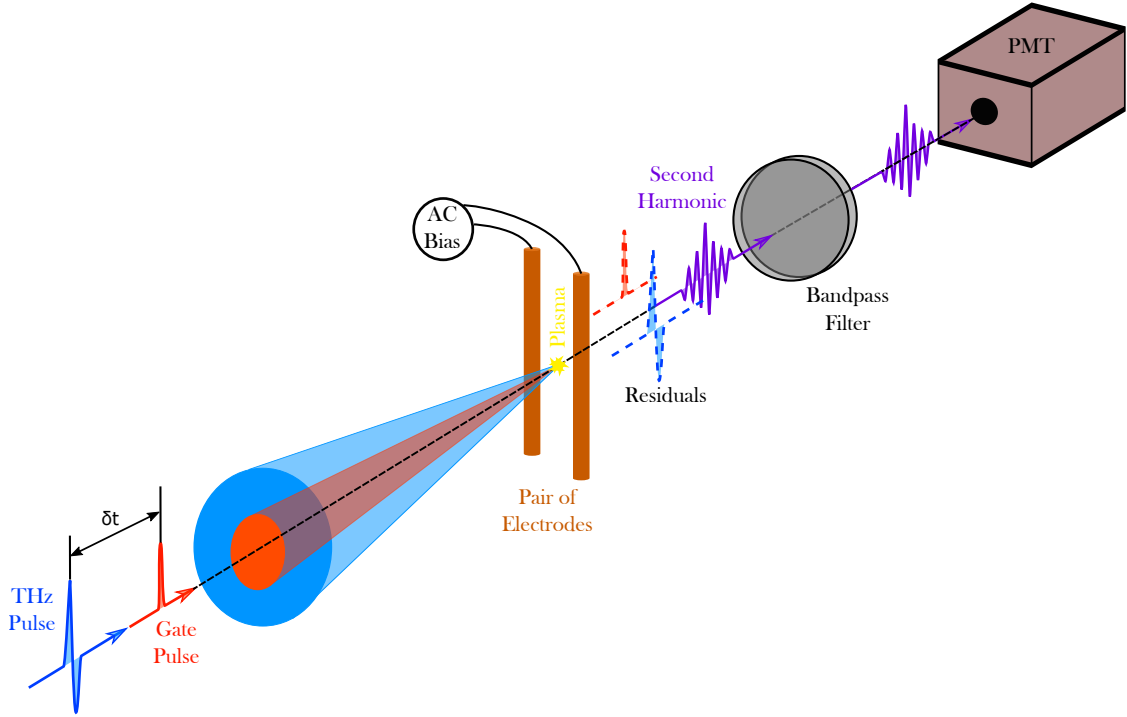


Figure 4.7: **Air-Biased Coherent Detection:** Schematic illustration of the ABCD process. The THz and optical gate pulses travel collinearly and overlap spatiotemporally in between the two electrodes. A very weak plasma is required in this case and the AC bias acts as a local harmonic oscillator generation the second harmonic of the gate pulse. The bandpass filter cuts off any residuals of the THz and optical gate. The second harmonic is quite weak in intensity and therefore a PMT is used to detect it.

can be deducted as background noise. Equation 4.27 can be reduced into a more compact and meaningful form as follows:

$$I_{2\omega} \propto \left[(\chi^{(3)} I(\omega))^2 I_{\Omega} + 2\chi^{(3)} I(\omega) E_{2\omega}^{\text{loc}} E_{\Omega} \cos \phi \right], \quad (4.28)$$

where ϕ is the phase difference between $E_{2\omega}^{\text{loc}}$ and $E_{2\omega}^{\text{THz}}$. Although this was a successful attempt to introduce coherence, the strong white light emitted from a plasma dominates the detection capability of a photomultiplier tube resulting in a very small signal-to-noise ratio.

N. Karpowicz and X.C Zhang built further on this method where one could bypass the requirement for an induced air-plasma at the detection. [279,280] Essentially, an AC bias replaces the role of the plasma as the local oscillator. The bias is provided by a pair of electrodes placed at the focal point where THz and probe beams overlap. Previously with the air-plasma induced SH generator, the method was termed as Air Breakdown Coherent Detection (ABCD). In this new scheme with the AC bias, the method was termed the Air Biased Coherent Detection (ABCD) scheme allowing for coherent heterodyne detection,

and is free of the noisy background. From this point onwards, ABCD will be referred to as the improved second version.

The basic concept of ABCD is depicted in Figure 4.7: a probe beam or gate pulse in the case of an OPTP setup, of frequency ω is sent to propagate along a controlled time delay path, in order to be able to manipulate the temporal distance between it and the pump beam. After the delay stage part, it is focused by a lens of long focal length. Usually as the probe beam is focused down, it propagates through a hole in a metal coated axis parabolic (OAP) mirror. The same OAP mirror is used to focus the THz beam. The probe and THz beams focus collinearly with overlapping focal points. Across the focal point, a pair of electrodes with a gap between them is placed, and an alternating voltage bias V is applied, with an amplitude on the order of some tens of kV and an alternating frequency half the repetition rate of the laser. If phase-matching is achieved, then the second-harmonic beam is generated, collected by a lens and focused to a light detector, usually a photomultiplier tube.

The SH induced by the local-oscillator field is then given by: [160]

$$E_{2\omega}^{\text{bias}} \propto \chi^{(3)} E_{\omega} E_{\omega} E_{\text{bias}} \propto \chi^{(3)} I_{\omega} E_{\text{bias}} \quad (4.29)$$

After passing through a bandpass filter, the residual beams are filtered out and the intensity of the detected SH is proportional to the square of the sum of the electric field amplitudes:

$$I_{2\omega} \propto (E_{2\omega}^{\text{THz}} + E_{2\omega}^{\text{bias}})^2 \propto [(E_{2\omega}^{\text{THz}})^2 \pm 2E_{2\omega}^{\text{THz}} E_{2\omega}^{\text{bias}} + (E_{2\omega}^{\text{bias}})^2] \quad (4.30)$$

In order to remove the constant background terms in the above relation, first and third, and only keep the cross term, a coherent heterodyne detection scheme can be utilised: [160] by modulating the bias field at a certain frequency, usually half the repetition rate of the pumping laser repetition rate, the other two terms can be discarded and only the coherent cross term is isolated.

This method introduces a significant advantage over the air-plasma SH induced signal: no plasma is required and therefore the pulse energy can be low and secondly through this heterodyne detection both SNR and the dynamic range are improved.

4.5 Experimental Setup: Building the Setup

This section is dedicated to the building of the setup including beam-path diagram and the various optical components the system comprises. A few points worth noting is first, in order to retain maximum bandwidth from the plasma, a compact system is preferable

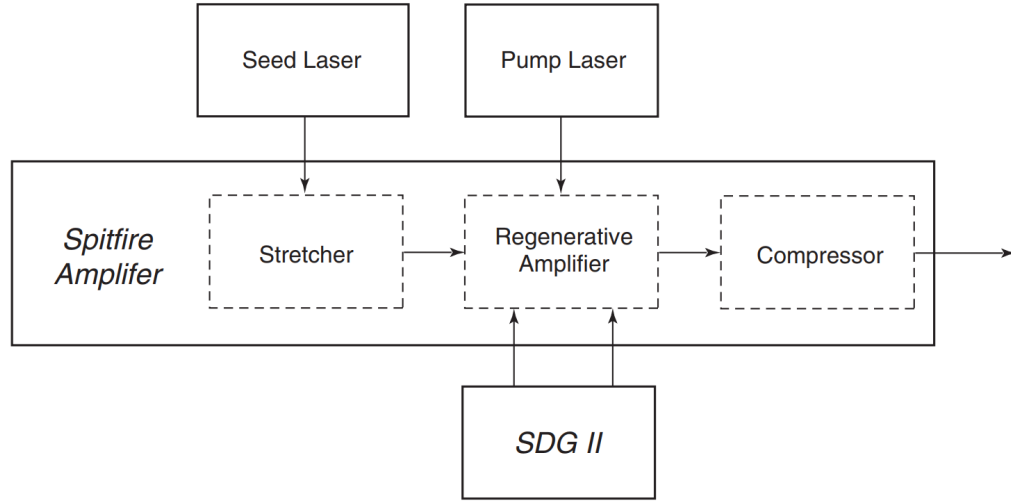


Figure 4.8: A block diagram showing the main parts of the Spitfire Ace regenerative amplifier.

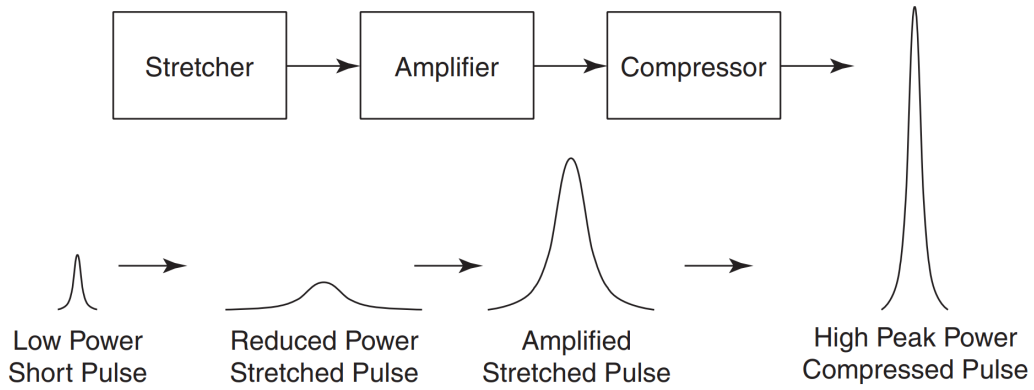


Figure 4.9: A block diagram showing the main parts of the Spitfire Ace regenerative amplifier.

and second the amount of space on the optical is quite small and therefore a challenging task to build a full OPTPS. We will begin by briefly describing the laser amplifier used and the principles behind pulse stretching and amplification. We then go on to describe the setup with a ray diagram drawn using Inkscape.

4.5.1 Laser Amplifier

A regenerative Ti:Sapphire laser amplifier (Spitfire Ace Spectra Physics) was used to generate 35 fs pulses centred at 800 nm at a repetition rate of 5 kHz with an average power of 8 W. Only a fraction of the 8 W was used for the air-plasma system: 3 W.

The Spitfire amplifier contains the optics and opto-mechanical devices for stretching, selecting, amplifying and compressing pulses from a seed laser (such as a Spectra-Physics Mai Tai or Tsunami). The Spitfire amplifier comprises the following three assemblies:

the optical pulse stretcher the regenerative amplifier the optical pulse compressor. These assemblies are each carefully optimized for the chosen wavelength range, the repetition rate of the amplified output, and the duration of the amplified pulses. Figures 4.8 and 4.9 give a brief overview of what goes on in the amplifier system. The Spitfire amplifier gain media is a titanium-doped sapphire (Ti:sapphire) crystal. Ti:sapphire was selected because of its two very useful properties: (a) it has a broad absorption band in the blue and green, which allows it to be pumped by the frequency-doubled output of a Nd:YLF or a Nd:YAG laser, and (b) it is tunable over a broad emission band of wavelengths in the near infrared.

4.5.2 Beam Paths

In this section we will try to provide an accurate description of the experimental setup of the broadband air-plasma terahertz spectrometer. As mentioned in the previous section, only a fraction of the 8 W was used for the OPTP setup. This is achieved through the use of beamsplitters where the energy is split into two smaller portions depending on the transmission-reflection ratio. The setup is shown diagrammatically in Figure 4.10.

Out of the 8 W from the Ascend laser amplifier, only 3 W in total is used. The main beam is split into three parts: the gate pulse (0.075 W), the THz pulse (1.07 W) and the pump pulse (0.36 W). The gate pulse is used to optically gate the measurement of the THz field intensity at the detection crystal. The THz pulse is designated as the fundamental or “pump” beam (which is different to the pump pulse), and along with its second harmonic generated by the β -BBO crystal, is used to induce the plasma formation and subsequently generating the terahertz radiation. The setup, marked by a black box in Figure 4.10, was enclosed in a box purged with dry Nitrogen gas in order to reduce the absorption lines in the THz spectrum due to water vapour in the air. The gate beam is fixed along a calculated path while the THz and pump beams move along motorized stage. Consequently, when building a system, extra care is needed to align the beams as straight as possible to avoid any beam spot movement during scans. This was achieved by using two alignment aids from Thorlabs which fluoresce when being hit by the 800 nm laser. To reduce any further errors in aligning, the two alignment aids need to be used in the same correct order at each alignment stage as they will both not be at the exact same height due to machining errors when designing holders.

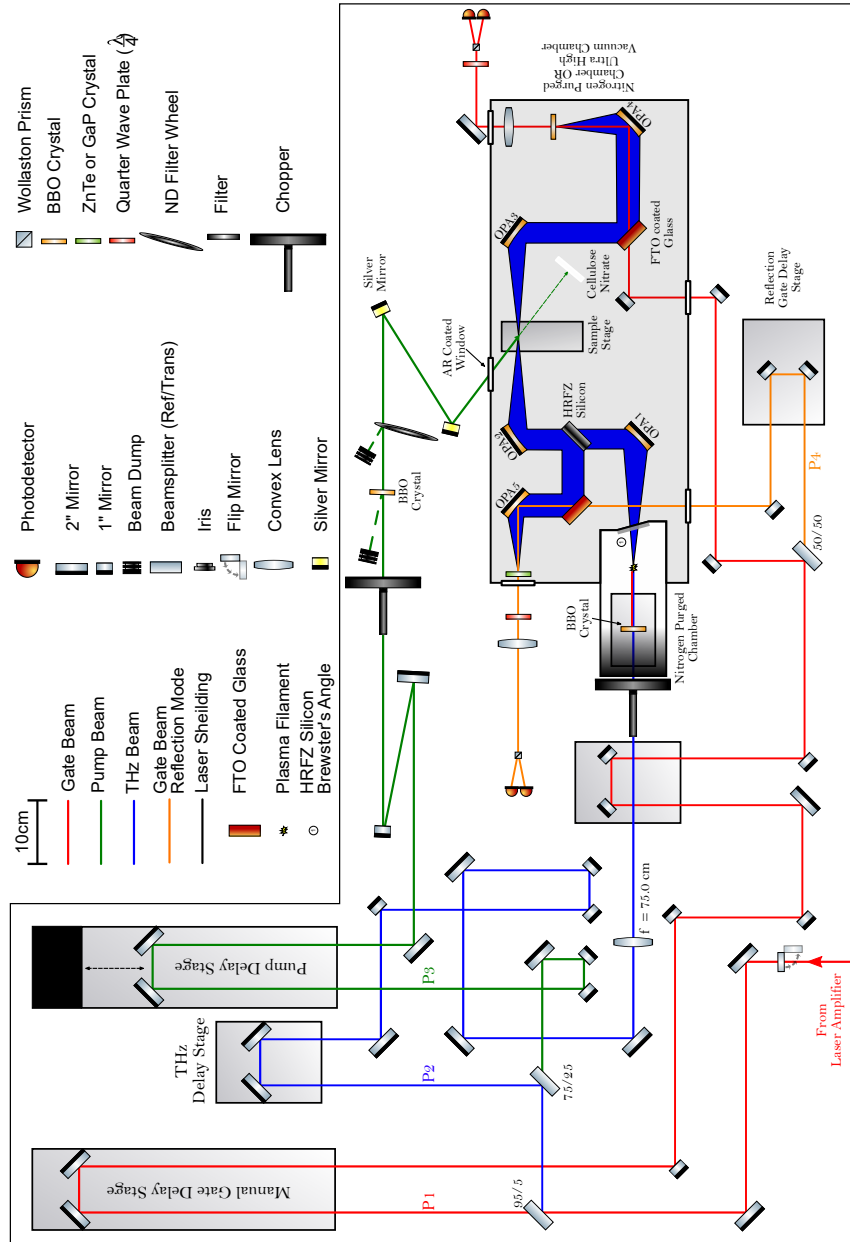


Figure 4.10: **Air Plasma System:** Schematic diagram showing the beam paths. P1, P2, P3, and P4 are the gate transmission, THz, pump, and gate reflection beams respectively. A 0.2 mm thick BBO crystal is used to frequency-double the fundamental beam (800nm) after which both harmonics are focused into an N₂-purged chamber under pressure. The high field intensity of the femtosecond laser breaks down the air and a plasma filament is formed which then emits THz radiation. An HRFZ-Silicon angled at the Brewster's angle is used to block the residual 800+400 nm and lets only THz through. At Brewster's angle, all *p*-polarized THz is let through without any attenuation. Off-axis parabolic mirrors (OAPs) are used to collimate and focus the THz onto the sample. In order to prevent water absorption of terahertz in moist, ambient air, a purged environment is required which is shown by the enclosed box.

4.5.2.1 THz generation

As can be seen from Figure 4.10, P2 is the beam which generates the plasma in the nitrogen-purged box. The THz pulse position is controlled by a high precision motorized stage, VP-25XL from Newport. This precision compact linear stage provides high-precision positioning performance in an ultra-compact form factor. The stage comprises an excellent minimum incremental motion of $0.01\ \mu\text{m}$ and, although quite short distance, a maximum travel range of 25 mm. This allows for high precision terahertz pulse waveform recovery which will in turn provide more bandwidth.

To generate the plasma, the fundamental beam needs to be focused in an air/gas medium and this was achieved by using an optical converging lens with an effective focal length (f) of 750 mm. It should be noted that by varying f , different plasma filament lengths can be achieved which will result in different THz field amplitudes at both the sample and detection positions. As P2 propagates, it is passed through a thin BBO crystal (cut at $\phi = 29.2^\circ$ with an effective thickness of 0.2 mm), and the second-harmonic wave is generated. The BBO crystal was mounted on a manual mechanical rotating stage, sitting on a manual positioning stage, which can move along the beam propagation path and it can also be rotated, in order to control the phase-matching of the SHG. A thin BBO was used as only a tiny amount of the second harmonic is needed to break the symmetry of the air as explained earlier in this chapter.

At the focal point, due to high intensity of the amplified femtosecond laser pulses, the ambient air/ N_2 gas is ionized by the combined fields and a plasma filament is induced. Due to the self-focusing Kerr effect, a longer filament length will be measured. Depending on the focusing length of the lens, the filament length will vary. As mentioned in section 4.4.2 according to the mechanisms, the THz beam is generated in a conical fashion. The THz diverges from the focal point, together with the residual fundamental and the second harmonic, and they all propagate towards the same direction. A high resistivity float zone silicon (HRFZ-Si) is used as a window, angled at 73° , to block the 800 nm and 400 nm beams whilst letting the THz through. 73° is the Brewster angle for silicon at THz frequencies, and in this particular configuration, all the p -polarized THz passes through without any attenuation. Off-axis parabolic (OAP) mirrors from Thorlabs, with protected gold-coatings will be used in this setup to direct the THz beam. OAPMs achromatically focus a collimated beam or collimate a divergent source, and their off-axis design separates the focal point from the rest of the beam path. The reflective design eliminates phase delays and absorption losses introduced by transmissive optics and makes these well suited for use with femtosecond pulsed lasers. A 2" diameter OAP1 with an effective focal length of 4" collects and collimates the THz. Next, a pair of

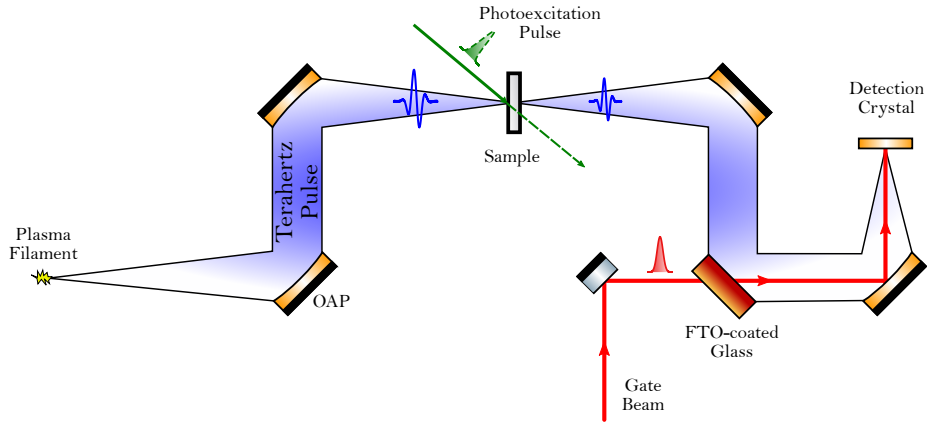


Figure 4.11: **THz Transmission:** in transmission mode, the THz pulse interacts with the material and is attenuated as it exits. The transmitted THz pulse now encodes all the required information from the bulk of the sample such as the dark conductivity or photoconductivity, complex refractive index, and dielectric response.

parabolic mirrors, OPA2 and OPA3 collect, focuses down and recollimates the THz beam. At the focal point of this section between the two mirrors is the sample position which sits on a motorized vacuum-compatible stage, MODEL: UTS50PPV6 from Newport.

Transmission Mode. In transmission mode, OAP3 collects and collimates the attenuated THz beam which now encodes any optoelectronic properties of the samples. An FTO-coated glass is used to reflect the THz as well as allowing the 800 nm transmission gate beam to pass through. OAP4 finally collects and focuses the two beams onto the detector crystal. This is illustrated in Figure 4.11.

Reflection Mode. In reflection mode, an additional HRFZ-Si, 2 mm thick beamsplitter is placed at 45° after the first OAP. When the THz hits the sample, depending on its physical and optical properties, some will pass through and some will reflect. The reflected signal bounces back with the sample acting as a source. OAP2 collects the beam and collimates it onto the silicon beamsplitter which in turn reflects onto an FTO-coated glass. The latter, as mentioned above, will also let the reflection gate beam through. Both beams are then collected and focused onto a detector crystal by OAP5. This is illustrated in Figure 4.12.

At the detector position, a second order nonlinear process will induce a polarization intensity change of the gate beam. Through a combination of quarter wave-plates, focusing lenses, wollaston prisms, and balances photodiodes, the signal can be recovered. The details of this process has been detailed in the previous chapter. The signal is amplified using a Stanford Research lock-in amplifier with a reference frequency of 2.5 kHz before being fed into a custom-built board, HM2. This detection system records 4 signals in 4 registers: register A, register B, register C, and register D. The signals are

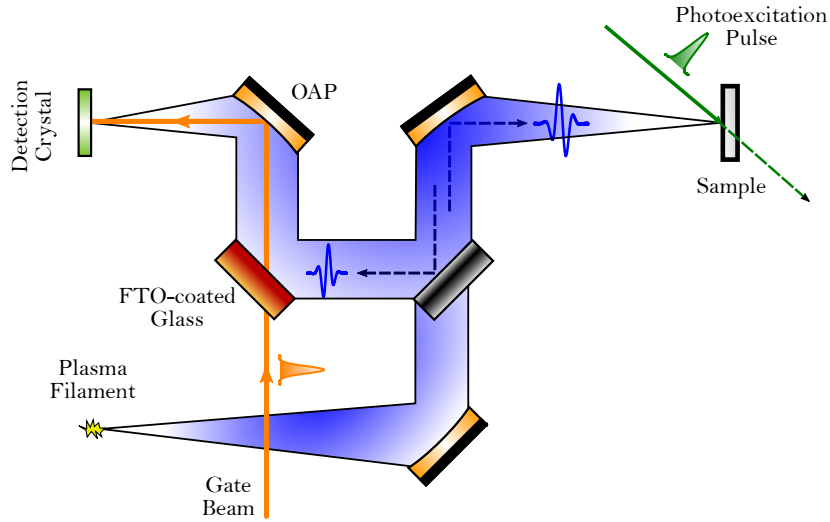


Figure 4.12: **THz Reflection:** in reflection mode, the THz pulse interacts with the surface material. As the THz pulse reflects back, it is attenuated similar to the case of transmission. The extra information derived from reflection is the surface behaviour of the sample under study. For optically dense materials, THz transmission unfortunately does not provide enough information. THz reflection therefore complements THz transmission should one wish to obtain full information of the sample.

related as follows:

$$T_{\text{THz}} = \text{Reg}_A - \text{Reg}_B$$

$$dT = (\text{Reg}_A - \text{Reg}_B) - (\text{Reg}_C - \text{Reg}_D).$$
(4.31)

4.5.2.2 The Pump Beam

The beauty of this system is the ability to switch from terahertz time-domain spectroscopy to terahertz time-resolved spectroscopy. This is achieved by a third beam known as the photoexcitation pump, represented as P3 in Figure 4.10. Similar to the THz beam path, the pump is also passed through a motorized delay stage, albeit of less precision but of much longer distance, 200 mm in total. A typical pump scan is done by sitting at the THz peak position and scanning the pump stage thereby probing temporal charge dynamics. Further details have been given already in the previous chapter.

A closer look at Figure 4.10 shows that the pump pulse has an additional four mirrors: T1, T2, S1 and S2. The former pair are what we refer to as telescope lenses and the latter pair are silver mirrors. Telescope mirrors play an important role in our setup to control beam waist size with minimal loss of energy and maximum efficiency. Since they are high reflectivity mirrors to focus and collimate the beam, the issue of dispersive loss is nicely avoided by ditching the use of optical lenses.

The laser amplifier's beam width is just short of an inch and our mechanical choppers have a finite width window ($\ll 1''$) that will chop the beam at the desired frequency (1.25 kHz). A more simplistic approach to deal with this conundrum would be to focus the beam through the chopper window into a point and collect the rest at the sample position. However, a quick judgement about this process reveals many faults such as the possible formation of a plasma in air at the focal point, or the chopper position needs to be carefully chosen as only at a minimum distance would all of the beam pass through without being clipped, or even the choice for the correct focal length of the lens for the beam size at the sample position to be big enough to ensure uniform photoexcitation. A clever trick to circumvent these issues would be to use telescope mirrors. The first mirror, T1, with a focal length of x focuses the beam down to a point just as a parabolic mirror would. Depending on how small we would require the beam to be in order for it to pass through the chopper window completely, the distance of the second mirror T2 from T1 is carefully measured. For our purpose, a reduction by 50% will suffice. This then creates a virtual focal point behind T1. T2 then sits at a distance of x cm which will in turn collimate the beam, now with a diameter of $\frac{d}{2}$.

4.6 THz Detection

The heterodyne THz detection scheme we employed for this setup is of two types: (1) free-space electro-optic sampling using GaP and ZnTe crystals, and (2) air-biased coherent detection in a gas. The former is used in both transmission and reflection modes, while the latter is only used in transmission mode. For the transmission mode, a rotating stage allows one to choose between FS-EOS and ABCD. This section will look at each method separately, including a detailed analysis for ZnTe electro-optic crystal.

4.6.1 Free Space Electro-Optic Sampling

A word of caution, part II: The concept of FS-EOS has been briefly touched upon in the previous chapter. For this ultra-broadband system, in order to extract the high frequency components of the THz pulse, an ultrathin ZnTe crystal is used. As discussed previously, the crystal thickness is directly proportional to the signal amplitude while being inversely proportional to the bandwidth. This section will attempt to quantify this effect mathematically along with some simulation results.

The ZnTe has an effective thickness of $20\text{ }\mu\text{m}$ and even though the signal is predicted to be quite low, the extreme THz electric field amplitude more than makes up for it and we are able to extract a reasonable voltage across the photodiodes. Although electro-optic

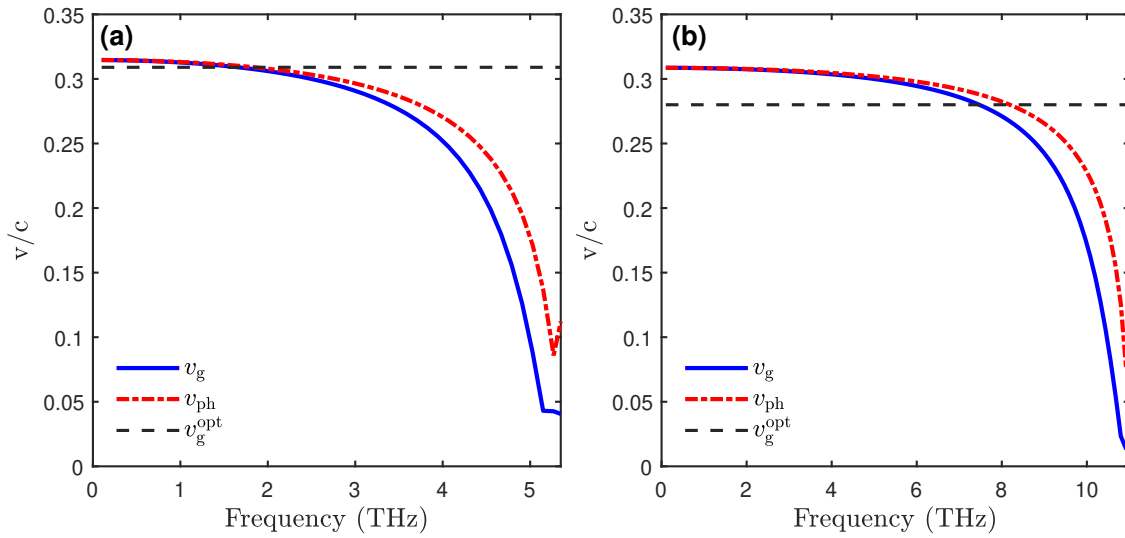


Figure 4.13: **Group Velocity:** Plots illustrating how the group velocities of the femtosecond optical gate pulse 800 nm and the pico-second THz pulse vary with in ZnTe (a) and GaP (b) in the THz range. v_g^{opt} is the group velocity of the optical gate pulse whereas v_g and v_{ph} are the group and phase velocities of the THz pulse in the crystal respectively.

sampling is a very straightforward process, it does possess two major downsides: (1) a material damage threshold, and (2) the material's transverse-optical (TO) phonon mode will limit the bandwidth. Of the two, the second one is the most important one as the optical gate pulse energy can always be decreased by using neutral density filters to avoid any damage at the expense of signal amplitude.

The phase mismatch of the electro-optic interaction between the optical probing pulse and the THz pulse is a parameter quantifying the phase lag between the two pulses. The complex refractive index of a material is usually frequency-dependent and therefore a material will have different refractive indices corresponding to the wavelength of the radiation passing through it. The optical gate pulse and the THz pulse have different dispersion and therefore will travel at different velocities across the material and will eventually accumulate a phase delay. The group velocity of a pulse is given by

$$v_g = \frac{c}{n} \left(1 + \frac{\lambda}{n} \frac{dn}{d\lambda} \right) = \frac{c}{\left(n + f \frac{dn}{df} \right)}. \quad (4.32)$$

A given optical wavelength will only be velocity matched to a certain THz frequency for a given EO crystal. This is illustrated in Figure 4.13. At low frequencies, the THz pulse will propagate at a higher velocity than the optical gate pulse and at higher frequencies, the opposite happens. At the resonances, the group velocity mismatch approaches zero. Hence, the response function of the sensor is entangled by the frequency-dependent velocity mismatching.

In THz FS-EOS, the highest efficiency corresponds to a zero phase mismatch whereby the optical gate pulse at 800 nm and the THz pulse remain overlapped for a fixed delay as they travel through the crystal. Evidently, this is attained only if the group velocity (v_g) of the optical gate pulse matches the phase velocity of the THz pulse as they propagate through the crystal. It is well-known that ZnTe has a high sensitivity for frequencies between 0.1 THz and 3 THz, since the phase velocity at this frequency range matches well with the group velocity of light within the tuning range of Ti:sapphire lasers. However, ZnTe cannot be used at higher frequencies because of the presence of a transverse-optical (TO) phonon resonance at around 5.3 THz. This is illustrated in Figure 4.14. One way to bypass this limitation is to use other detector crystals such as InP or GaP with TO phonon modes present at higher frequencies of 9.12 THz and 8.06 THz respectively. [281–287]

TO Phonon Mode: It is often assumed that the EO detected signal is a perfect reconstruction of the THz waveform. Unfortunately, this is not the case and it arises from complications induced by several effects such as dispersion and absorption of the THz pulse in the EO crystal, reflections at the boundaries of the materials used for both the generation, and detection and phase matching of the electro-optic sampling process. These effects result mainly from the presence of strong TO-phonon resonances at THz frequencies in the crystals. Modelling these effects can be of great value, since it permits a reconstruction of the original THz pulse. In this section we describe how the distortive effects can be accounted for.

The TO-phonon resonances resulting from lattice vibrations of the individual atoms couple strongly to the THz radiation. This in turn causes the frequency components at which the phonon mode oscillate to propagate as mixed light-polarization states denoted as phonon polaritons. A THz pulse for which the frequencies are close to a TO-phonon resonance will thus propagate as a dispersive phonon–polariton wave packet and therefore will not appear in the spectrum. [287–289] This appears as “holes” in the Fourier transformed data. To overcome this, one has to calculate the complex response function of the crystal over the frequency range one would expect the system would give. This acts as a reference. By dividing the experimentally extracted spectrum with the reference, one is able to recover missing frequencies.

In this analysis, multiple reflections within the detector is ignored as usually they sit on an inactive substrate that filters out Fabry–Perot effects. At the crystal position, the THz beamwidth is much larger than the optical gate pulse. In this limit, the gate pulse can be considered as a delta function centred at λ_0 . Assuming a monochromatic wave, the THz pulse takes the form of an exponential function, $\exp(i\omega t)$. As both pulses propagate

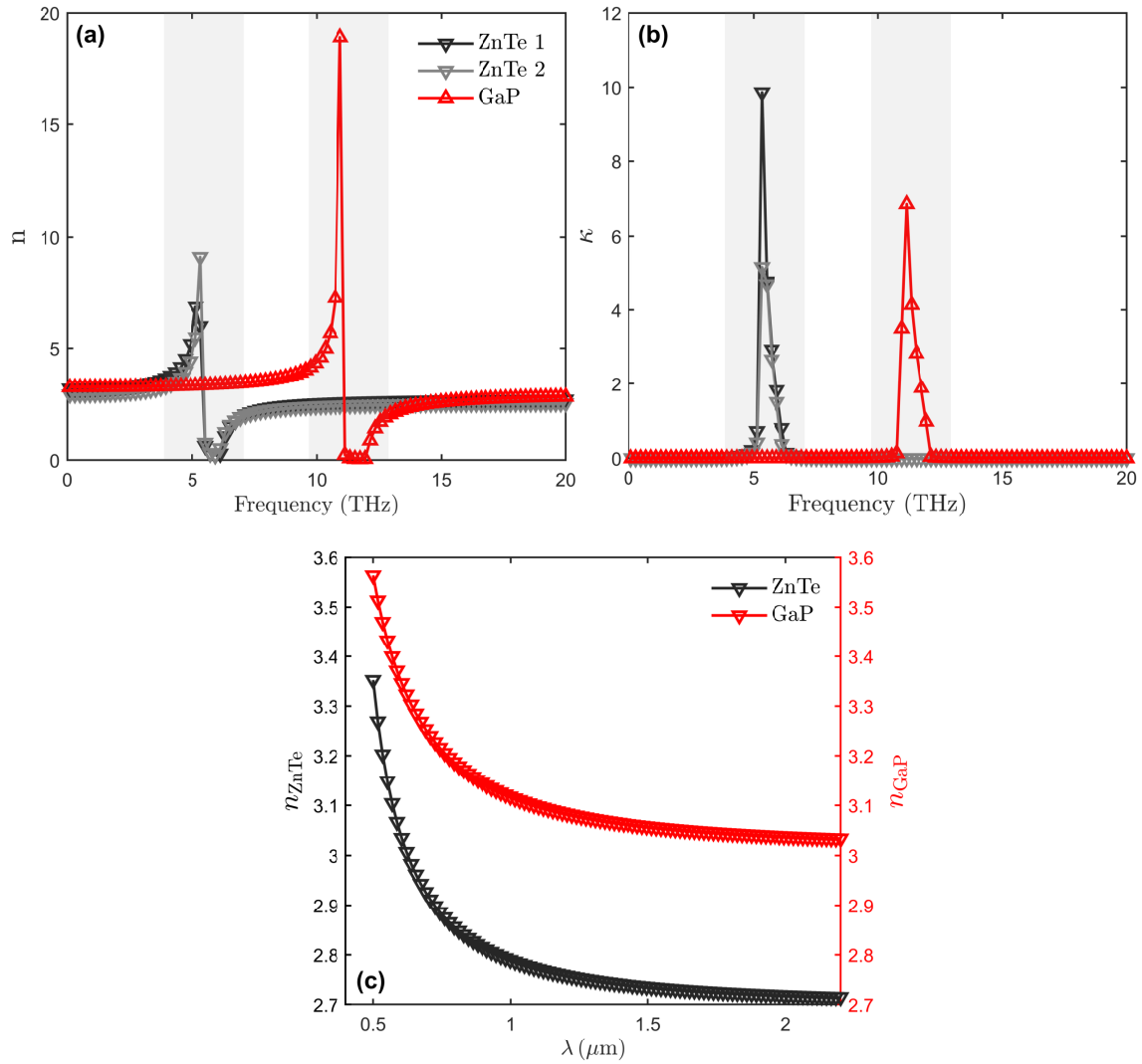


Figure 4.14: **Refractive Index of EO Crystals:** Plots illustrating the complex refractive index of GaP and ZnTe in both the THz and visible region of the electromagnetic spectrum. (a) and (b) are the real and imaginary parts in the THz regime with clear sharp changes in the region of the TO phonon mode. The crystals have negligible absorption otherwise.

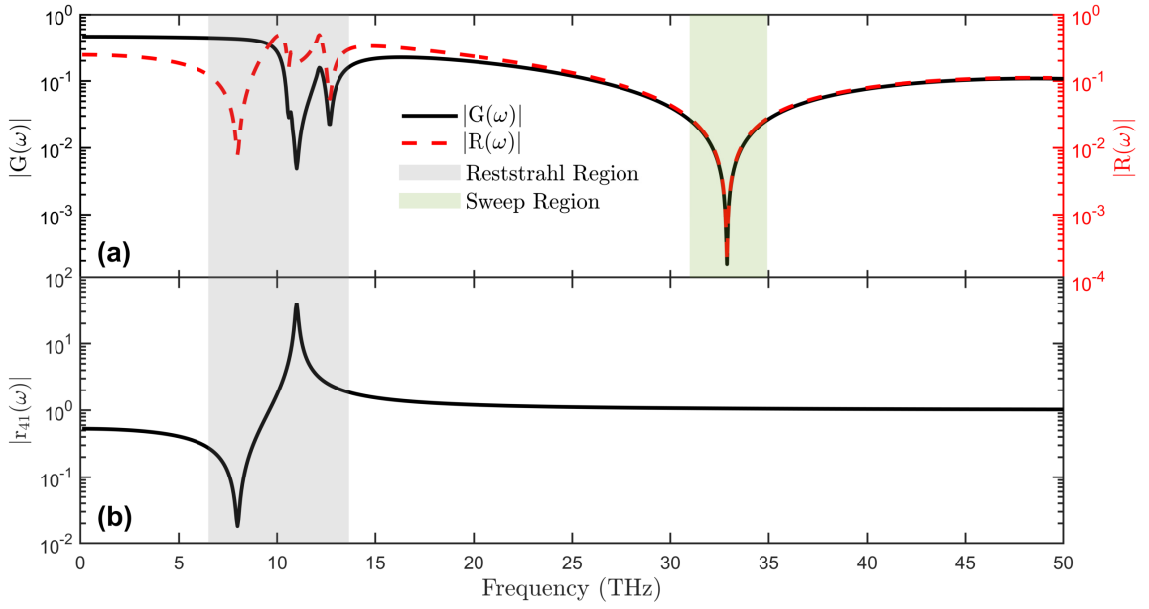


Figure 4.15: **Complex Response Function:** The absolute values of the sensor response behaviour plotted as a function of frequency for a $13\mu\text{m}$ GaP detector crystal. In (a) we have both the uncorrected (dark solid line) and the corrected response (dashed red line) for the nonlinear EO coefficient. (b) displays the EO coefficient as a function of frequency.

through the EO crystal of thickness l , they acquire a phase lag and the accumulated group velocity mismatch (GVM) time is given by:

$$\delta(\omega) = \frac{n_g(\lambda_0) - n(\omega)}{c} l, \quad (4.33)$$

where $n_g(\lambda_0)$ is the optical group index at the optical wavelength. This data is available from dispersion value tables reported in previous works. $n(\omega)$ is the frequency-dependent complex phase index of the THz radiation and is parametrised by the dielectric response of a harmonic oscillator:

$$n(\omega) = \sqrt{\left[1 + \frac{(\hbar\omega_{\text{LO}})^2 - (\hbar\omega_{\text{TO}})^2}{(\hbar\omega_{\text{TO}})^2 - (\hbar\omega)^2 - i\gamma\hbar\omega}\right]} \times \epsilon_\infty, \quad (4.34)$$

where $\hbar$ is the modified Planck's constant, ω_{LO} and ω_{TO} are the longitudinal and transverse optical phonon modes, γ is the lattice phonon damping parameter, and ϵ_∞ is the high frequency dielectric constant. The amplitude and phase of the complex EO modulation, $G(\omega)$, of the THz electric field is then given by: [287,290,291]

$$G(\omega) = \frac{2}{n(\omega) + 1} \times \frac{c[\exp(-i2\pi\omega d(n_g(\lambda_0) - n(\omega))/c) - 1]}{-i2\pi\omega d(n_g(\lambda_0) - n(\omega))}. \quad (4.35)$$

$G(\omega)$ is not the full complex response function of the EO crystal. The EO coefficient, r_{41} , of the material is unfortunately not frequency-independent and has to be incorporated into the response function for a complete analysis. This is particularly significant in

the region of the phonon mode where r_{41} exhibits strong dispersion and resonance enhancement. r_{41} is given by the following analytic expression: [292,293]

$$r_{41}(\omega) = r_e \times \left[1 + C \left(1 - \frac{(\hbar\omega)^2 - i\hbar\omega\gamma}{(\hbar\omega_{\text{TO}})^2} \right)^{-1} \right], \quad (4.36)$$

where C is the Faust-Henry coefficient. It relates the ionic part to the electronic part of the EO effect at $\omega = 0$. r_e is the electronic nonlinearity and is taken to be constant in the far-infrared regime. Combining both Equations (4.35) and (4.36) then gives the full complex response function of the detector, $R(\omega)$:

$$R(\omega) = G(\omega) \times r_{41}(\omega). \quad (4.37)$$

Figure 4.15 (a) shows the calculated amplitude spectrum of the response function for a 13 μm GaP detector with parameters from reference. [290] Of particular interest are the two shaded regions. The light grey is the Reststrahl region where the phonon mode of GaP is situated. This is manifested as a dip in the spectrum due to the high absorption of the crystal and the large velocity mismatch at the lattice resonance. The amplitude signal is recovered right after but the envelope decreases smoothly as the time delay accumulates at higher frequencies. At around 32 THz, the time-delay accumulation is such that the optical gate pulse sweeps over exactly one THz cycle as they both pass through the crystal. There is no polarization change as the birefringence is not felt and the orthogonal components of the polarization are of exactly the same magnitude. The photodiodes then reads no signal. This is indicated by the light green shaded region.

As for (b), the EO coefficient displays strongly a distortion around the phonon mode (8 THz – 11 THz) that results from an interplay of the electronic and lattice contributions. At 8 THz, they cancel each other while at 11 THz, they reinforce each other and r_{41} is resonantly enhanced. By using $R(\omega)$ as a reference signal, we are able to correct for the signal's phonon-drop in the spectrum, thereby recovering the "lost" frequency components. What follows is the implementation of this correction on both ZnTe and GaP crystals of varying thicknesses.

GaP and ZnTe: In this section, we compare and contrast the performance of GaP and ZnTe EO crystals as THz detectors. The sensitivity and bandwidth of the detectors are done for a range of thicknesses and both the uncorrected and corrected response functions are plotted as a function of frequency. The full complex response function, $R(\omega)$, and the EO coefficient were simulated as shown in Figures 4.16 and 4.17.

Low Frequency Correction: A quick look at Figure 4.17 shows that the complex response function is flat at very low frequencies whereas this is not the case in reality. In any

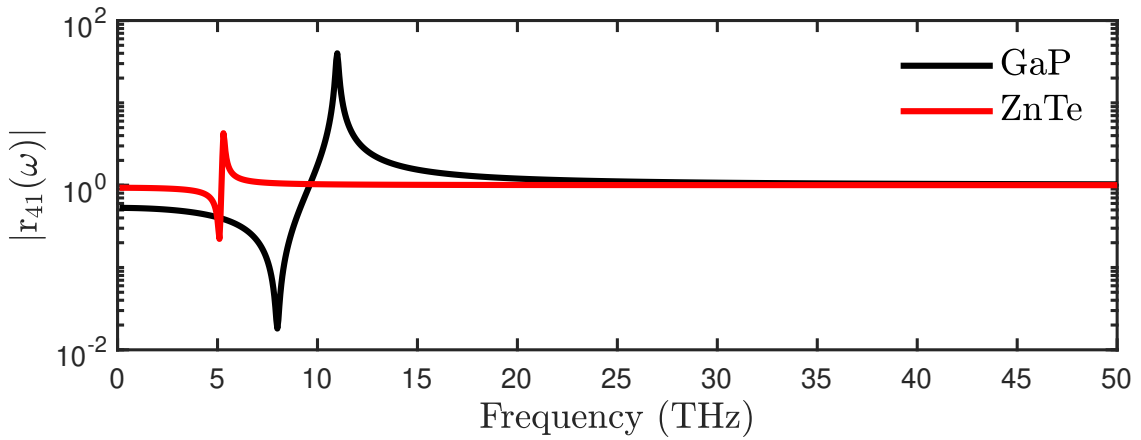


Figure 4.16: $r_{41}(\omega)$: The EO coefficient as a function of frequency. The two graphs feature the strong resonance near the TO phonon modes of the two crystals: ≈ 11 THz for GaP and ≈ 5.3 THz for ZnTe. The parameters used can be found from reference. [290]

THz experiments, the THz radiation source is often approximated as a point source. The waves are collected and collimated and focused using OAPMs. Diffraction therefore plays an important role in determining the beam shape at the focal positions such as the sample or the detector. As will be shown in §4.7.4, the beam can be approximated as a Gaussian and the low frequencies are on the outer edge of the beam line. The dimensions of the optics chosen for a reasonably sized experiment are such that their finite apertures will not be able to capture all the energy of the low frequency components that have diffracted to a size larger than the diameter of the collimating optics. This is the origin of the sharp rise in the amplitude spectrum at low frequencies and needs to be included in the complex response function to accommodate for the low part of the amplitude spectrum.

Cote *et al.* in 2003 [294] developed an approximation that reproduces the effect of losing low frequency components in THz experiments. Most THz systems will consist of pairs of OAPMs with matched focal lengths. Within certain approximations, this particular arrangement can be treated as a single optical component with an effective focal length of $f' = f/2$. They further assumed that the scenario can be studied as a beam, with a Gaussian spatial profile, going through a single lens. The approximation function is then given by

$$F_{\text{low}}(\omega) = \text{erf}^2\left(\frac{2\omega R\sigma}{cf}\right), \quad (4.38)$$

where ω is the angular frequency, R is the radius of the OAPMs, c is the speed of light in vacuum, and f is the effective focal length of the OAPM. For our setup, the function has a sharp rise and peaks at around 1 THz after which it is a flat function. This is consistent with the fact that low frequencies diffract more than high frequencies. While the latter

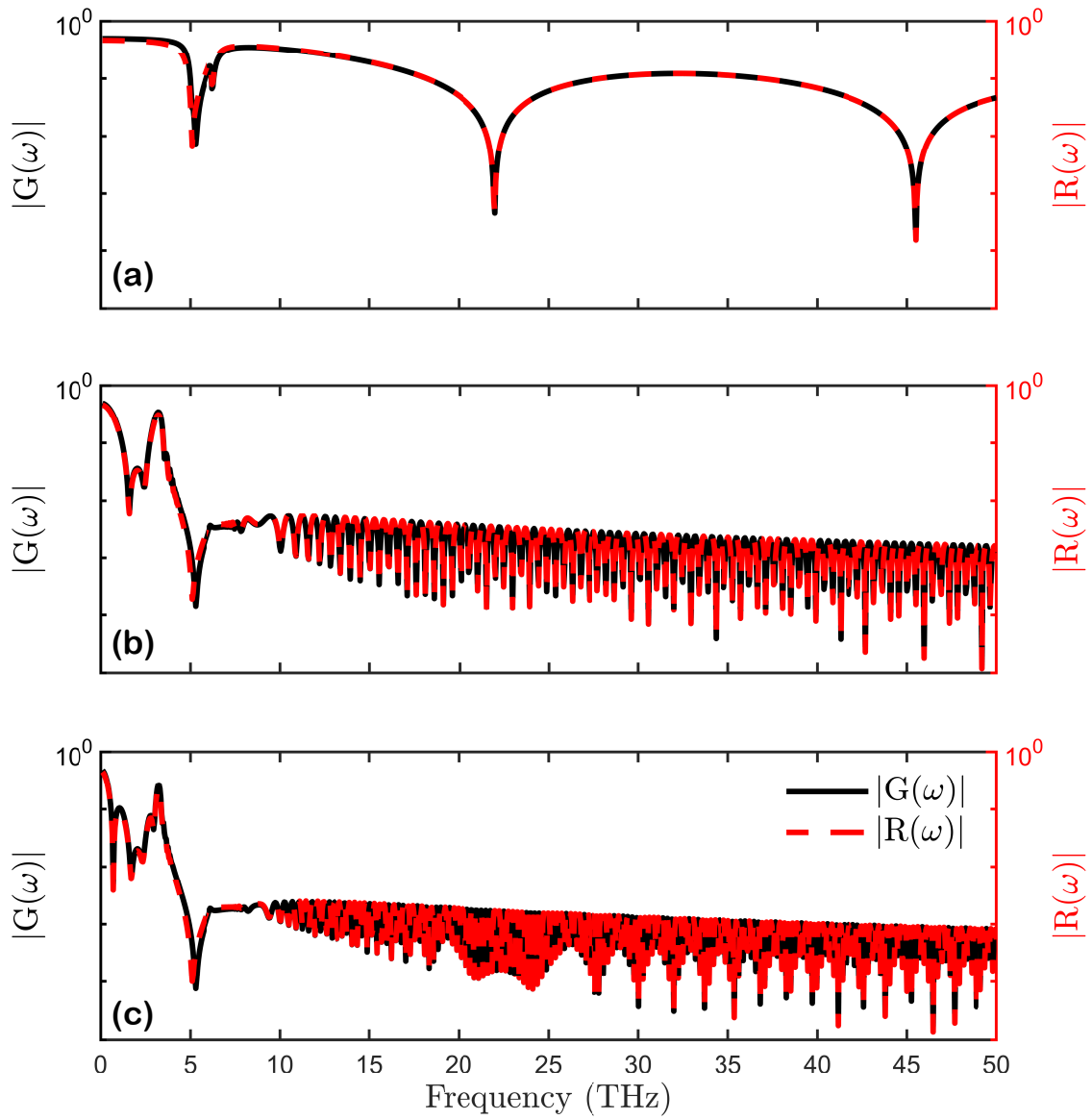


Figure 4.17: $G(\omega)$ and $R(\omega)$: The amplitude spectra of the complex response of ZnTe EO crystals for varying thicknesses: (a) $20\ \mu\text{m}$, (b) $1000\ \mu\text{m}$, and (c) $1930\ \mu\text{m}$. It is evident that with decreasing thickness, the maximum bandwidth that can be extracted is larger.

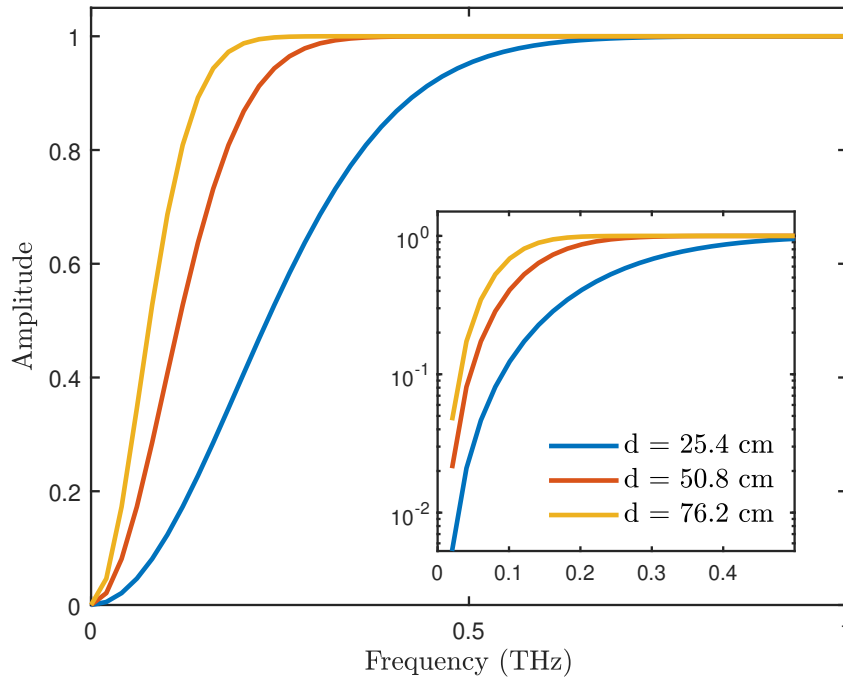


Figure 4.18: $F_{\text{low}}(\omega)$: The amplitude spectra of the low frequency response correction for various OAPM diameter with focal lengths of $f = 15 \text{ cm}$ and $\sigma = 0.9 \text{ mm}$. The graph features a sharp rise in the amplitude at low frequencies until it reaches a plateau. As the diameter increases, the OAPM is able to capture more frequencies and the plot plateaus earlier. The inset shows the same plot but on a logarithmic scale.

will be entirely collimated, the former will diffract more. Figure 4.18 displays the effect of the OAP diameter on the approximation function.

The full complex response function is now given by:

$$\begin{aligned} F^{\text{FULL}}(\omega) &= R(\omega) \cdot F_{\text{low}}(\omega) \\ &= G(\omega) \times r_{41}(\omega) \times \text{erf}^2\left(\frac{2\omega R\sigma}{cf}\right). \end{aligned} \quad (4.39)$$

The complex response is shown in Figure 4.19 which is now a better approximation to the experimentally determined bandwidth.

4.7 Results and Discussions

This section tries to capture the capabilities of this state-of-the-art terahertz spectrometer. In order to understand how one can tap into the ultra-high broadband regime, a series of measurements were performed to test its performance and the full system characterised. As the spectrometer is still in the manufacturing stage, ABCD detection technique was not implemented and neither was the effect of gas pressure. Hopefully, once the THz

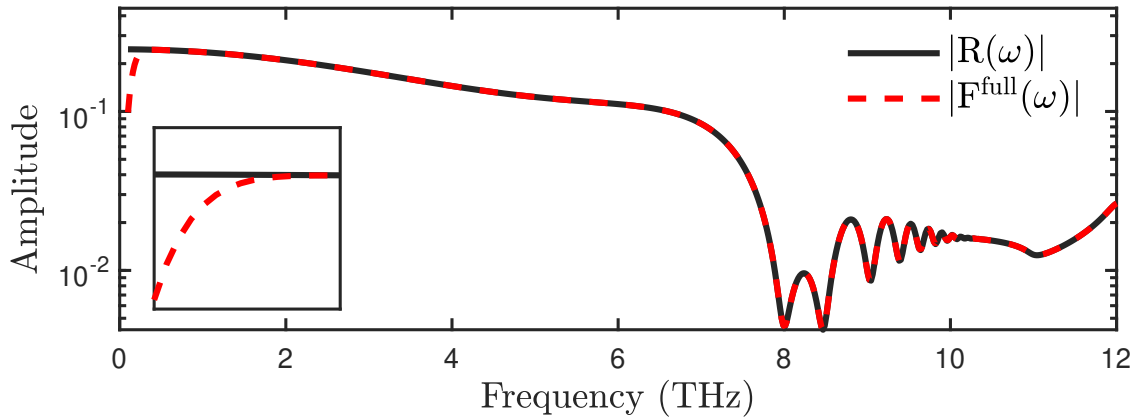


Figure 4.19: $F^{\text{full}}(\omega)$: Amplitude of the full response function with the low frequency correction.

box is made, both EOS and ABCD detection techniques will be available under a high vacuum and pressured environment respectively.

4.7.1 THz Pulse

As a reference, THz pulses were recorded in the time domain and then Fourier transformed to the frequency domain to obtain the corresponding spectrum. A purge box was built temporarily, enclosing most of the optics from the plasma filament until the detection crystal. The measurements were done under both ambient air and under a dry nitrogen-purged environments in order to compare the effect of water vapour absorption on the spectrum.

4.7.2 Laser Pulse Energy Dependence

From the FWM model described earlier, it was shown that the field-induced second-harmonic intensity has a square dependence on the probe beam intensity. To verify whether this relation holds, and consequently what is its effect on the detection of the THz field and the performance of the spectrometer, as described by the signal-to-noise ratio, and whether or not the saturation regime of the field-induced second harmonic intensity can be reached.

The THz pulse trace for various intensities of the probe beam were recorded. The power, and subsequently the pulse energy of the probe beam was controlled by adjusting a neutral density (ND) filter in its path, prior entering the purge box and the setup. The power was measured with a power meter after the ND filter, and the actual power that reaches the interaction volume, after part of it has been absorbed by filters and windows along the way, was deduced by a conversion factor. The plot is shown in Figure 4.21.

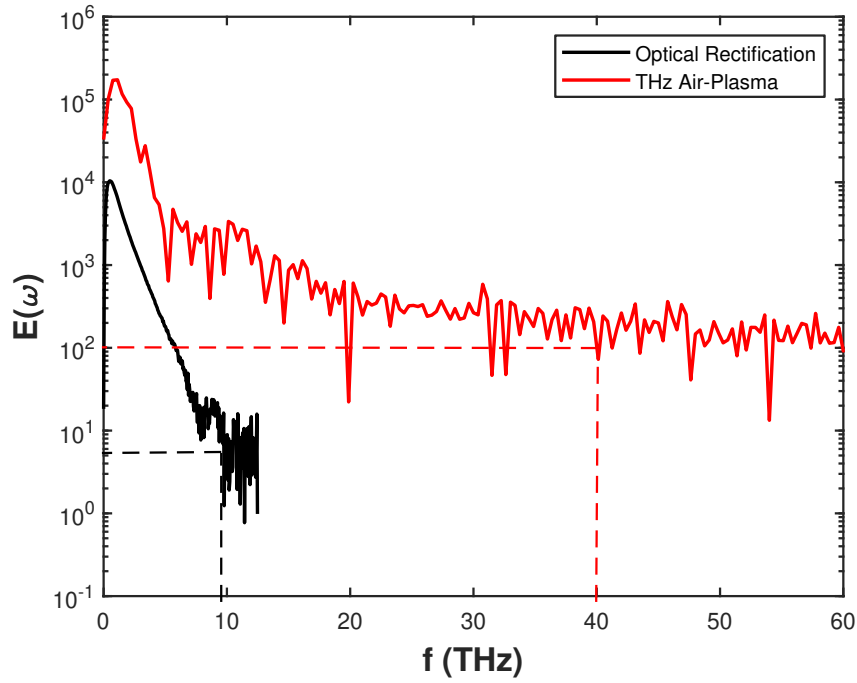


Figure 4.20: **Spectrum Comparison:** Figure illustrating the bandwidth comparison between optical rectification/spintronic emitter to the plasma generation. For the latter case, a maximum bandwidth of around 40 THz can be extracted. The spectrum has a few oscillation and dips which can be further improved by waiting for an hour of purging with dry nitrogen gas. For the spintronic emitter, the bandwidth drops to the noise level very quickly after 8 THz.

This is in accordance with what the FWM model predicts and is proof that there needs to be a plasma for THz emission to be possible.

4.7.3 BBO Angle Dependence

In the air-plasma system, the plasma filament is formed by combining the fundamental beam 800 nm with its second harmonic 400 nm, all focused into a gas. The second harmonic is achieved by using a thin BBO crystal of 0.1 mm thickness. THz emission from a gas plasma is not yet fully understood but the concept of phase-matching, as introduced earlier in this chapter, is of great important. This is reflected in the 3D plot in Figure 4.22 where the angle of the BBO crystal was varied and the THz emission was measured.

Changing the angle of the BBO changes both the conversion efficiency of the 800-400 nm and the phase delay between the two pulses. Figure 4.22 shows a colour map of the dependence of the THz pulse against the rotation angle of the BBO. The detection crystal was unchanged and the full angle-dependent spectrum was recorded. The THz peak changes with rotation but there are no clear mathematical link. Figure 4.24 shows the change of the spectrum with BBO angle which is very critical.

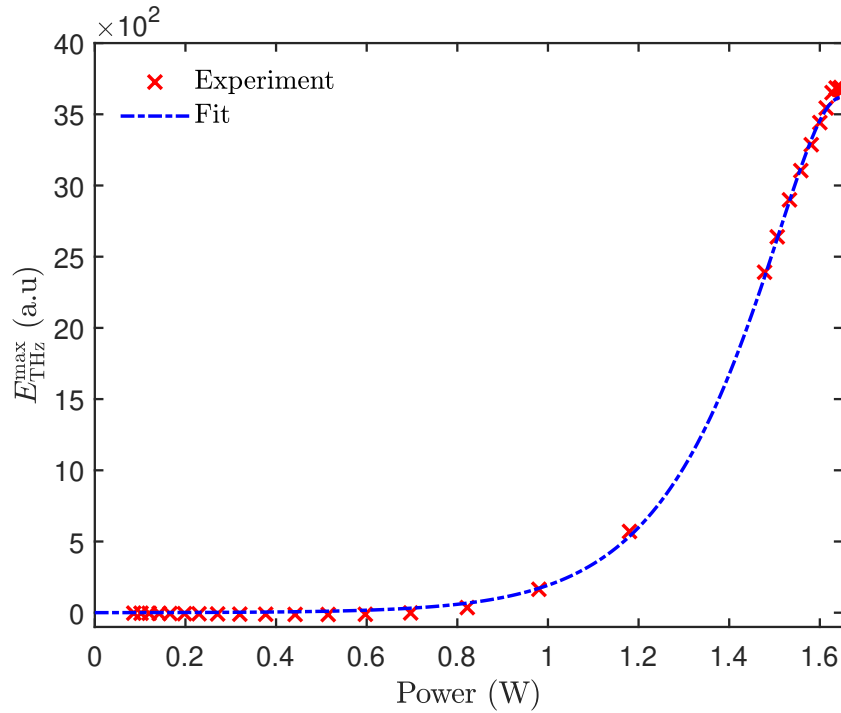


Figure 4.21: **Power Dependence:** the fundamental beam intensity was varied from its maximum to minimum using a filter wheel. The peak of the THz was measured for each one of them and plotted. An exponential was then used to fit the data. From the plot, it is evident that there is a threshold above which the plasma is formed and emitting THz whilst below this value, the gas is not broken down yet for a plasma to form.

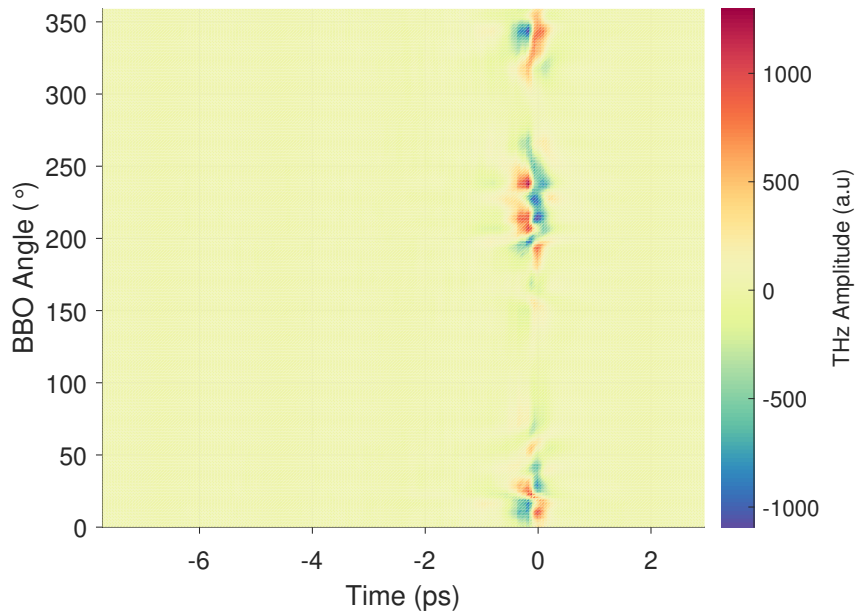


Figure 4.22: **Angle Dependence:** 3D plot illustrating the effect of the BBO angle on the THz pulse. As mentioned before, the concept of phase-matching is critical in this setup. Changing the BBO angle will change the SHG efficiency and this is reflected in this diagram. What also changes the polarization emission of the THz.

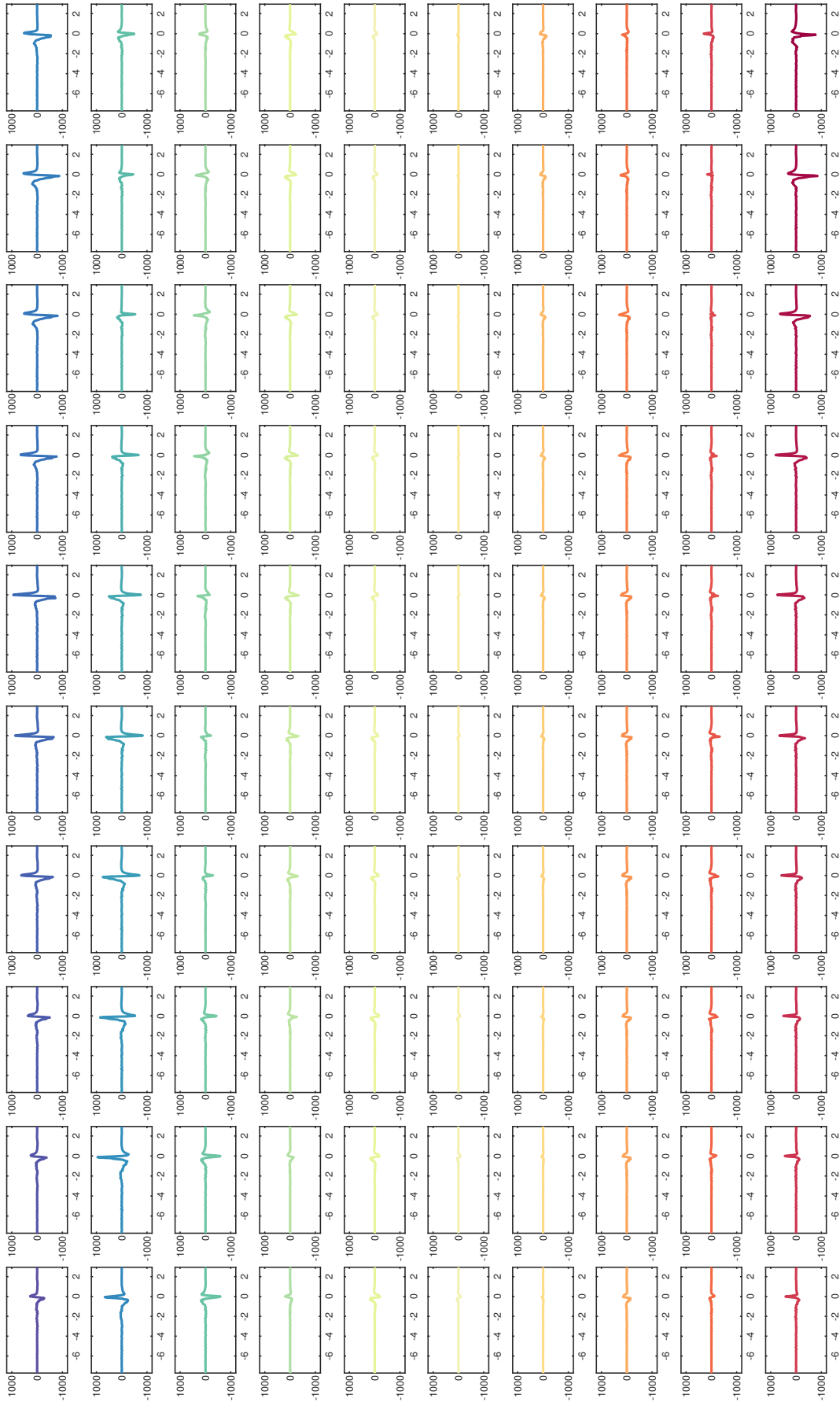


Figure 4.23: **Angle Dependence:** Plots showing the variation of the THz pulse transient with the BBO Angle. The x-axis is time in picoseconds and the y-axis is the amplitude of the THz pulse in arbitrary units.

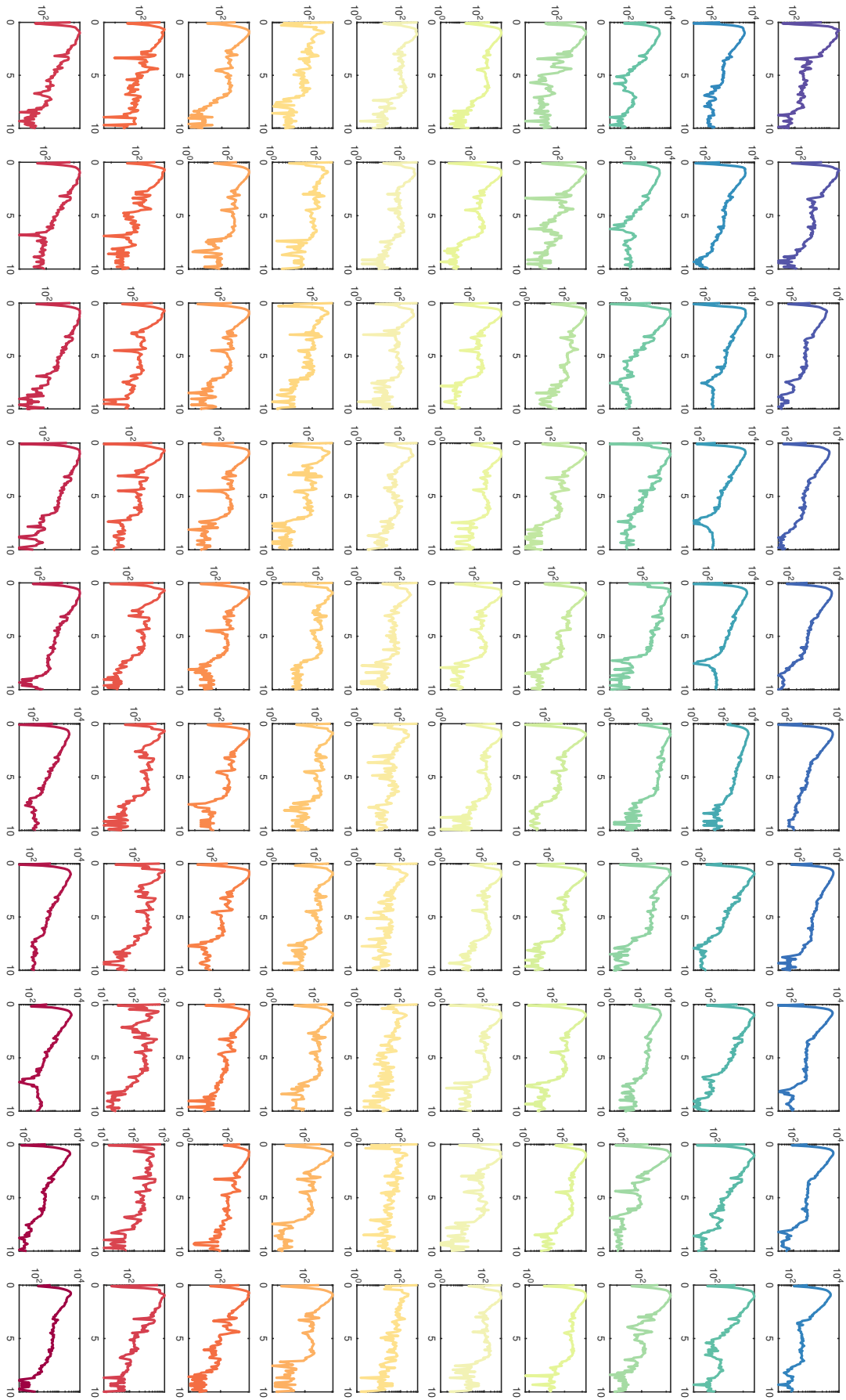


Figure 4.24: **Angle Dependence:** Plots showing the variation of the bandwidth with the BBO Angle. The x-axis is frequency in terahertz and the y-axis is the spectral amplitude (magnitude of the Fourier-transformed data) of the THz pulse.

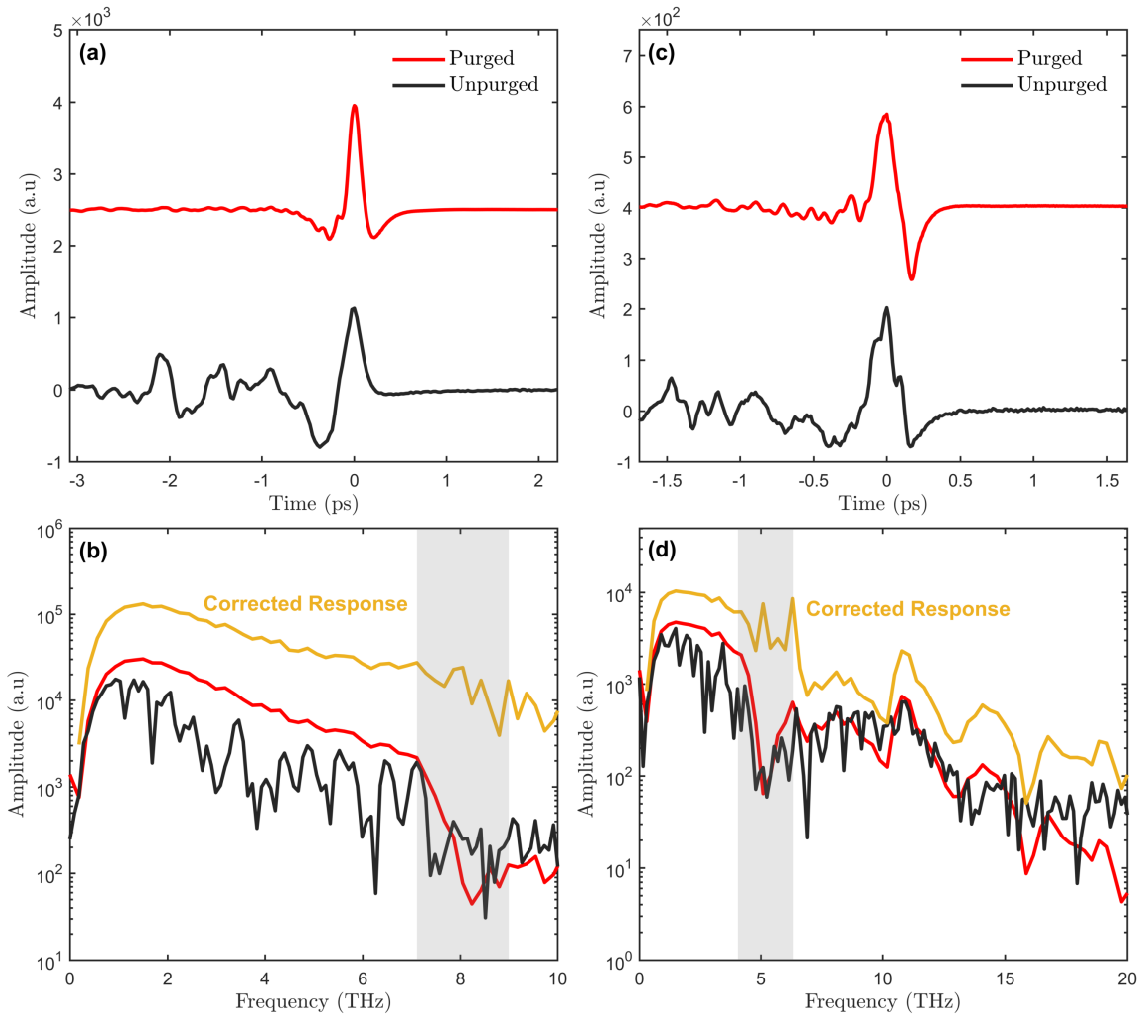


Figure 4.25: **Water Vapour Absorption:** Plots illustrating the effect of water vapour absorption from ambient air on the THz pulse. (a) and (c) are the THz transients for GaP and ZnTe Eo crystals respectively, and (b) and (d) are their corresponding spectra. The shaded grey blocks represent the Reststrahl regions affected by the TO phonon mode as explained earlier in this chapter. Also presented are the corrected response for the detector crystals where the dips due to the lattice resonance were effectively screened and the full spectra recovered.

4.7.4 Maximum Bandwidth

The THz-air-plasma setup was built as it is able to provide high intensity THz fields and a large bandwidth that will enable us to study the behaviour of semiconductors in the multi-THz region. For this reason, it would be useful to show the maximum bandwidth we were able to extract using FS-EO sampling with both an ultrathin ZnTe crystal ($0.2 \mu\text{m}$) and a relatively thick GaP crystal ($0.4 \mu\text{m}$).

As discussed in the previous section, the detector response function can be applied to circumvent and correct for the lattice resonance absorption of the EO crystals such that a smooth spectrum is obtained without losing any information. Figure 4.25 shows the

effect of water vapour absorption on the THz spectrum. Also shown are the corrections to the detector crystals by applying the correct complex response function. The plots show that it is indeed possible to get the corrected response such that the maximum bandwidth can be seen.

4.7.5 Off-axis Parabolic Mirrors

Astigmatism & Aberrations: THz spectroscopy requires the THz beam to be tightly focused at both the sample position and the detector position. This ensures that a high THz peak field is obtained at the sample and the perfect overlap with the optical gate pulse for maximum bandwidth extraction at the detector. When dealing with pump-probe setups, the high density of optics on an optical bench is usually an issue with less space for freedom. In a particular OPTP experiment, the OAPMs used to focus and collimate the THz pulses are placed in an open configuration, Figure 4.26. This allows for more space around the optics to set up other beam paths such as for FS-EOS or a reflection pathway.

OAPMs are central and interesting especially in the THz spectral range. They are achromatic and nearly lossless in comparison to refractive lenses which possess inherent Fresnel losses and absorption/dispersion. In using OAPMs, one is able to eliminate such issues thereby preserving the detected high E-field amplitudes without any pulse echoes. In addition, the off-axis configuration ensures no central obscuration that will otherwise damp the middle transferred spatial frequencies. [295]

Even though OAPMs are strong candidates to be used as THz mirrors, they are not however perfect. The wavefront errors of OAPMs have been characterised previously [296, 297] and they have shown that the off-axis geometry of these mirrors introduce astigmatism and coma. Moreover, the optimal arrangement for off-axis ellipsoidal mirrors has been derived where it has been shown that Gaussian beam profiles are distorted leading to mode conversion. In 2010, Bruckner et al. investigated further the inherent aberrations of OAPMs through various combinations of the mirrors. It was found that the arrangement with the parent parabola axes coinciding gave the least geometrical optical spot of confusion, i.e. the OAPMs being arranged in a closed configuration as shown in Figure 4.27. [295]

Holes and Bandwidth: When dealing with pump-probe setups, the high density of optics on an optical bench is usually an issue as there is less space for freedom. Severe spatial requirements in optical-pump-probe experiments have led to the development of OAPMs

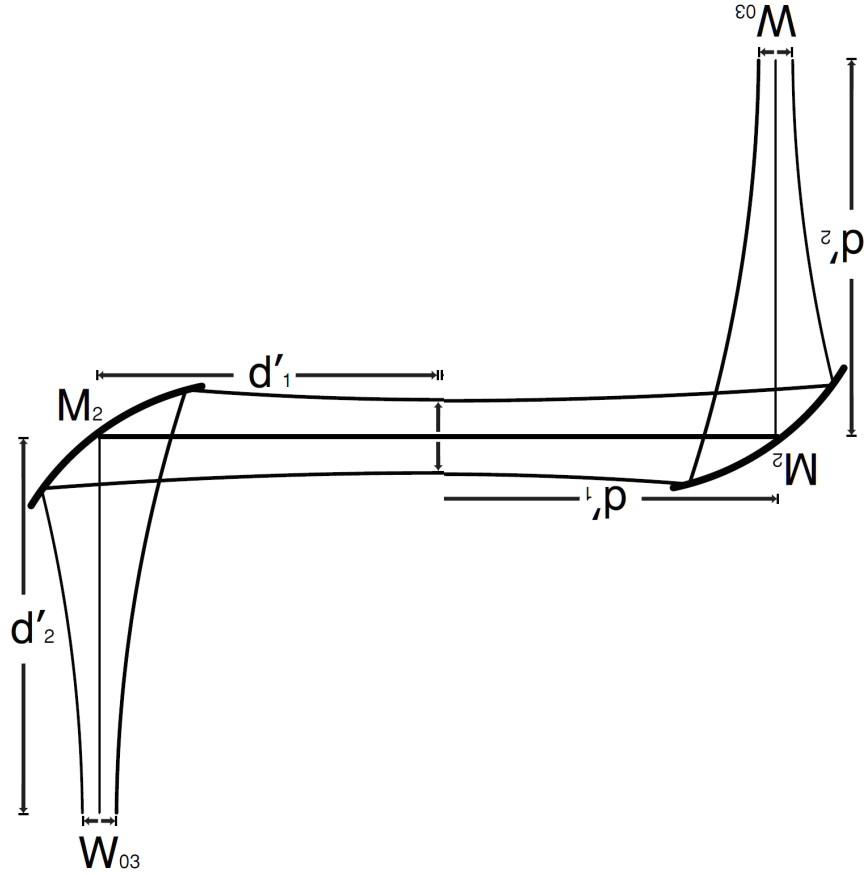


Figure 4.26: **OAPMs Z-configuration:** The two OAPMs in an open configuration. This allows for more space around the optics to manoeuvre other pieces of equipment such as a sample stage or extra beam paths.

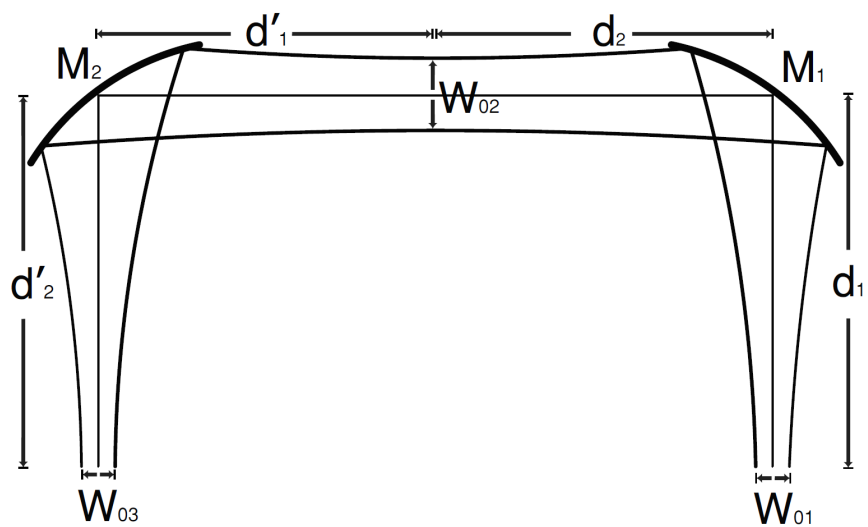


Figure 4.27: **OAPMs U-configuration:** The two OAPMs in a closed configuration. Although space-restricted, this setup minimises the astigmatism in the THz beam.

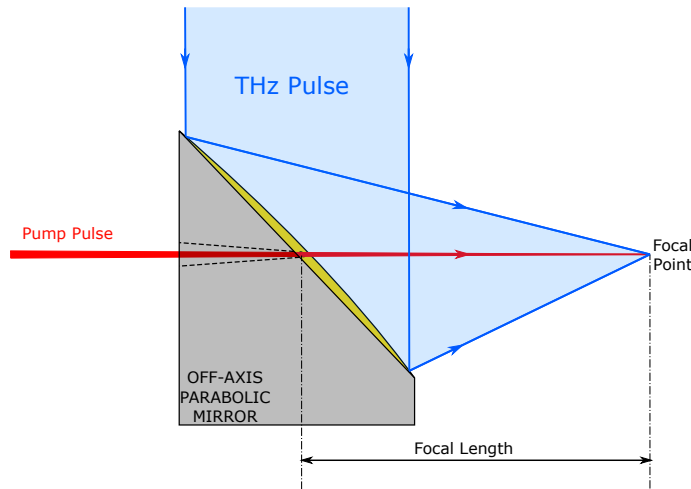


Figure 4.28: **OAPMs**: Schematic of the most common off-axis parabolic mirror used in spectroscopic setups. The hole in the gold-coated area, here represented by the black dot, allows the photoexcitation pump pulse to propagate along the same line as the probe pulse.

with a hole in the middle of the paraboloid surface that allows the photoexcitation beam to pass through it directly onto the sample in a linear geometry, Figure 4.28.

A standard theoretical treatment of the description of laser beam propagation is based on a Gaussian beam profile theory. The beam waist at a distance z can be written in terms of the Rayleigh range as follows

$$w(z) = \sqrt{w_0 \left[1 + \left(\frac{z}{z_0} \right)^2 \right]}, \quad (4.40)$$

where z_0 is the frequency-dependent Rayleigh range, and w_0 is the beam waist size at $z = 0$. Unlike the propagation of a single-frequency beam, a THz pulse is a superposition of many frequencies. Consequently, the waist size and Rayleigh range are not single-valued for the different frequency components of the THz pulse. For a pulse spread over a circular geometry, it can be shown that the higher frequencies have the smallest beam waist sizes and appear in the middle of the pulse while the lower frequencies are more spread out. [146] This then dictates that for an OAPM with a hole in the middle, the high frequency components are effectively lost and the bandwidth will be smaller. This is shown in Figure 4.29 where the performance of an OAP with a 3 mm hole was used to focus the THz was compared with a normal OAP. It is quite clear that the latter has retained the high frequencies. Since the air-plasma was primarily built for higher power an broad bandwidth, OAPMs with no holes were used and FTO-coated glass was set in place for merging the optical gate pulse with the THz beam at the detector, whilst the photoexcitation pump pulse was set an angle.

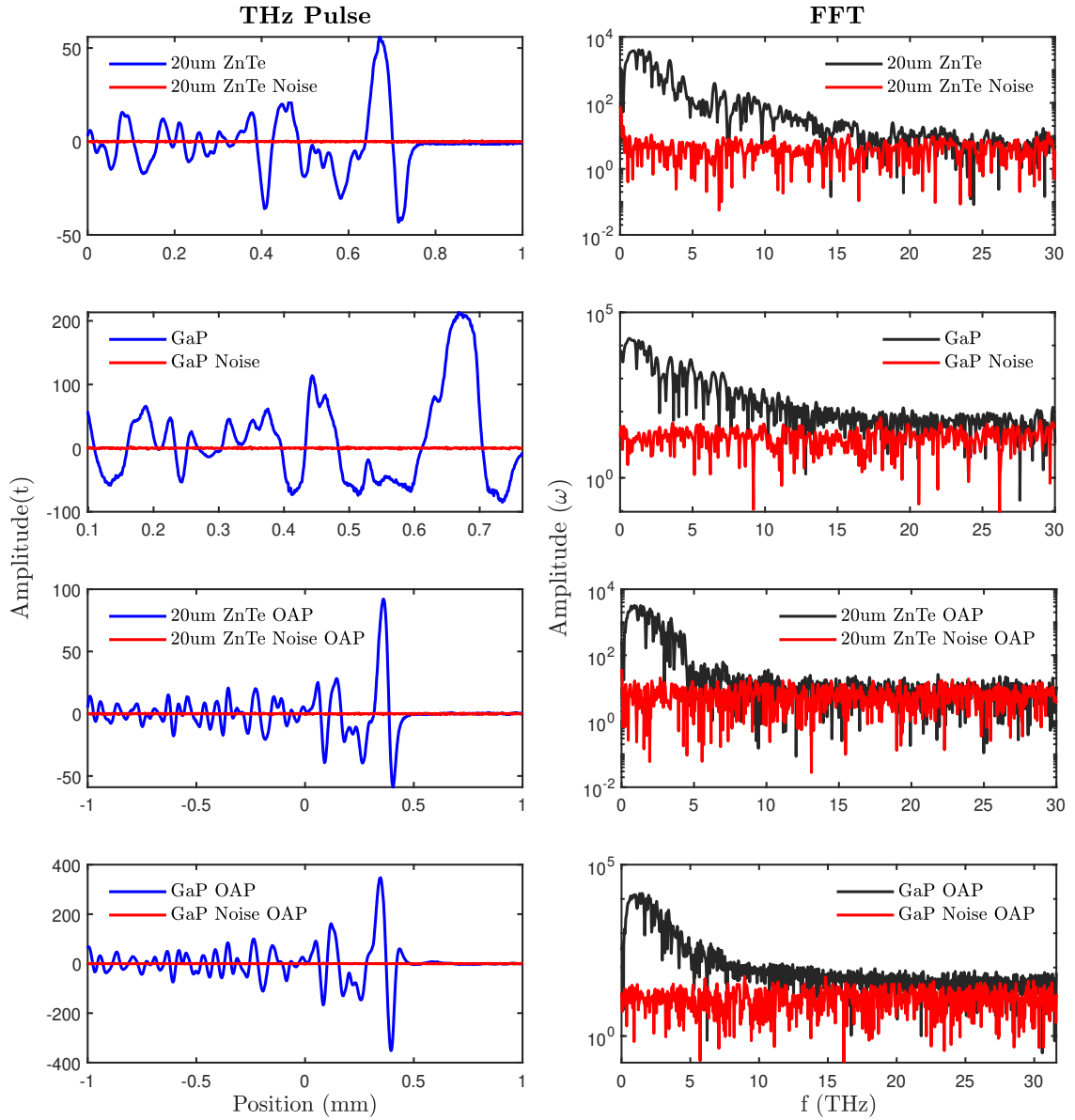


Figure 4.29: **OAPMs & Holes:** Plots illustrating the effect of having a hole in an OAP focusing a THz pulse. The plots on the left are the THz transients and the plots on the right are their respective spectrum. Comparing the spectra of the top two with the bottom two shows that more bandwidth is extracted for OAPMs without holes. These measurements were done in air, hence the water vapour absorption lines in the spectra.

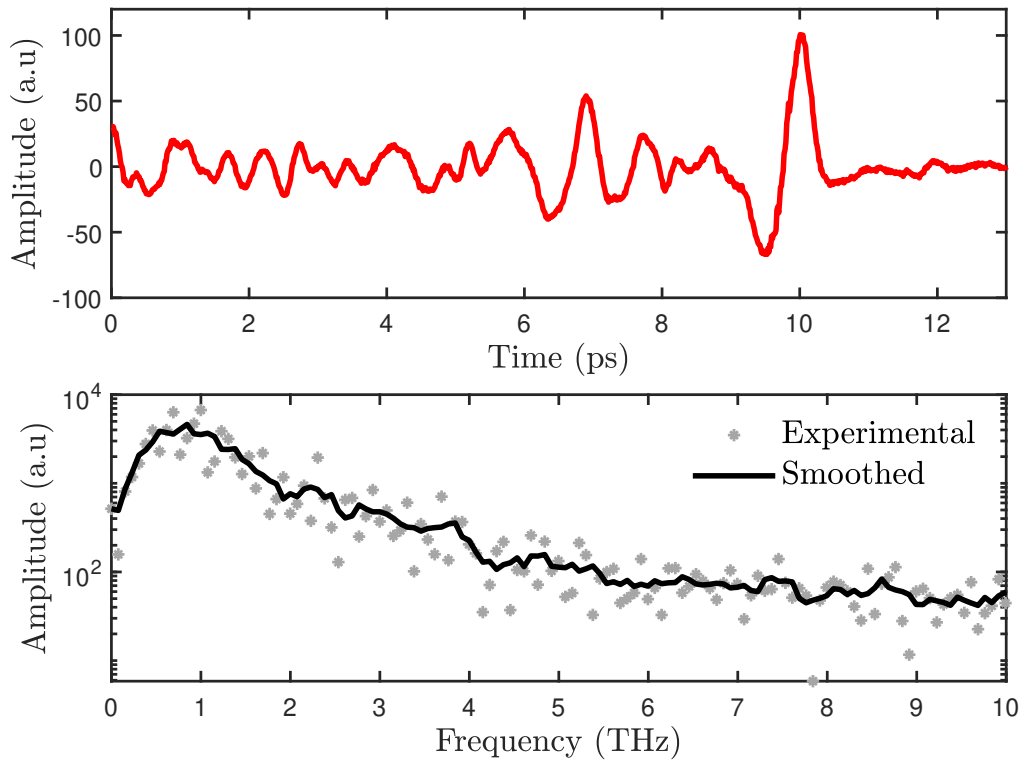


Figure 4.30: **Reflection Setup:** Plot showing the THz waveform and the spectrum in reflection mode. The measurement was taken in ambient air and the water vapour absorption lines are quite evident (grey dots) as well as the THz transient not decaying to zero. The smoothed spectrum shows that even in reflection mode, it is possible to recover up to 8 THz.

4.7.6 Reflection Setup

The air-plasma setup is not only capable of transmission measurements but also operates in reflection mode. This is mostly important for samples with high absorption and reflectivity coefficients. However, all samples can be studied in both transmission and reflection simultaneously and this greatly reduces the time needed on the system.

For this reflection setup, high resistivity float zone silicon (HRFZ-Si) was used as a beamsplitter and a second gate pulse was introduced for the detection. FS-EOS was the detection technique of choice given its simplicity as space restriction became an issue. Nevertheless, the bandwidth of the reflection beam for a silver mirror was measured and found to be as good as in the transmission mode.

4.8 Conclusion

This chapter looked at THz generation using a gas-plasma and two of the main theories put forward to understand the physical nature of this generation. Although either theories

fail to give a full picture of this complex process, there is still scope to dive deeper into the theory of plasma physics. The new setup has shown an incredible bandwidth extending beyond 10 THz with a 20 μ m thick ZnTe crystal and a clean spectrum of up to 8 THz for a 200 μ m thick GaP crystal which was huge improvement compared to the previous setups. The new system also features some upgrade which will enable users to extract maximum benefit in taking measurements. The THz box (*i.e.* the optics consisting of the off-axis parabolic mirrors and the sample stage) will feature a monolithic stage setup which will enable easy swap between different experimental geometries. Additionally, the system is capable of simultaneous transmission and reflection measurements with the detection of THz pulses in the transmission mode being done in either of two ways: free-space electro-optic sampling or air-biased-coherent-detection. Drawings of the THz measurement chamber with optics are shown in Figures 4.31, 4.32, 4.33, 4.34. These have been designed by Nicholas Callaghan, a member of our physics clarendon workshop.

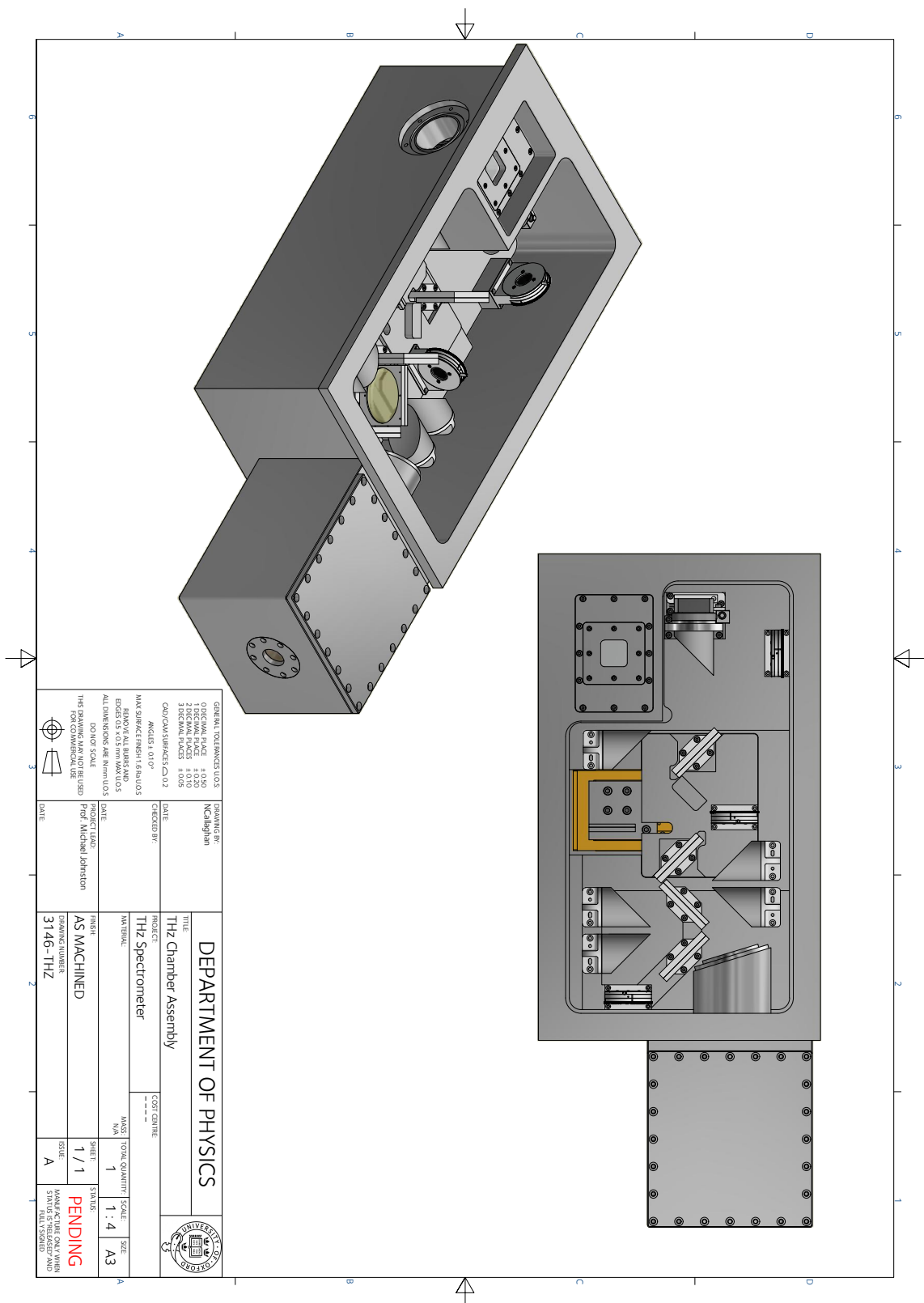


Figure 4.31: Top and Angled Views of the THz Vacuum/Purged Box: The sealed compartment is where the two-color plasma will be formed.

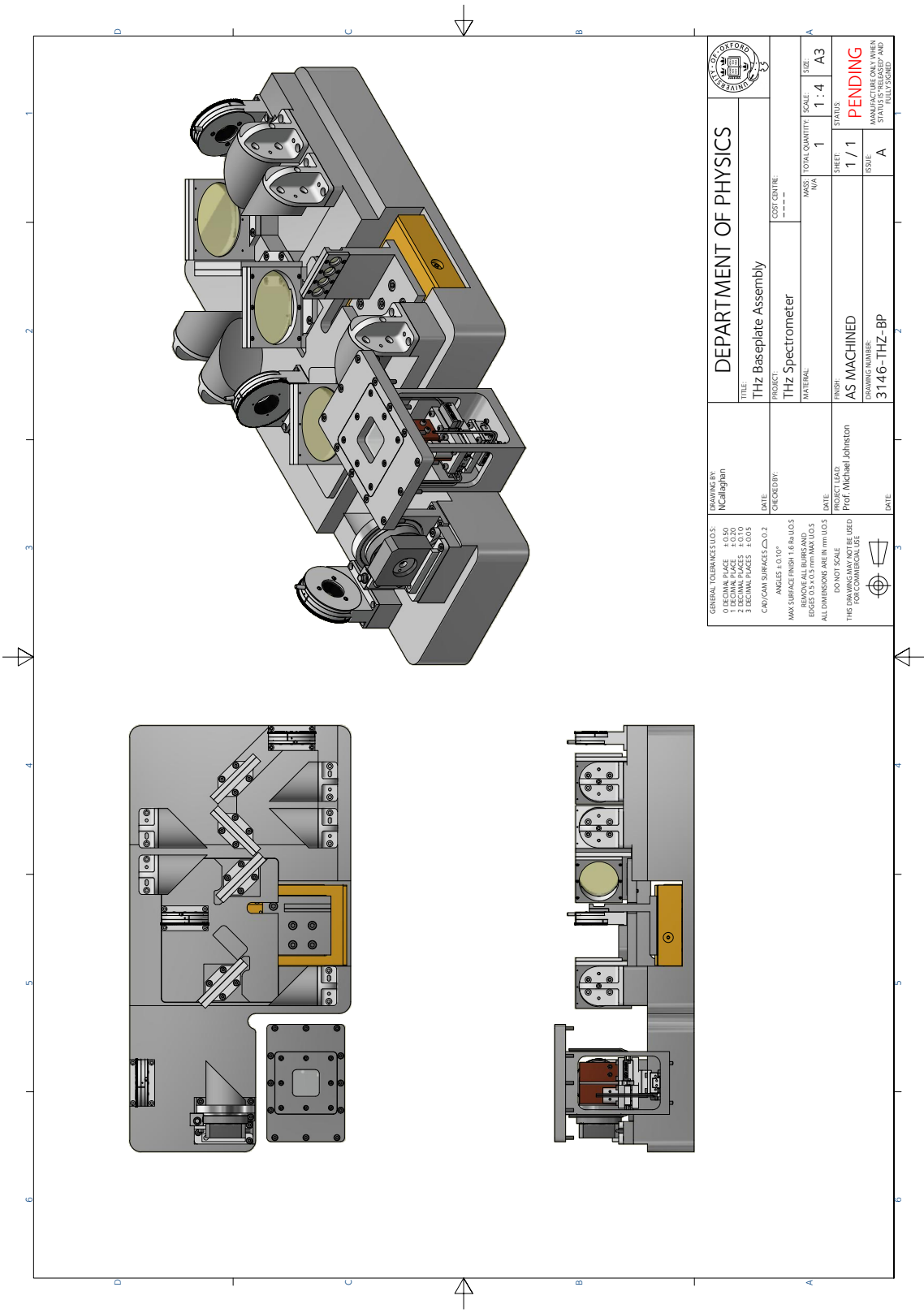


Figure 4.32: The Inside of the THz Vacuum/Purged Box.

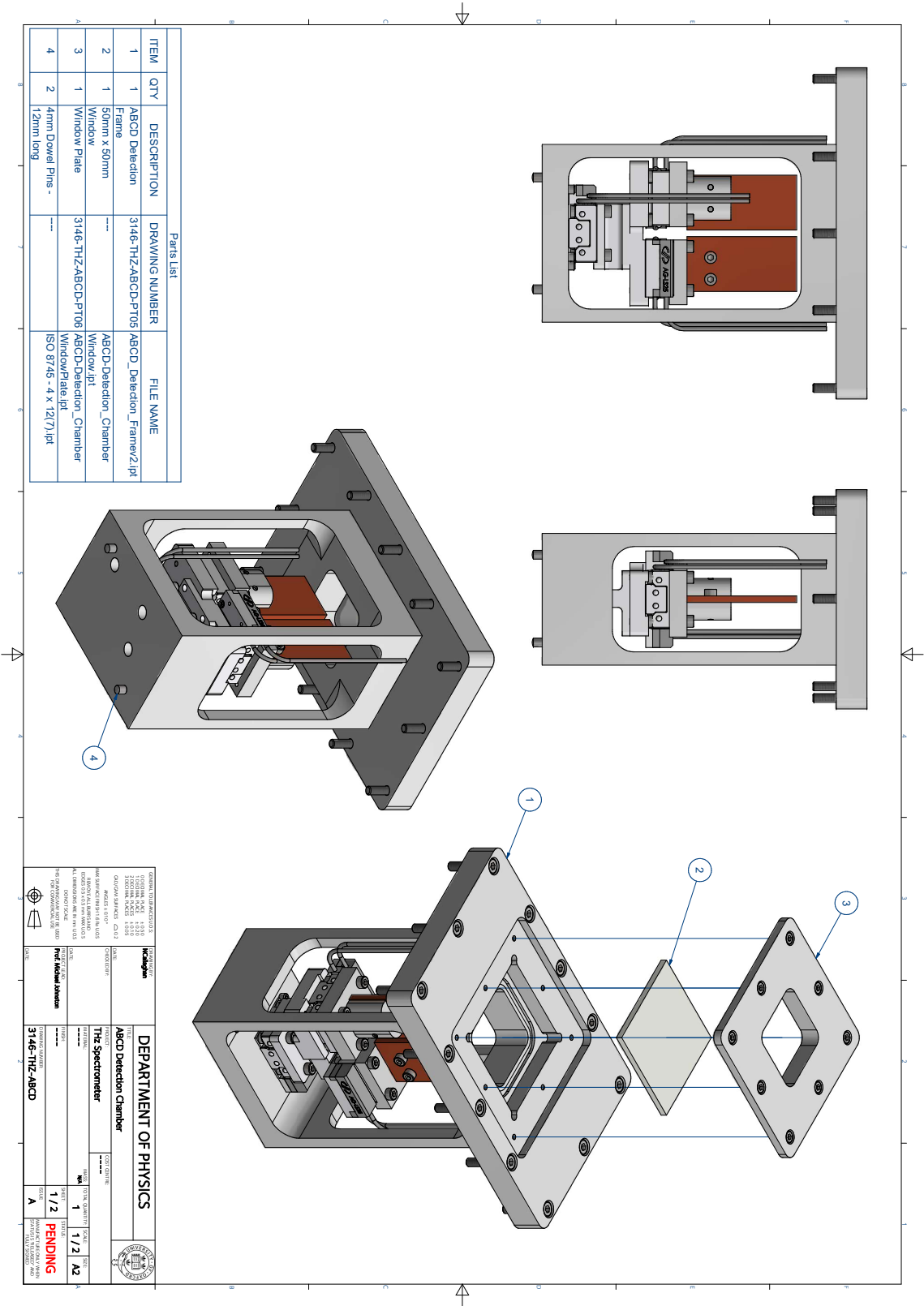


Figure 4.33: The ABCD Setup.

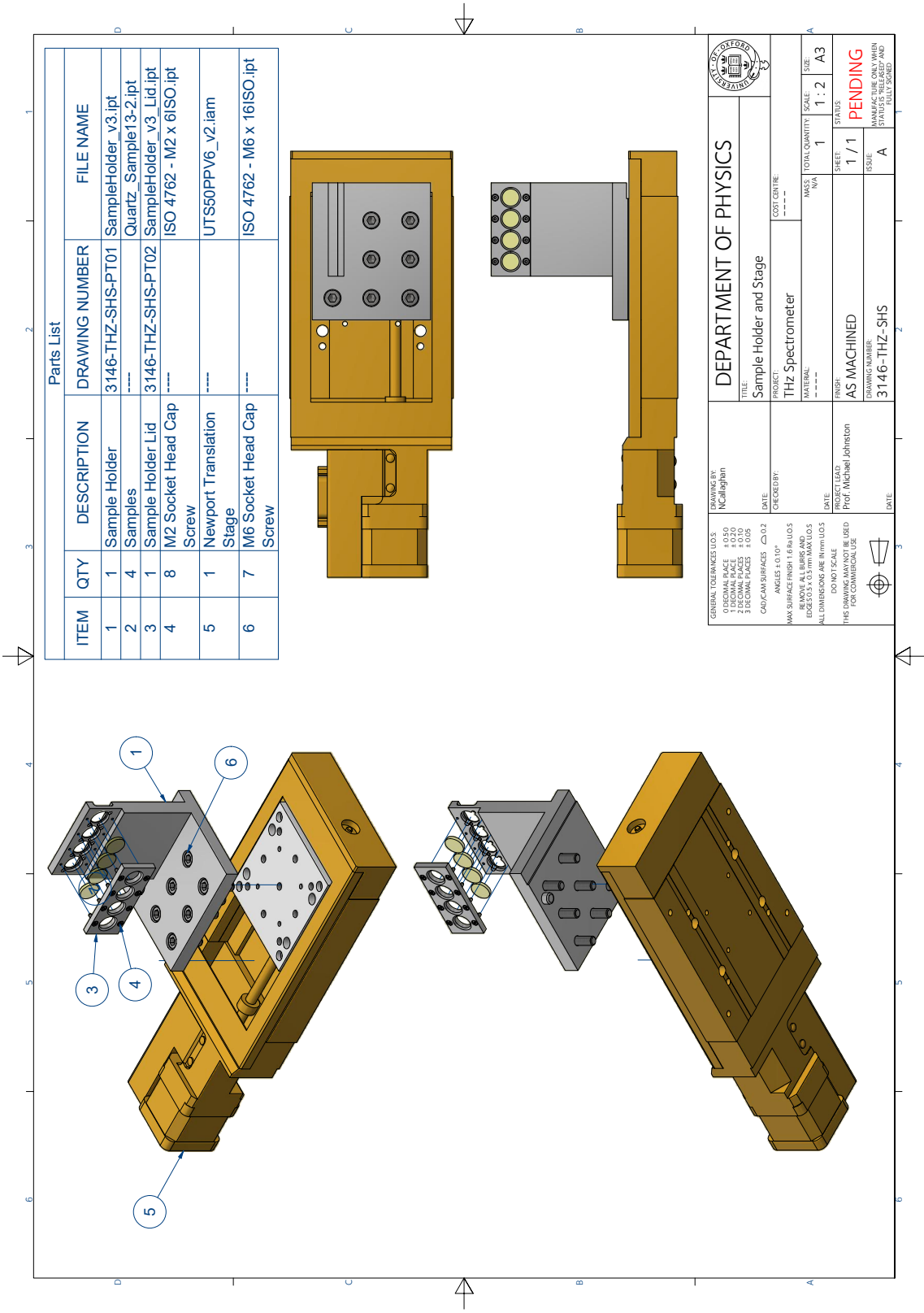


Figure 4.34: The Sample Stage.

Length-Dependent Plasmon Resonance in GaAs & InP Nanowires

III-V semiconductor nanowires are playing an increasingly important role in the field of condensed matter physics. From nanoscale components [28,42,298] to highly efficient photovoltaic devices, [299,300] there is a strong urge to have a solid fundamental understanding of their optoelectronic properties. In the terahertz frequency range, surface plasmons (SP) are the staple oscillations in III – V nanowires, and strong correlations have been found relating to the nanowire thickness, surface defects, and charge carrier density amongst others. [14,75,79] In this chapter, we go on to show that there is a direct relation between the nanowire length and the frequency of the SP resonance in the terahertz regime. Both gallium arsenide and indium phosphide nanowires have been grown to various lengths via MOCVD and theoretical calculations have been done to further strengthen this study. Additionally, the simulations revealed higher electron mobilities than the previously reported values. Previously, the plasmon resonances were fitted using a Lorentzian model which had an extra factor called the g -factor which depended on the NW geometry and how the THz pulse interacted with the sample. The plasmonic behaviour is determined by considering the normal Drude response of the complex dielectric function and thereafter fitting the experimental data to the finite-difference time-domain (FDTD) simulations.

5.1 Introduction

III – V semiconductor nanowires (NWs) have attracted a lot of interest as strong contenders for next generation ultrasmall optoelectronic devices. Their fascinating opto-

electronic properties have elicited their use in a plethora of fields such as nanoscale lasers, [301–303] photovoltaics, [299, 300, 304, 305] THz modulators [76–78, 306] and detectors, [307–309] waveguides, [310] LEDs, FETs [6, 311, 312] amongst others. Their inherently large surface-area-to-volume ratio and quasi-1D geometry have earned NWs significant advantages over their bulk counterparts such as the ability to tune their bandgaps, carrier lifetimes, and charge mobilities. [31] Moreover, the rich physics underlying NW optics and photonics that arise mainly due to the interaction with electromagnetic radiation has sprouted research in plasmonics. [313–316]

The field of NW growth is now well-established. Both gallium arsenide (GaAs) and indium phosphide (InP) NWs, the two III-V materials studied in this work, have been highly studied in the past owing to their very interesting and attractive optoelectronic properties as will be described below. In the past, electrical methods such as Hall measurements or field effect transistor measurements used to be the experiment of choice but at the expense of material damage and the introduction of several external factors such as contact resistance, and capacitance which add to uncertainties within the data. Terahertz spectroscopy has offered a new avenue as a non-invasive, contact-free probe to determine the various optical and electronic parameters of these NWs.

Semiconducting GaAs NWs have been at the forefront for various reasons: direct bandgap, low Auger recombination rate, high absorption coefficient and high electron mobilities. The THz conductivity of Au-seeded MOCVD (see chapter 2 for more details about the growth method) grown GaAs NWs was first investigated via OPTP spectroscopy on MOCVD grown GaAs NWs with diameters of 50 nm. [75] The photoconductivity data, $\Delta\sigma(\omega)$, featured a Lorentzian response with $\text{Im}(\Delta\sigma(\omega))$ crossing the frequency axis at the peak of $\text{Re}(\Delta\sigma(\omega))$. The plasmon resonance displayed a red-shift with decreasing photoexcitation fluence and electron density, as previously seen for localised surface plasmon (LSP) modes. By fitting of a Lorentzian plasmon model to the photoconductivity spectra, the electron mobility was found to be around $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ which was a factor of 6 lower than the bulk material. This reduction in electron mobility was attributed to electron scattering at the NW surface. Additionally, the temporal dynamics of the photocarrier showed a very short lifetime of less than 10 ps due to rapid charge trapping at the NW surface. [75] Joyce *et al.* in 2013 [14] performed a series of measurements on bare, unpassivated GaAs NWs of varying diameters and found that the surface recombination velocity was extremely high at $5.4 \times 10^5 \text{ cm s}^{-1}$ (see chapter 3 for how to extract surface recombination velocities).

Furthermore, the photoconductivity traces displayed a monoexponential decay as a result of carrier trapping at the surface. There was a direct correlation between the carrier

lifetime, τ , and the NW diameter, d . With decreasing d , τ was found to decrease as well, an effect attributed to the higher surface area-to-volume ratio, which allows for saturable carrier trapping at the NW surface. [14] Following this work, further research was performed in accordance to surface effects. The surface passivation of GaAs NWs was then investigated by Yong *et al.* in 2012, [79] with numerous experiments on the effect of overcoating of GaAs NWs with aluminium gallium arsenide (AlGaAs) shells. The shell drastically changed how photocarriers behave. Being a higher bandgap material, the charge carriers are no longer moving across the trap-rich surface but instead are forced to move freely in the GaAs NW core. Twin defects in the GaAs core are also reduced, preventing carrier scattering and increasing the carrier mobility. From measurements of the photoconductivity decays of both bare GaAs NWs and GaAs NWs coated with AlGaAs shells the carrier lifetime was found to be improved by a factor of 4, as a direct result of surface passivation from the AlGaAs shell. [79] The photoconductivity lifetimes increased with increasing photoexcitation fluence, suggesting the existence of trap states that saturate at higher photoexcited carrier densities. Through fitting of the carrier decays with a coupled rate equations, the trap density was extracted to be 82% lower in the AlGaAs-coated NWs.

Photoconductivity spectra were also taken and a plasmon resonance was observed around 1-2 THz for all samples. Through fitting of a plasmon model to these spectra, the electron mobility was determined as $2250 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for the core-shell GaAs/AlGaAs NWs and $1200 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for the bare GaAs NWs. An increase in electron mobility of over a factor of 2 was observed for the coated NWs, owing to a reduction in the surface-related scattering due to the AlGaAs shell. Further studies have shown that by optimisation of the AlGaAs shell growth conditions and thickness, the surface-related scattering can be reduced to optimise the electron mobility to reach up to $3000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, comparable with bulk values. [31] This increase in mobility is consistent with an increase in photoconductivity lifetime of up to 1.6 ns with the thickest AlGaAs shells. [14,30,32,33,75]

Boland *et al.* went even further to investigate the effects of dopants in GaAs NWs. Both *n*- and *p*- type doping were studied revealing lower carrier mobilities than undoped ones. However, there was an increase in the carrier lifetime demonstrating a strong suppression of non-radiative surface and defect-mediated recombination. *p*- type doping also showed an ultrafast decay within the first 25 ps after photoexcitation which was a result of band bending. [33] All these effects offered great insights into the optoelectronic properties of GaAs which have been key to using them in many devices such as lasers and solar cells.

Indium phosphide (InP) is an important III – V semiconductor that has been extensively studied, as their long lifetimes make them useful as potential building blocks for NW photovoltaic devices. Its ability to exist in two crystalline forms namely wurtzite (WZ) and zinc blende (ZB) (see chapter 2 for crystal structures) possessing direct band gaps of 1.42 and 1.35 eV at room temperature respectively makes the material a highly promising candidate for construction of viable nano-integrated circuits. [309,317–321] Quantum confinement is highly regarded in InP owing to the nanoscale dimensions in the radial direction attributing novel physical properties to nano-sized InP as compared to bulk materials. One-dimensional geometry on the nanometre (10^{-9} m) scale provides an extremely high surface area with a nanoscale radius of curvature and great mechanical flexibility. These properties are advantageous in many chemical and mechanical applications. InP semiconductors among other III–V semiconductors are used in high power and high-frequency electronics because of high electron velocity when compared with other III–V semiconductors, for instance, GaAs. Moreover, InP has the longest lived optical phonons among the compounds with ZB crystal structure. [322] Lastly, InP has a large dielectric constant that minimises losses in solar cells. All of these various physical, optical and electronic properties have sprouted a plethora of research for InP.

Just as with GaAs NWs, similar measurements have been performed on InP NWs. High quality MOCVD-grown InP NWs have been studied via OPTP with the measurements performed at various fluences, for various diameters. The photoconductivity decays the InP NWs were shown to exhibit long carrier lifetimes over 1 ns. For very high fluences, a slow rise in photoconductivity was initially seen which was attributed to the fact that electrons are promoted into multiple high energy valleys possessing different curvatures and therefore different effective masses (larger in this case) leading to a reduction in the mobility and hence an initial hump in the carrier decay. In contrast to GaAs NWs, the carrier lifetime was found to be independent of the NW diameter, suggesting that the lifetime is dominated by trapping at planar crystallographic defects rather than at the NW surface. A low surface recombination velocity of 170 cm s^{-1} was determined by fitting the lifetimes for the varying diameters. Its low value was attributed to the spatial separation of electrons and holes, which prevents carrier recombination and leads to a much longer lived photoconductivity lifetime. [14,79] Photoconductivity spectra were also measured for all InP NWs with a similar Lorentzian response observed as for GaAs NWs. The surface plasmon model fitted gave very low electron mobilities between 120 and $660\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were extracted which were also independent of the NW diameter, suggesting that the dominant scattering mechanism for these NWs result from ZB-WZ boundaries rather than being a surface effect. [29]

The above literature survey mentions only the use of the surface plasmon model. However, in the extraction procedure and fittings of photoconductivity data and related parameters, several models have been proposed and developed over time including and not restricted to (1) localized surface plasmon (LSP) modes, (2) the Drude model, and (3) the Drude–Smith model, which is an extension of the Drude model (all three models are discussed in detail in Chapter 3). [4] The latter model introduces a further parameter, c_n , which is related to the incomplete randomisation of carrier momentum upon scattering and simulated models can be seen in §3.7.1.6. These are the three most important ones and while the Drude–Smith model can produce comparable shapes of the frequency-dependent conductivity to the surface plasmon model (when $c_1 \approx -1$, $c_n > 1 = 0$), it would require a time-varying backscattering parameter to model the data, which has no obvious physical origin. Parkinson *et al.* preferred the surface plasmon (or Lorentzian model) approach to model the conductivity. [75] Terahertz radiation can couple into the (normally forbidden) plasmon mode due to the narrow width of the nanowires and the interaction between the modes on adjacent sides of the same nanowire. [323]

Surface plasmon modes, in contrast to bulk plasmons, are coherent oscillations of the electron–hole plasma at the surface of a dielectric upon interaction with light. [75, 323–325] The relationship between the carrier density N and the plasmon frequency ω_p is given by

$$\omega_p = \sqrt{\frac{gNe^2}{\epsilon_0\epsilon_\infty m^*}}, \quad (5.1)$$

where m^* is the effective mass of the electron, ϵ_∞ the high-frequency dielectric response of the NWs, and g is a factor dependent upon the surface geometry and the surrounding dielectric medium. The values g can take varies from 0 to 0.5. Parkinson *et al.* in 2007 showed that for a terahertz electric field E polarized perpendicular to the axis of a cylindric nanowire in vacuum, $g = 1/2$ or $g = 1/3$, while for E parallel to the nanowire’s axis, $g = 0$, and the only conductivity response is due to the bulk plasma mode. [75] Fotev *et al.* further investigated the g -factor for both longitudinal and transverse fundamental modes and found values ≈ 0.228 and ≈ 0.93 respectively. [250]

This chapter looks at plasmonic behaviour simulated using finite difference time domain calculations. The method is described in detail in the section below. Rather than probing the photoconductivity, one looks at the scattering intensity. As the THz pulse impinges onto the NW surface, some of it will pass through while some of it will be scattered. The physics of this scattered light was pioneered by Lord Rayleigh in 1871 through the concept of electric dipoles. [326] It is assumed that the phase of the electromagnetic radiation is constant over the region of interest. The homogeneous field induces a polarisation which then scatters the light. It is worth noting that the NWs act as dipoles and that

higher order scattering modes (quadrupoles and octupoles) are not taken into account. The polarisation response of the NWs is then determined from the dielectric function which is approximated using the classical harmonic oscillator formalism introduced by Lorentz. [324]

At the plasmon resonance frequency, the light no longer goes through the NW but travels on the surface of the NW which in turn leads to a high scattering intensity. In the determination of photoconductivity and mobility values, previous works have developed models based on the surface plasmon equation taking into account a factor known as the g -factor. As mentioned above g depends on how the THz electric field interacts with the NW geometry and the rubbing technique for transferring NWs onto a substrate does not allow for a full control on the morphology or NW distribution due to randomisation thereby introducing uncertainties in the determination of this factor. The InP NW samples used in this study were all transfer-printed ensuring that the majority of the NWs are all aligned with the THz electric field. The model used however drops this factor and the mobility values obtained are higher than previously reported. This will hopefully shed some light on how the photoconductivity fitting works and gives a bigger picture for NW photoconductivity in general to try and reconcile theory with experiment.

5.2 Sample Fabrication

Gallium Arsenide (GaAs) & Indium Phosphide (InP): The GaAs and InP nanowires were grown at the Australian National University using MOCVD and selective-area epitaxy (SAE) respectively - the former having been described in detail in chapter 2, and the latter schematically in Figure 5.1. For SAE, briefly, a $\langle 111 \rangle$ A InP wafer substrate was used as the base for the InP growth. For SAE, the growth is controlled via patterning individual 'holes'. To achieve this, a 30 nm thick SiO₂ layer (evaluated via ellipsometry) was deposited onto the substrate by plasma enhanced chemical vapour deposition (PECVD) at a temperature of 300°C. Thereafter, hexamethyldisilazane (HMDS) was spin-coated at 500 rpm for 5 seconds and at 4000 rpm for the next 45 seconds. This was followed by another spin coating procedure of ZEP 520A resist at the same settings. The hexagonal array patterns were defined at high resolution onto the resist using electron beam lithography (EBL). The resist was then developed after which a plasma etcher was used (300 watts, 2 mins, 300 sccm O₂) to remove residues of the resist before being etched in a solution of 40% hydrofluoric (HF) acid diluted with ammonium fluoride in a ratio of 1:45. ZEP stripper was then employed to remove the ZEP initially used, and the surface was further plasma-etched for a deep clean. Since there is a possibility that the exposed InP surface might have been damaged during the SiO₂ layer deposition, an extra step is

required to ensure uniformity: 10% H_2O_2 was used to oxidise the InP layer followed by the removal of the oxide layer with 10% H_3PO_4 solution for 2 mins. This process was repeated 5 times for best results. The sample was then transferred into a metal-organic vapour-phase epitaxy (MOVPE) reactor for the NW growth.

The patterned array of InP NWs, Figure 5.2, were grown in an AIXTRON 200/4 MOVPE reactor operating at a base pressure of 100 mbar and H_2 as carrier gas. The precursors for the III-V elements were trimethylindium (TMIn) and phosphine (PH_3). By mixing precise molar fractions of the solutions and engineering the correct thermodynamics of the NW growth, various lengths for the NWs, $1\text{ }\mu\text{m}$ to $11\text{ }\mu\text{m}$, were achieved. SEM was used to structurally characterise the NWs and the images are shown in Figure 5.3.

Nanowire Transfer Printing: The NWs were subsequently transferred onto z-cut quartz discs with a diameter of 13 mm and a thickness of 2 mm. Quartz discs have been chosen as the substrate as it has negligible dielectric response at terahertz frequencies. [256] Nanowires have strong anisotropic terahertz absorption along their long axis and therefore it is imperative to have most NWs aligned with the polarisation of the THz pulse. [76–78] To achieve perfect alignment of all the NWs on the quartz disc, a special technique developed at the University of Strathclyde was employed: [327] transfer printing (TP). TP enabled the easy manipulation and organisation of the NWs. At the core of this technique is the polymer-based micro-stamp (μ -stamp) fabricated in polydimethylsiloxane (PDMS) that has a sticky surface. This then allows one to controllably capture NWs from the growth substrates and effectively transfer them onto the desired substrates for spectroscopic measurements. A brief description of how the process works is as follows: the equipment consists of an in-built microscope that allows for easy targeting of NWs. One the μ -stamp is made, it is aligned with a NW bundle and pressed against it. Upon contact, the μ -stamp deforms and conforms to the NW shape thereby embedding and capturing it. The μ -stamp is then lifted off from the surface and dragged onto a specific site onto the desired final substrate. In doing so, the μ -stamp returns back to its original shape and form whilst the NW is still stuck onto it. The Van der Waals forces between the NWs and the resulting substrate is sufficient to have them detached from the surface of the μ -stamp. A full in-depth review of the nanoscale mechanisms involved during this procedure is given in Reference [327].

Theoretical Framework: The nanowire length-dependence of plasmonic resonance in the THz regime was seen theoretically. Finite difference in time domain (FDTD) simulations were performed using a commercial software package: Lumerical. The scattering intensity of the NW was calculated as a function of frequency when a simulated THz electric field is incident onto the NW. This is related to the magnitude photoconductivity of the NWs

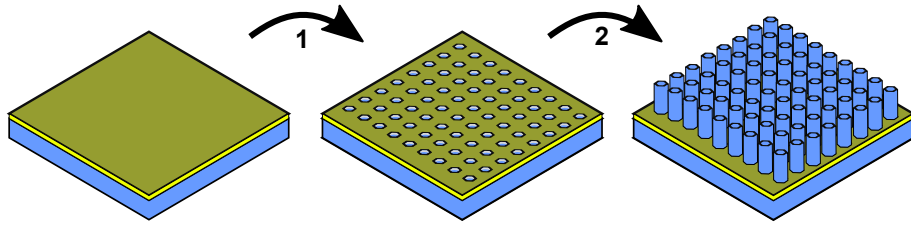


Figure 5.1: **Selective-Area Epitaxy:** Schematic of the growth technique used for InP growth. From left to right: InP $\langle 111 \rangle$ A wafer substrate with a thin layer of SiO₂ (30 nm), hexagonal arrays were patterned onto the SiO₂ for controlled growth, and finally the InP NWs grow vertically through the holes.

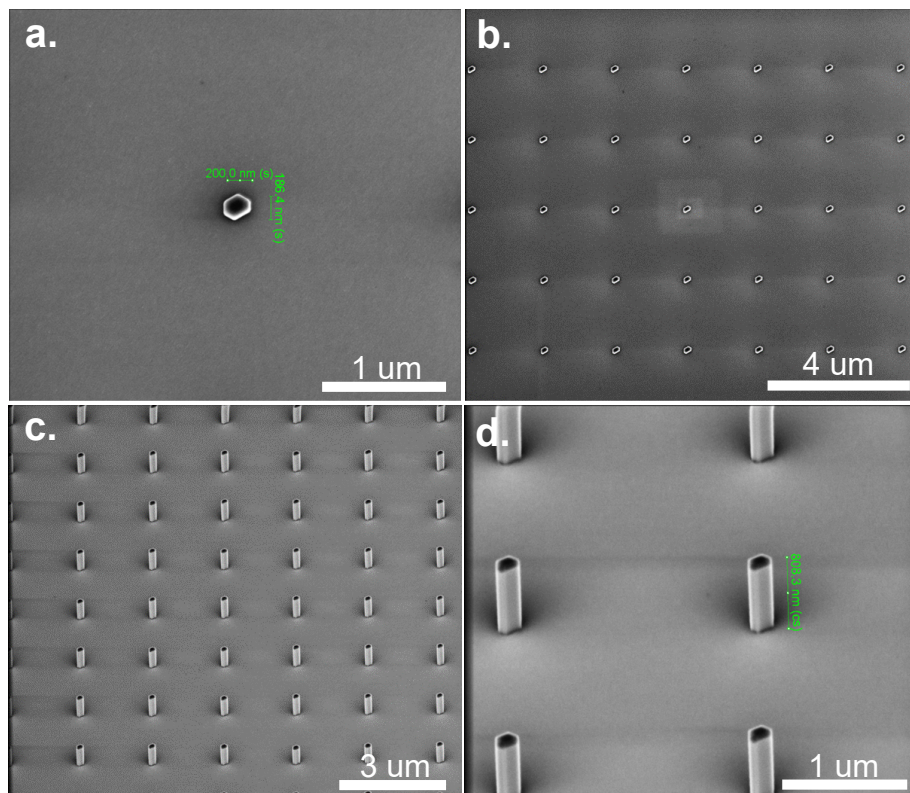


Figure 5.2: **0.8 μm NW:** Scanning Electron Microscope images of the InP nanowires as grown via SAE. (a) and (b) show the top view projection and (c) and (d) show an angled view. The nanowires are all roughly about the same lengths.

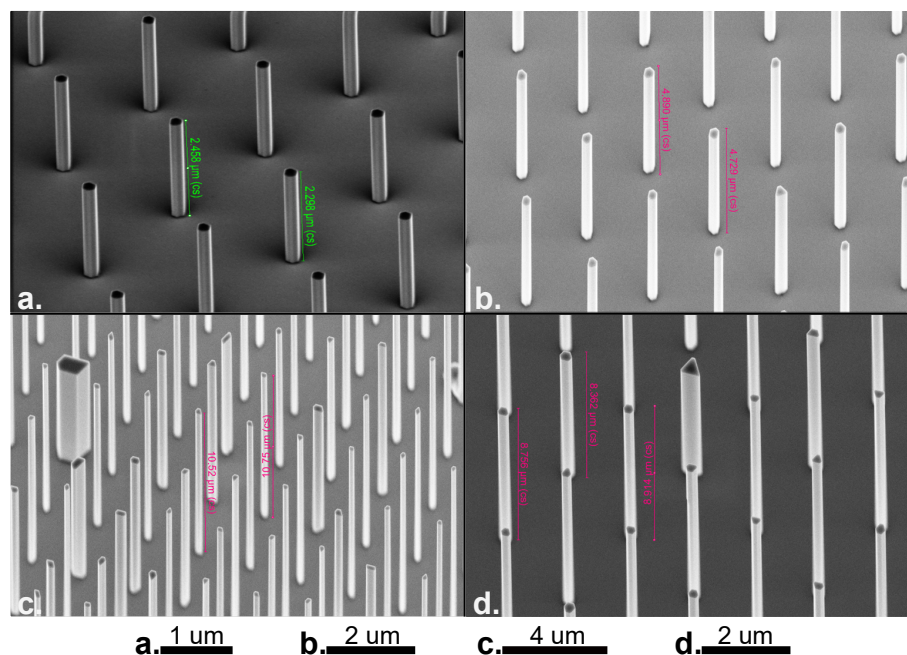


Figure 5.3: **Length Dependence InP:** Scanning Electron Microscope images of the various lengths of the InP. The scale bars are shown at the bottom for their respective labelled images.

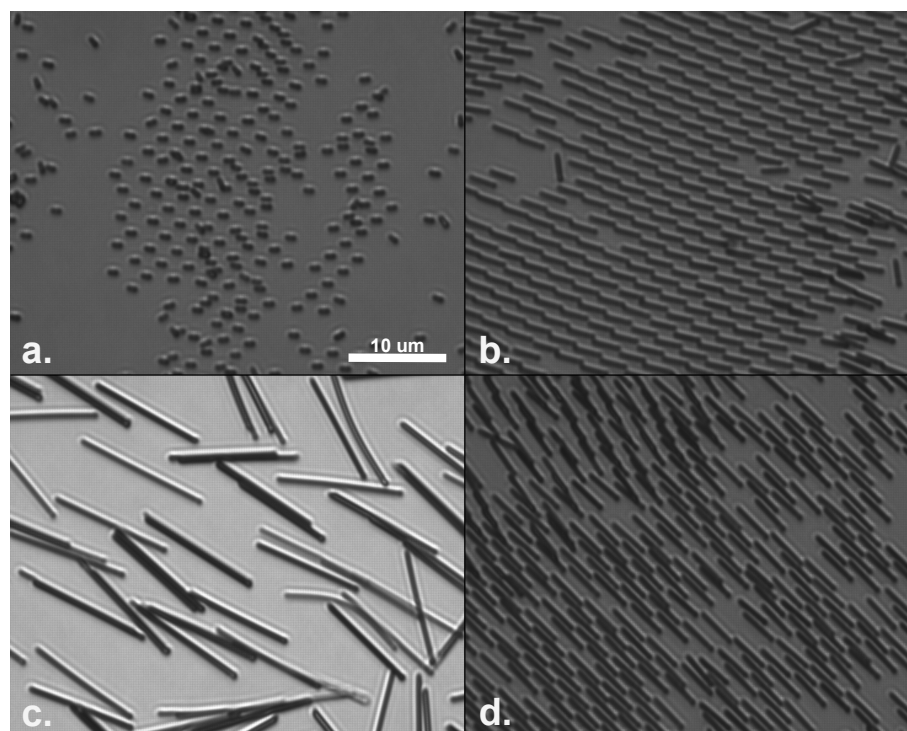


Figure 5.4: **Samples:** Optical microscope images of the samples after transfer printing. The NWs are highly aligned with reasonable densities around the main.

one obtain from OPTP. The simulation collects the scattered light in all directions and generate the intensity. The permittivity of the GaAs/InP NWs was approximated by that of a free electron gas described by the Drude model. This approximation has been proven to be valid for semiconductors at THz frequencies. The frequency dependent complex permittivity resulting from the Drude model of free charge carriers in the NWs can then be modelled using:

$$\epsilon = \epsilon_H - \frac{\omega_p^2}{\omega^2 + i\Gamma_e\omega} + \frac{(\epsilon_L - \epsilon_H)\omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\Gamma_p\omega}, \quad (5.2)$$

Where ϵ_H and ϵ_L are the high and low frequency dielectric constants, ω_{TO} and Γ_p are the transverse optical phonon resonance and damping coefficient. ω_p is the plasma frequency given by the following expression:

$$\omega_p = \frac{Ne^2}{m_{eff}\epsilon_0}, \quad (5.3)$$

where N is the charge carrier concentration per unit volume, m_{eff} is the electron effective mass. Γ_e is the momentum scattering rate and can be calculated via the following equation: $\Gamma_e = e/m_{eff}\mu$, where μ is the mobility. The optical constants are determined for different carrier density and mobilities and used to calculate the plasmonic response of nanowires. A TFSF (Total Field Scattered Field) source, polarised parallel to the axis of the nanowire illuminates the nanowire. The scattered light is detected with a box of monitors around the nanowire in the scattered field region. The scattered intensity is then directly related to the NW photoconductivity response with maximum scattering occurring at the plasmon resonance frequency.

Data was simulated for a range of values of mobilities, and photoexcited carrier densities. The latter parameter was obtained by fitting the experimental data with the surface plasmon model as shown in Figure 5.11. The simulations were then compared to experiment and it has been observed that a resonance shift was shift for NWs with carrier mobilities beyond $2900 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for unpassivated, undoped, bare NWs. These values are much higher than the ones previously reported. It has previously been shown that the plasmon resonance in a particular material is directly proportional to the square root of the photoexcited charge carrier density. Figures 5.5, 5.6, and 5.7 plot the simulations and show how the plasmon resonance behaves with NW length, the photoexcited carrier density, and charge carrier mobility for GaAs (InP also showed similar plots and for the purpose of brevity we will not show them here). For the purpose of this work, carrier densities around $1 \times 10^{17} \text{ cm}^{-3}$ will be considered for the simulations as the maximum photoexcited carrier density obtained from the experimental photoexcitation pulse energy density will give around that same value.

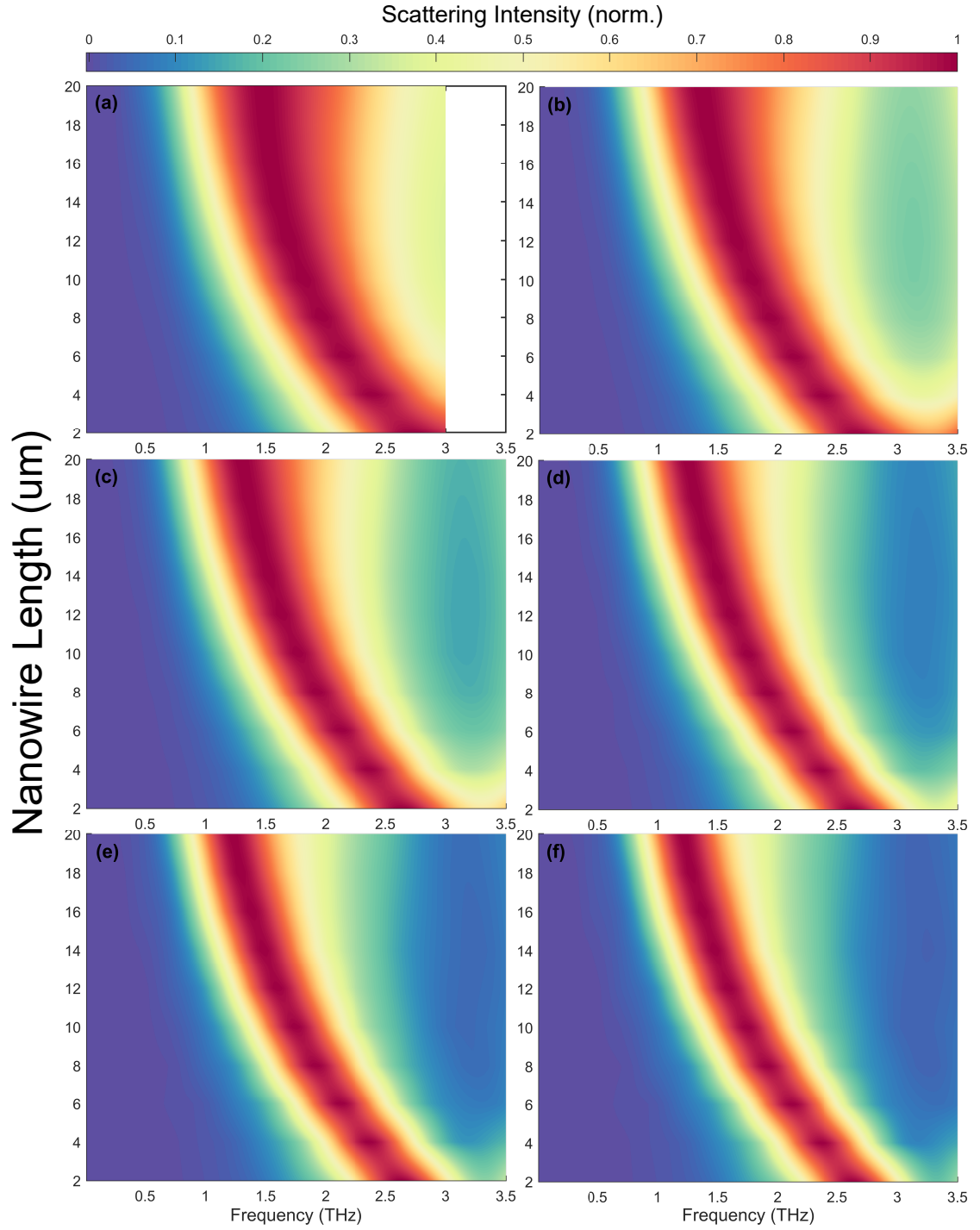


Figure 5.5: **Scattering Intensity vs. Nanowire Length:** Simulations illustrating the dependence of the plasmon resonance on the nanowire length ($2\ \mu\text{m} - 20\ \mu\text{m}$). Plots (a) - (e), all normalised, refer to mobilities equivalent to 3000, 3500, 4000, 4700, 5500, 6000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively. The resonance becomes more pronounced as the mobility increases.

In Figure 5.5, the mobility is varied while keeping the photoexcited carrier density constant, and in Figures 5.6 and 5.7, the photoexcited carrier density, N , is varied while keeping the mobility, μ , constant. As for the latter, the plasmon resonance frequency changes drastically with N and has a square root dependence as has been shown in previous works. [14,75] Most mobility values reported in other works have been in the range of $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ – $3000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. [14] The simulation data however did not show any resonances for values below $3000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ indicating the possibility that the models used in the past may not be accurate enough. One of the reasons why this could be the case is the introduction of the so-called g -factor which is the geometrical factor depending on the NW material, its geometry and the surrounding dielectric medium and has values between 0 and 1. g has a direct relation to the plasmon frequency: $\omega_0 = \sqrt{g}\omega_p$. Parkinson *et al.* [75] argues for only three distinct values: 0, 0.33, and 0.5. Fotev *et al.* extracted values around 0.23 and 0.93 for longitudinal and transverse modes. For the simulated results, this factor is dropped and clear resonance peaks are seen. However, the magnitude of the photoconductivity which is indicative of the scattering intensity did not match as a fitting.

5.3 Experimental Methods

The length-dependent plasmonic response of the NWs was assessed experimentally via an OPTP setup. The measurements were performed using an amplified Ti:Sapphire laser generating 35 fs pulses centred at 800 nm at a repetition rate of 5 kHz and 4 W average power as described in Chapter 3. Single-cycle picosecond THz transients, photoexcitation of the samples, and THz detection were achieved by splitting the main beam into three paths: the first beam generates THz pulses via a spintronic emitter (mechanism explained in Chapter 3 of this thesis), the second beam is used to photoexcite the sample and the third beam is used as an optical gate beam for free-space electro optic sampling using a $200 \mu\text{m}$ thick gallium phosphide (GaP) crystal (mechanism explained in Chapter 3 of this thesis). The energy density impinging on the sample was varied by using a neutral density filter wheel that allowed for photoexcitation at 100%, 75%, 50%, 25%, 10%, 5%, and 1% of the total energy (corresponding to 395, 296.25, 197.5, 98.75, 39.5, 19.75, and $3.95 \mu\text{J cm}^{-2}$). At the sample position, the optical pump beamwidth was ensured to be larger than the THz beam such that the area probed was uniformly photoexcited. The area of coverage of the sample was estimated to be around $3 \text{ mm} \times 3 \text{ mm}$. To maximise the signal-to-noise (SNR), an average of 5 scans were taken for each sample (boxcar average of 50000). The THz electric field, E , and the photoinduced change, ΔE were detected using a pair of balanced photodiode in a heterodyne fashion. Fluence-dependent photoconductivity

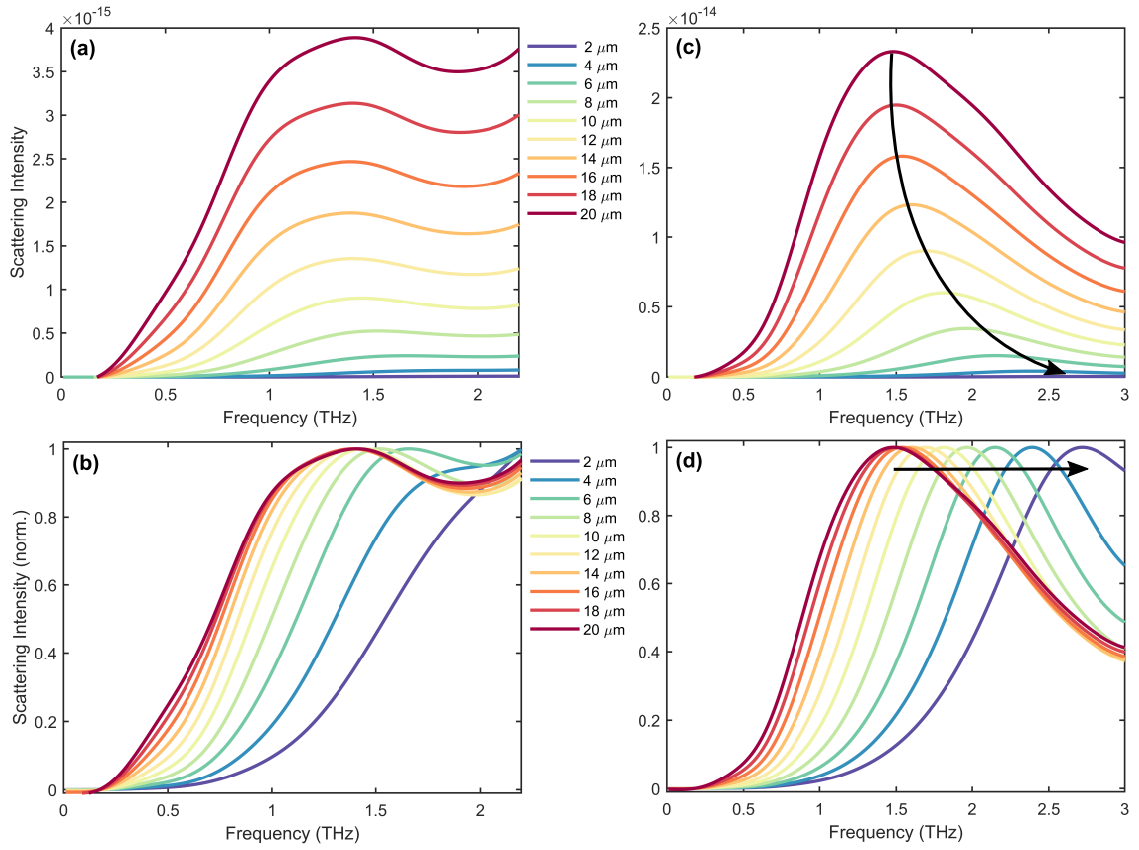


Figure 5.6: Effect of Photocarrier Density: Simulations illustrating the dependence of the plasmon resonance on the photoexcited carrier density. (a) and (c) show the carrier intensities for a charge density of $5 \times 10^{16} \text{ cm}^{-3}$ and $1 \times 10^{17} \text{ cm}^{-3}$ respectively and (b) and (d) are the corresponding plots but normalised. (a) and (c) show that as the length of the NW decreases, the scattering intensity decreases while (b) and (d) show the shift in plasmon resonance with nanowire length.

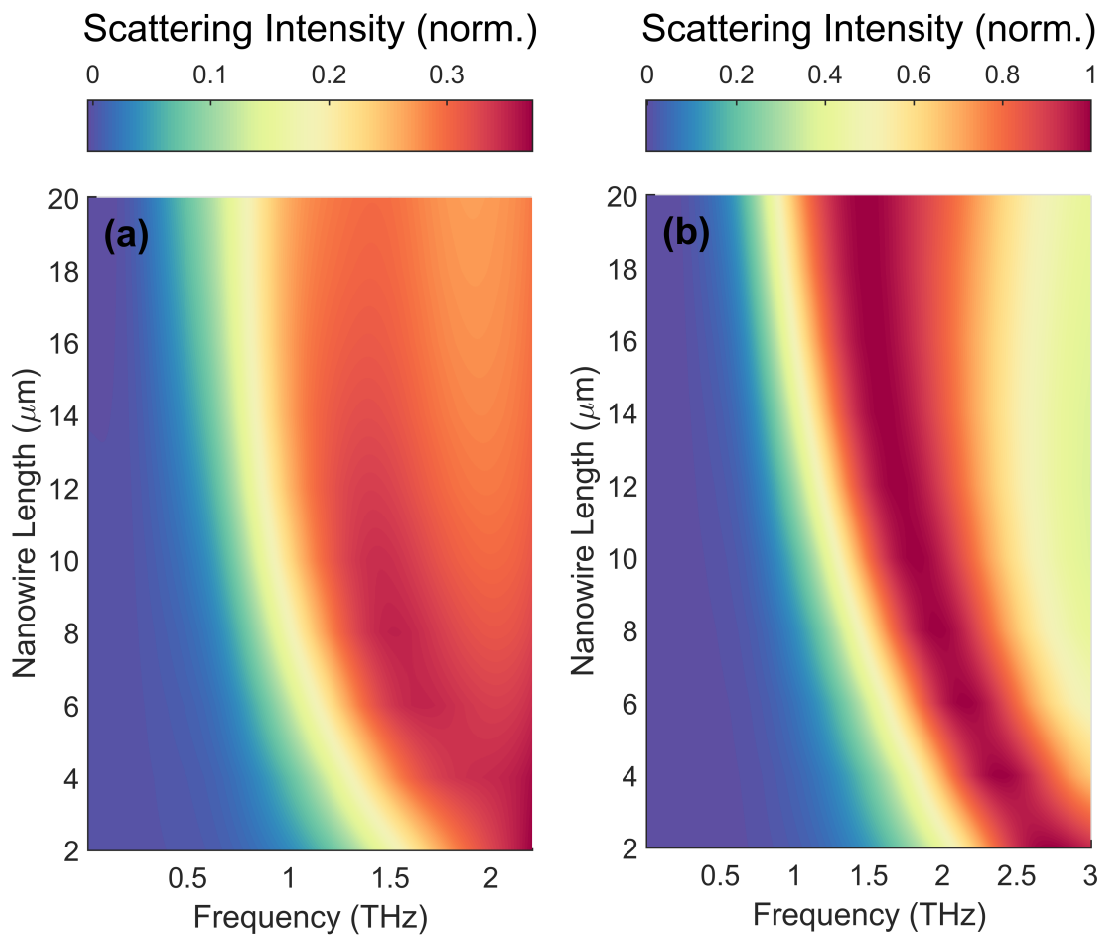


Figure 5.7: 3D Plots of the Photocarrier Density Dependence: Simulations illustrating the dependence of the plasmon resonance on the nanowire length ($2\ \mu\text{m} - 20\ \mu\text{m}$) as the photoexcited carrier density is changed.

decay and spectral scans were measured by varying the pump and THz stage positions accordingly. All the measurements were performed at room temperature under a vacuum ($\approx 1 \times 10^{-2}$ mbar) to minimise water vapour absorption by the THz pulses.

Spectral Scans & Photoconductivity Decay: For the spectral scans, the time delay of the THz transient probe pulse was varied while keeping the delay of the photoexcitation pulse fixed. The transmission of the electric field of the THz probe pulse through the NWs can then be measured in the time domain, $E(t)$, and then Fourier transformed to the frequency domain, $E(\omega)$. The electric field transmitted through the sample without photoexcitation (at equilibrium) is given by E_{off} . Upon photoexcitation, free charge carriers are pumped into the conduction band in the NWs and these carriers interact with the THz wave to reduce the transmission to E_{on} . The photoinduced change in THz transmission through the NWs is denoted by $\Delta E = E_{\text{on}} - E_{\text{off}}$. The value of $-\Delta E/E_{\text{off}}$ is then proportional to the photoinduced conductivity of the NWs and directly related to the photoexcited free carrier concentration. $t = 0$ ps is defined to be the pump-probe delay at which $-\Delta E/E_{\text{off}}$ is maximum, i.e. the peak photoconductivity. As for the photoconductivity spectra, the pump delay line was kept fixed and the THz delay line was scanned to obtain the change in THz transmission. Fabry-Perot reflections within the substrate were time-windowed out and the data then converted to photoconductivity.

5.4 Results & Discussion

Figure 5.8 shows the photoconductive decays of both the GaAs and InP. GaAs NWs have high surface recombination velocities due to the high density of surface states providing route for fast recombination and therefore the photocarriers decay within 1 picosecond. InP, on the other hand exhibited prolonged photoconductivity and a remarkably low electron trapping rate at surfaces, even without surface passivation. Of particular interest is the low mobility region in InP for early time scales. At the onset of the photoconductivity for high fluences, electrons are photoexcited into the additional side valleys which possess higher effective masses owing to the different curvature of the bands. Therefore, a low mobility is probed until all the excited electrons relax back into the valence band after which a monoexponential decay is recovered. At low fluences however, the first conduction band is not filled completely and therefore there is little scattering into the side valleys. A monoexponential behaviour is expected as shown in Figure 5.8. Figure 5.9 gives a visual explanation of this process by considering band structure diagrams.

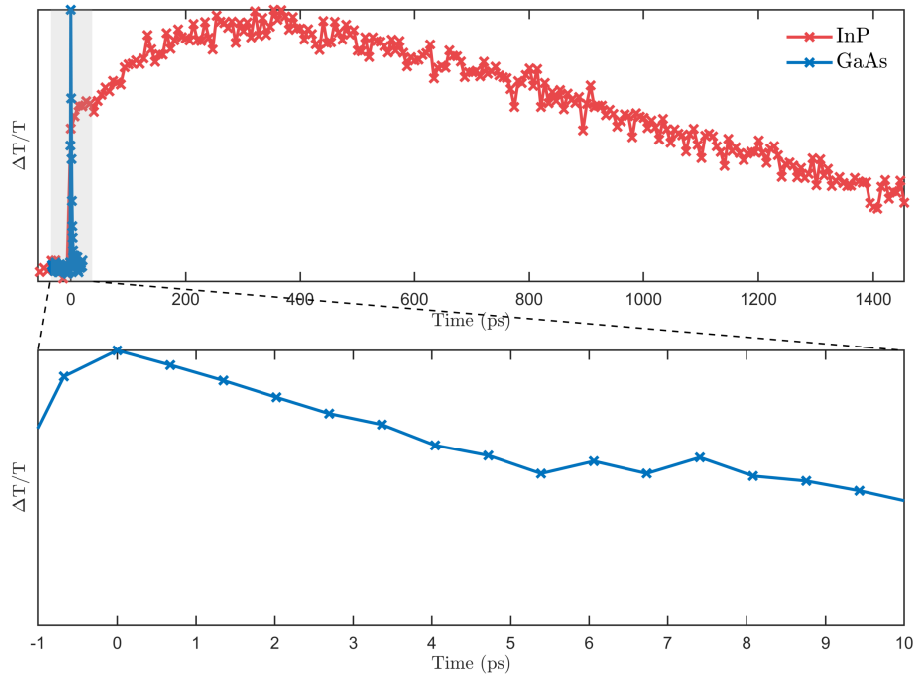


Figure 5.8: **Photoconductivity Decay for both the longest InP and GaAs:** Plots showing the photoconductivity decays for both material. The very fast decay for GaAs makes the top plot difficult to read on a very long time scale (logarithmic scale). The bottom plot is a zoomed in version for the first 20 ps showing the decay on a normal scale.

The photoconductivity spectra of the GaAs and InP taken at specific times: 0.5 ps after the onset of the photoconductivity for GaAs, and 667 ps after the onset of the photoconductivity for InP. Figures 5.11 and 5.12 shows photoconductivity spectra collected for both the GaAs and InP nanowires. The photoconductivity responses were obtained for various lengths of the NWs (2, 6, 8, and 12 μm for GaAs and 2.3, 4.9, 9, and 10.5 μm for InP) and at different photoexcitation fluences ranging from 4 $\mu\text{J cm}^{-2}$ to 395 $\mu\text{J cm}^{-2}$ (specifically at 1, 5, 10, 25, 50, 75, and 100% fluence). All the conductivity spectra feature a pronounced Lorentzian response. The resonance shifts to higher frequencies with increasing photoexcitation fluence, as indicated by the arrows in Figure 5.10. This fluence dependence is typical of localized surface plasmon modes, for which the resonant frequency depends on carrier density and, therefore, fluence. [75] This is consistent with previous work on GaAs nanowires, which also exhibit surface plasmon modes in the terahertz range. [14,29]

As for the length dependence shown in Figures 5.11 and 5.12, there is a clear shift of the plasmon resonance to higher frequencies as the NW length decreases. This is indicated by the crossing of the frequency axis of the imaginary part of the photoconductivity. The arrows show a clear trend. For the case of InP, the smallest NW shows a plasmonic resonance lower than the expected value. However the real part of the photoconductivity

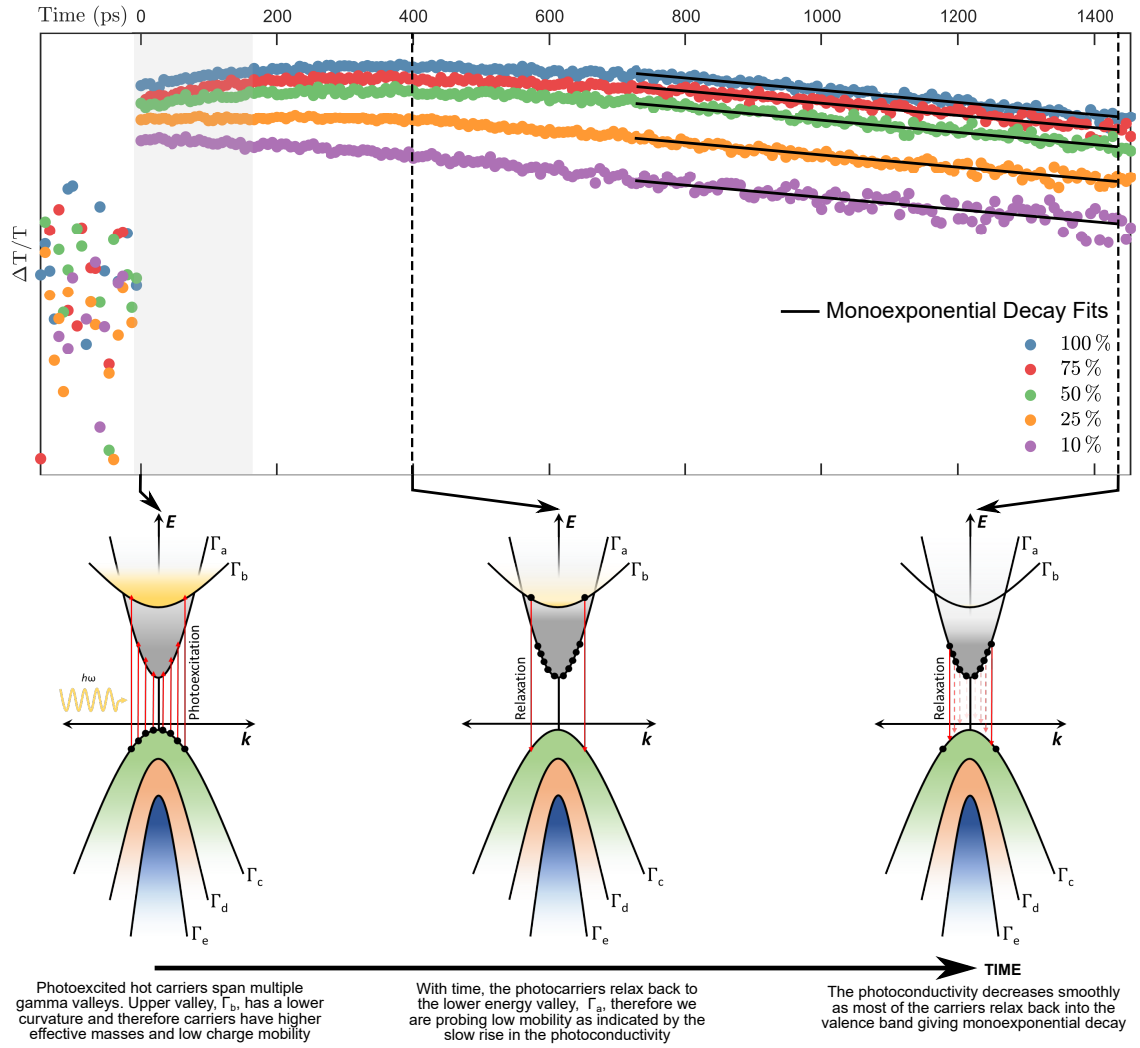


Figure 5.9: **Photoconductivity Decay for InP NWs:** A cartoon illustration depicting the reason why there is a slow photoconductivity rise at early times for high fluences.

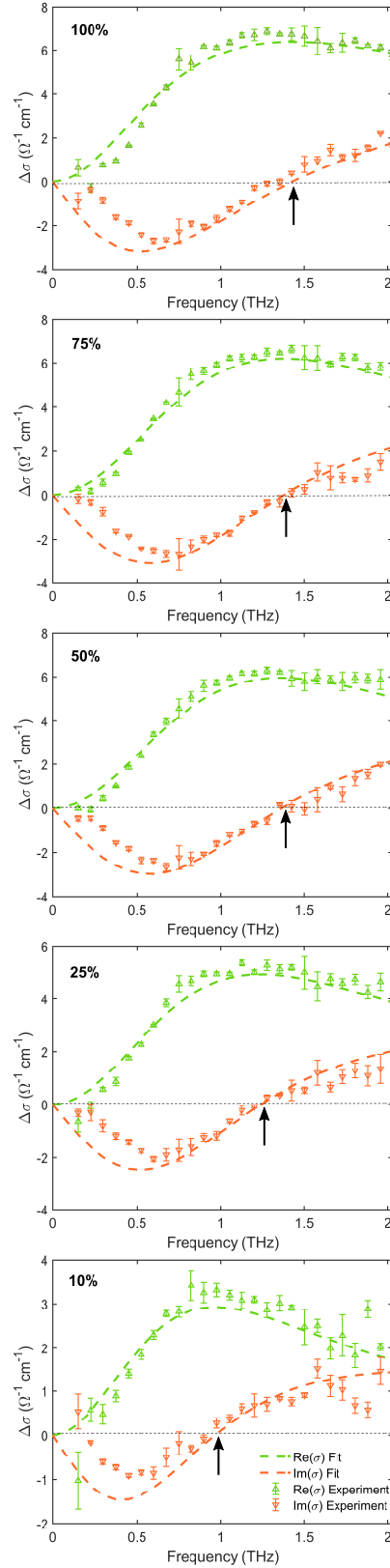


Figure 5.10: **InP Photoconductivity Spectra, Fluence-Dependence:** Plots showing the photoconductivity spectra of the InP NW (10 μm) at various fluences. We can see a clear increase in the plasmon resonance frequency with fluence indicative of the square root dependence as reported previously. [14,33,75]

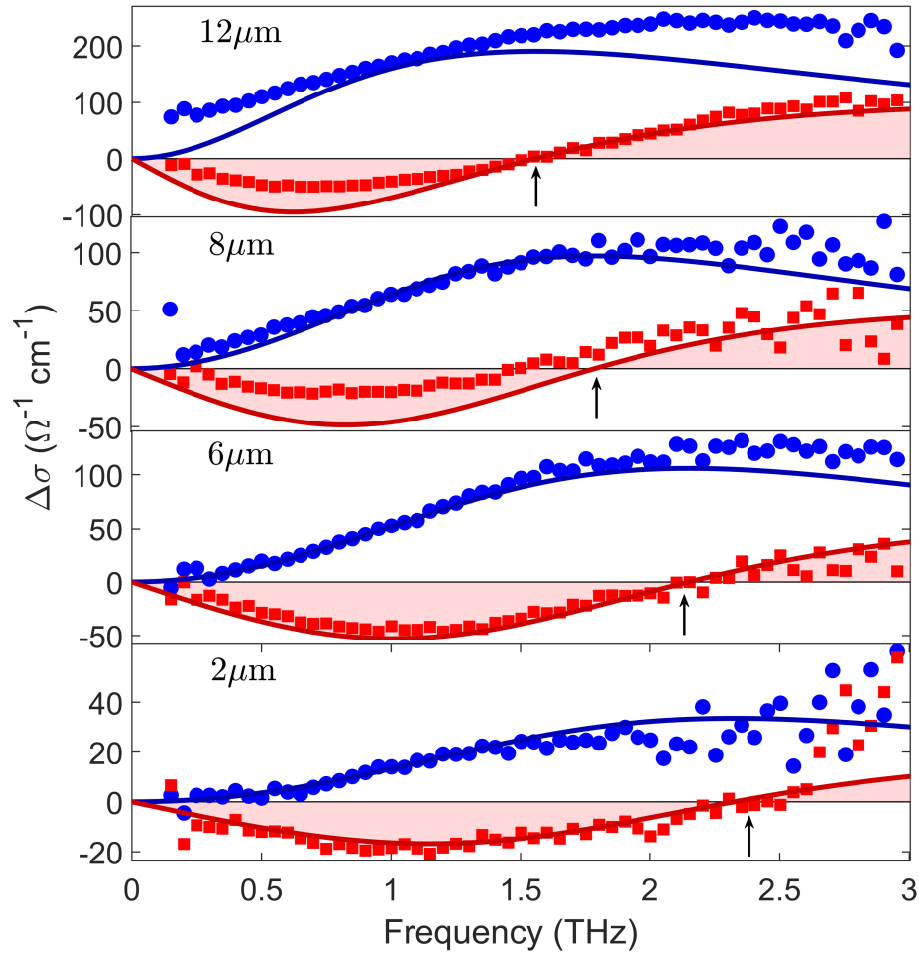


Figure 5.11: **Plasmon Resonance Dependence on NW Length for GaAs:** The above plots demonstrate photoconductivity spectra of the various lengths for the GaAs NWs. A clear dependence and shift is seen as we increase/decrease the length. This is also in good agreement with simulation models shown later in this chapter.

seems to be rising and has a peak beyond 2.5 THz. The imaginary part crosses earlier indicating the possibility that we are observing higher order modes. This can be attributed to the NW behaving not like a dipole but as a quadrupole. Further work is required to confirm this. Figure 5.13 collects both theoretical and experimental data.

5.5 Conclusion

In conclusion, the photoconductivity spectra of both GaAs and InP NWs displayed a strong plasmonic response. The plasma frequency showed an inverse relationship on the NW length which was as predicted via simulation. The theoretical model used was the Drude model for free carriers and in contrast to previous works, the geometrical factor was dropped. Resonance peaks were observed, however with charge carrier mobilities higher than previously reported. The relation between scattering intensity and the

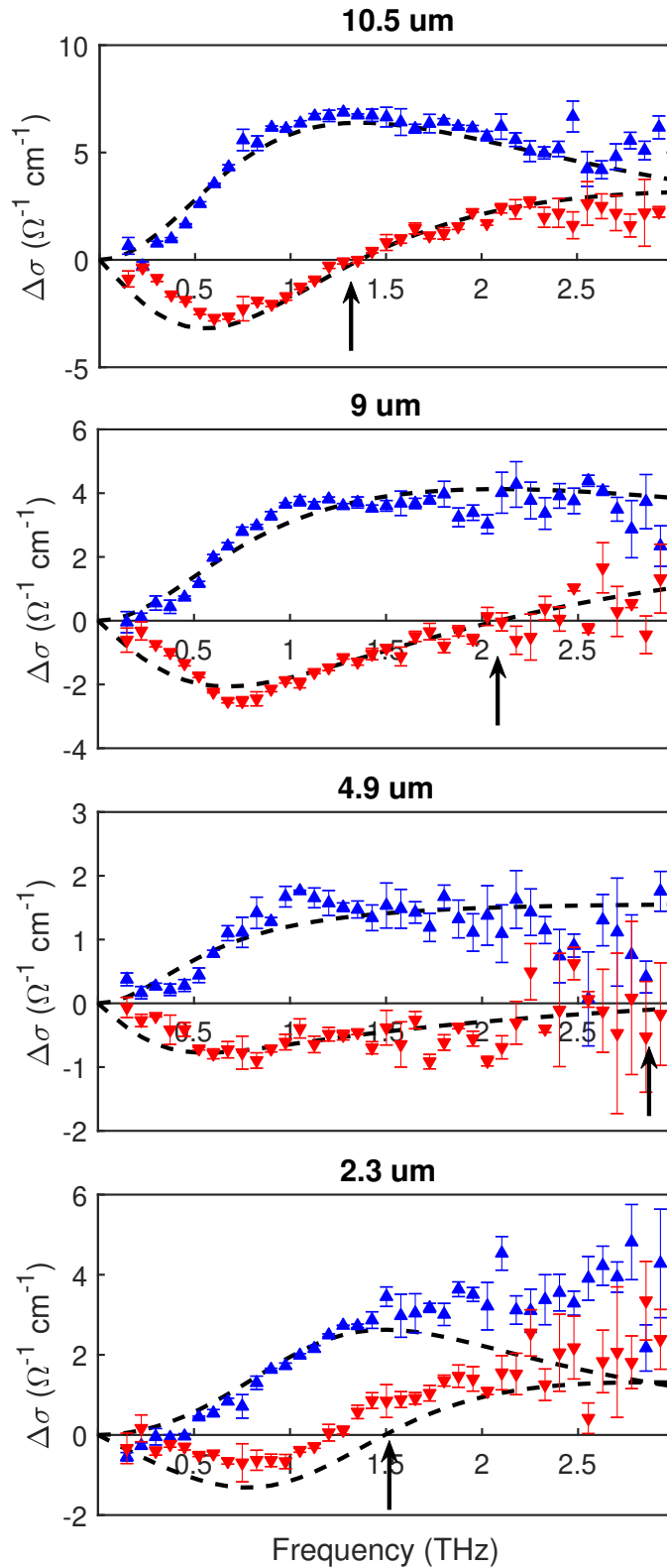


Figure 5.12: **Plasmon Resonance Dependence on NW Length for InP:** The above plots demonstrate photoconductivity spectra of the various lengths for the GaAs NWs. A clear dependence and shift is seen as we increase/decrease the length. As we reach the smallest length, the plasmon resonance for the first order mode is already beyond 3 THz. The second order resonance is therefore seen at much lower frequency even though the real part of the photoconductivity seem to still be rising with a maximum beyond 3 THz.

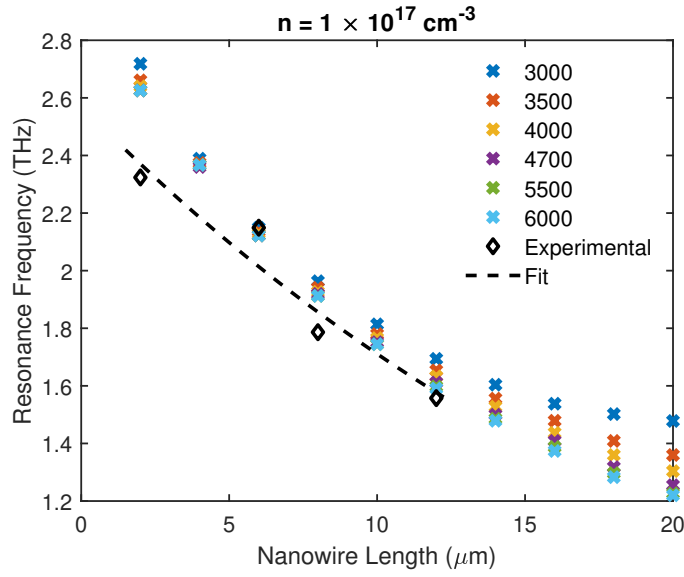


Figure 5.13: **Theory vs. Experiment:** Plot showing the resonance frequency with nanowire length for both theory and experiment. As for the theory, data were simulated for various mobilities with a photoexcitation density of $1 \times 10^{17} \text{ cm}^{-3}$. As the mobility is increased from $3000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $6000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ the trend shifts closer to the experimental data suggesting the possibility for the NWs having mobility values greater than or closer to $6000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

photoconductivity is still somehow unclear and more work has to be done to establish the correct relationship.

THz Polarisation Modulation using GaAs Semiconductor Nanowires

As terahertz technology progresses, THz modulators capable of high tunability of both intensity and phase are primordial for the effective control of THz light. Despite the recent advances in that field, there is still a lack of broadband devices able to achieve high modulation depth at fast switching speeds to integrate into high speed communication equipments. In this work, we will demonstrate two novel ultrafast THz modulators based on GaAs semiconductor nanowires operating at very high THz bandwidth. The modulator devices were fabricated using a highly flexible and cheap substrate – parylene-c. Through the use of multiple layers of this substrate, we show that for stacked layers, a deep modulation depth can be achieved without affecting the bandwidth over which the devices can operate. A terahertz air-plasma setup was built which allowed us to assess the devices over a broad range bandwidth of 0.1 THz – 40 THz.

6.1 Introduction

Lying between the infrared and microwave regions of the electromagnetic (EM) spectrum ($\approx 0.1 - \approx 40$ THz), THz radiation possesses a unique combination of desirable properties capable of non-invasive imaging and spectroscopy of materials. The generation of single-cycle pulses in the terahertz regime has enabled the resonant time-domain observation and control of fundamental low-energy excitations in condensed matter. Since its inception, THz radiation has found enormous applications in fields such as in biological and medical sciences, non-destructive evaluation, security, and ultrafast

computing. [328,329] One of the major bottleneck at the beginning was a lack of intense sources and detectors of THz radiation. [330,331]

However, over the past two decades, new advances in different technologies have made the previously unused terahertz (THz) frequency regime accessible and progress in this specific region of the electromagnetic spectrum has since undergone major development at a rapid pace. Significant research and effort went into building a plethora of THz sources and detectors in order to be able to integrate with state-of-the-art 21st century devices and techniques, [32,33,81,82,101,138,140,255,332–342] and yet ultrafast THz communication and imaging is still to be made possible due to a lack of compact and efficient THz phase and intensity modulators. In order to achieve this, active THz components that can directly manipulate and process THz radiation are essential.

Modulators are the most basic and yet the most important components of THz technology, which can modulate the transmission and also reflection of THz radiation. Much research has been done on THz modulators, mainly focusing on the material of choice and the various approaches to fabricate them. Depending on which property of light needs to be controlled, THz modulators can be categorized in primarily three forms: intensity modulation, [343,344] phase modulation, [345,346] and spatial position of the transmission and reflection coefficients of the THz electric field. [347,348] Much of the research that has been done in the past focused mainly on the modulation of THz intensity, with early demonstrations based on two-dimensional electron-gas (2DEG) structures [349,350], birefringent liquid crystals, [351,352] and static THz polarizers. [353–356] Recently, THz modulation has also been realised with metamaterials, [144,343,345,347,355,357–360] optical cavities, [361,362] and carbon nanotubes, (CNTs) [346,363,364] each with their own merits and weaknesses.

Graphene is another contender material for THz modulators. It is an ideal material for nanoscale photoelectronic devices due to its unique properties. [365–370] Graphene has been particularly attractive in the THz region because of its tunable conductivity, typically from comparatively high-resistance state to semi-metal state. [371–374] The first graphene THz modulator is demonstrated by Sensale-Rodriguez *et al.* demonstrated the first every graphene THz modulator with a modulation depth of 15% [375] operating on a wide bandwidth. Since then, improvements have been made in terms of the geometry and structures but these could not overcome the above-mentioned problems. Therefore, there is still a lack of an effective fundamental approach to achieving a broadband device with deep and wideband modulation range.

Group IV materials, such as silicon and germanium, have been used for THz modulators albeit with very poor performance with the modulation depth being quite low. Since

then, many new materials have been proposed with particular emphasis on metamaterials. High-speed THz modulators can be realized by combining metamaterial with semiconductors. However, the bandwidth of such modulators is still very narrow due to the fixed structure and the fabrication process is quite complicated. Despite these difficulties, metamaterial-based THz modulators have been presented which achieved high modulation depths, with Karl *et al.* in 2014, [376] demonstrating a dynamic range of over 20 dB and Chen *et al.* showing a modulation depth of $\sim 50\%$. [144] Nonetheless, the low bandwidth issue is still present, with the device operating at a designed wavelength, while also currently being limited to switching speeds with microsecond temporal resolution. On the other hand, gallium arsenide (GaAs) nanowires have been shown to possess a very short carrier lifetime on the order of a few picoseconds which will be very useful for fast switching speeds in devices.

THz amplitude modulators based on Fabry-Perot semiconductor cavity designs have also been demonstrated, with a modulation depth of $\sim 90\%$, yet only microsecond switching speeds. [362] Graphene-based modulators have also been shown with an improvement in switching speeds, through the utilisation of intraband absorption to obtain a modulation depth of $\sim 16\%$ and nanosecond modulation time. [375] In 2009, Ren *et al.* [363] fabricated static CNT THz polarizers by depositing aligned nanotubes onto a sapphire substrate featuring an extinction ratio of 10 dB in the optical and THz range, whereas in 2011, Kyoung *et al.* [364] demonstrated an extinction ratio of 37 dB by using a CNT stack fabricated from aligned nanotube arrays to produce static THz polarizers. However, in order to realise ultrafast THz communication, modulation times on the order of picoseconds are required. CNT-polymer based modulators can offer such high switching speeds. An ultrafast switchable CNT THz polarizer, demonstrated by Docherty *et al.* in 2014, [346] which could be optically controlled and was capable of polarization and intensity modulation of THz radiation with a time resolution on the order of 1 ps, although it suffered from a low modulation depth of around -27 dB.

Zephen *et al.* from the MacPherson group [377] recently demonstrated a graphene-based modulator with an impressive modulation depth of 99% while Burdanova *et al.* went on to show a modulation depth of 60% for pristine single-walled carbon nanotubes. [378] These results show that research in THz modulators are still ongoing although significant improvement is needed. Thus, there is still a need for the development of a practical THz modulator with a high modulation depths. Fast picosecond and sub-picosecond switching speeds are highly desired as we move into a world of THz technology, and modulators which can be electrically or optically controlled, and can be easily integrated into current Si-based technology are on high demand.

Previous Work: Earlier on in 2016, we presented the first THz intensity and polarization modulator based on III–V semiconductor nanowires (NWs) that was capable of both picosecond switching speeds and a reasonably high modulation depth of around 15%. [76] Semiconductor nanowires have attracted a great deal of attention for applications in THz technology. Their quasi-1D structure renders them particularly special as they feature unique optoelectronic properties. Their high electron mobilities ($\approx 1000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) and their ability to be integrated with silicon-based devices [379] have made them apt for technological applications.

In particular, GaAs NWs were chosen as the material of choice for THz modulation, as they possess a direct bandgap, high absorption coefficient at terahertz frequencies, and tunable optoelectronic properties, such as carrier lifetimes and mobility via doping. [14,33] Additionally, the NWs possess high anisotropic THz absorption along their axis and the way to render them active is via photoexcitation above bandgap. Once conductive, THz radiation polarized parallel to the long axis of the NW will be absorbed, thus reducing the THz transmission [31]. As such, they can offer a practical, cost-effective alternative to other THz modulation techniques, while providing a system that can not only modulate the intensity of the THz radiation but also the polarization, allowing for an increase in information that can be encoded on the THz wave and the realization of high-speed THz communication.

In this chapter, we go on to assess the modulator devices over a broad bandwidth for the THz transmission between 0.1 THz and 40 THz. To achieve this exceptionally large bandwidth, we designed a state-of-the-art terahertz air-plasma generation in an optical-pump terahertz-probe (OPTP) setup with an ultrathin, $20\text{ }\mu\text{m}$, zinc telluride (ZnTe) electro-optic crystal at the detection. The THz NW polarisers were fabricated in the Joyce group at Cambridge University from highly aligned GaAs NWs embedded in a parylene-*c* membrane and their optoelectronic properties characterised via OPTP spectroscopy. A photoconductivity lifetime of approximately 1 ps was extracted for the devices allowing for sub-picosecond switching speeds, even faster than those demonstrated by carbon nanotube (CNT) polarizers. [346] A photoinduced change in THz transmission of around 50% was observed for the champion device. which was a significant improvement on the previous devices. Furthermore, we went on to show that this modulation depth was achieved for up to 40 THz enabling a large bandwidth for THz modulation that exceeds values previously seen for other THz modulators. THz modulation is demonstrated by changing the polarization of photoexcitation of the NWs and through laminating several layers together, the modulation depth can be varied.

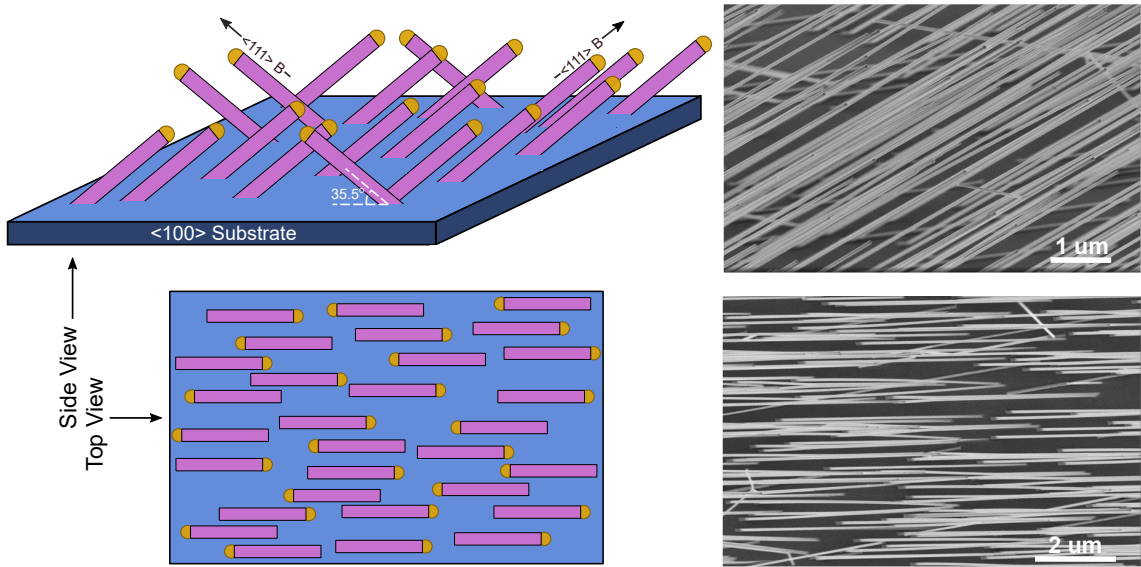


Figure 6.1: **GaAs Nanowires:** Cartoon illustration and SEM images of the GaAs as grown via MOCVD. The SEM images show the NWs poking up the $\langle 100 \rangle$ substrate surface at an angle of 35.5° . If we project this onto the $\langle 100 \rangle$ plane (top view image), we most of the NWs are lying down parallel to one another. Unfortunately, the growth technique is not perfect and occasional stray NWs will grow as is depicted in the SEM image.

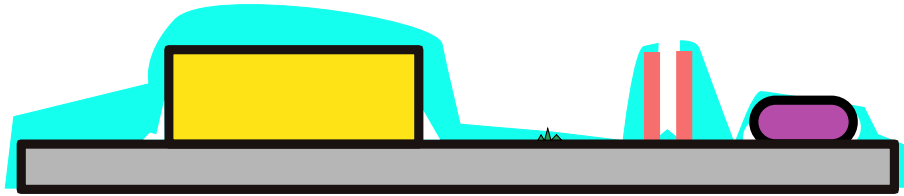
We also fabricated and tested a novel device based on a wire-grid conformation comprising of an epitaxial GaAs layer which was patterned into a grid using electron beam lithography. This device was fabricated at the Australian National University. Although the photocarrier lifetime was increased by a factor of 10, which meant that we are still getting sub-picosecond temporal resolution, his device showed an impressive 50% modulation depth as well. These results are very promising for future use in THz technological devices with efficiency and switching speeds comparable to those achieved by graphene-based THz modulators and outperforming those seen for optically-activated CNT THz polarizers.

6.2 Device Fabrication

GaAs Stacked Layer: Unpassivated and undoped GaAs NWs were selected as the active modulating elements due to their properties of a high anisotropic THz conductivity when photoexcited coupled with a short photoconductivity lifetime of less than 5 ps. These properties together should enable strong modulation of THz transmission on ultrafast timescales. [14,89]

High-density arrays of GaAs NWs of diameter 50 nm were grown via Au-seeded MOCVD in $\langle 111 \rangle B$ directions at an angle of 35.3° to the GaAs $\langle 100 \rangle$ substrate. Figure 6.1 shows both a plan-view and top-view cartoon schematic and scanning electron microscope

CONVENTIONAL LIQUID COATING



PARYLENE COATING



Figure 6.2: **Parylene Coating:** Schematic showing the difference between conventional liquid coating and parylene coating. Parylene is highly conformal. Unlike the former method, parylene is not applied but it basically “grows” onto the surface it is protecting. The coatings are applied in a vacuum chamber via a vapor deposition polymerization (VDP) process and adds virtually no weight to the device/sample.

(SEM) image of the GaAs NWs grown on these substrates. Although the NWs were grown on a $\langle 100 \rangle$ GaAs substrate, the NWs grow at an angle in the $\langle 111 \rangle$ B direction. This is advantageous to us as will be mentioned shortly when making the devices. Furthermore, it can be seen that the NWs are highly directional and are well-aligned with respect to each other. There are however a few stray ones due to the non-perfect growth conditions and techniques. The density of these stray NWs are too small to contribute any significant effect on the polariser devices. The NWs were grown via a two-temperature process that gives high uniformity in NW diameter, a twin-free zinc-blende structure and high charge carrier mobilities. [25,89]

Parylene Conformal Coatings: Parylene-c polymer coating is an ultra thin film that is uniform, stable, elastic and hydrophobic. It provides an alternative route that is significantly better and more efficient than conventional coatings. Being highly conformal in nature, parylene-c provides a consistent pin-hole free barrier that is able to coat evenly all types of surfaces reaching deep into crevices and round sharp edges as illustrated in Figure 6.2. This is due to its ability to effectively grow on the surface compared to other types of coatings. Moreover, parylene-c is transparent in the terahertz range and has been shown to have minimal absorption. [76] Its flexibility has enabled it to be widely used across all fields, from metals to electronics to plastics.

For experiments at terahertz frequencies, z-cut quartz is usually the substrate of choice as it has negligible dielectric response. [256] Additionally, quartz is highly resistant to

damage and has a near-constant complex refractive index over a range of 0.1 THz to 4 THz. However, as THz technology progresses, we are in dire need of devices that are flexible, cheap to manufacture, and robust. Parylene-*c* was the ideal route for making our devices.

The polymer-coating which was part of the device fabrication was also done in the Joyce group at the University of Cambridge where parylene-*c* was deposited onto the GaAs substrates having the grown NWs onto them using the Gorham process. [76] This is a low-pressure chemical vapour deposition process done at high temperatures where dichloro[2,2]-paracyclophane dimer was used as a precursor molecule. This dimer undergoes sublimation at around 130°C and pyrolysis at 650°C before subsequently condensing and polymerising at room temperature onto the substrate.

A step-by-step fabrication process is outlined as follows:

1. 8.6 μm of Parylene-*c* is deposited onto the nanowire samples. The parylene thickness is chosen to be 8.6 μm because the nanowire ‘vertical angle height’ ranges from 4-7 μm and we wanted to make sure that the nanowires are fully buried underneath the parylene(Parylene Coater: SCS PDS-2010);
2. Afterwards, the parylene-coated samples are divided into the desired dimension of 4x6mm, which is the minimum dimension for the terahertz characterization, using a razor blade. Note: we simply used the razor to slice the parylene layer into the dimensions we want; the underlying substrate is unharmed;
3. Next, the divided sheets of parylene are mechanically removed (peeled-off) from the substrate. This is achieved by first scratching the thin layer of parylene at the sides/edges of the samples with a razor blade and then followed by peeling the thin sheet of parylene (with nanowires embedded) from the substrate using the tweezer. The final devices will be used to test for polarisation modulation of THz radiation and therefore, it is very important to keep track of the sheet orientation;
4. The peeled-off sheets of parylene with embedded nanowires are then stacked on top of each other while maintaining similar orientations of each layers. The parylene sheets are stacked as 1, 2, 4, 8, 16, and 32 layers;
5. The stacked parylene layers are then laminated at the temperature of 130°C and pressure of 20 Bar for 300 seconds using the nanoimprinter (OBDUCAT NIL-25 Nanoimprinter). This will eliminate the air gaps in between the layers and make sure that the layers do not fall off;

6. Next, 5 μm of parylene-C is coated onto the quartz substrate. The stacked nanowire-parylene layers are to be mounted onto these quartz substrates for support;
7. The stacked nanowire-parylene layers are then laminated onto the prepared parylene-coated quartz substrate at temperature of 130°C and pressure of 10 for 300 seconds.

The highly conformal nature of the parylene C coating ensures the voids between the NWs are filled, hence providing excellent encapsulation for the NWs. Parylene C is also robust, flexible, simple to manufacture, and highly transparent to THz radiation with a low THz refractive index of 1.6, making parylene particularly suitable as a host medium for the photoconductive GaAs NWs.

In order to increase modulation depth, multiple layer samples were created to increase the effective areal NW density and therefore increase THz absorption. The thin film layers of NWs-in-parylene C were laminated together whilst preserving the alignment of the NWs. The layers were subsequently hot-bonded together as mentioned above.

GaAs Wire Grid Polariser: The GaAs thin films were grown using metallo-organic chemical vapor deposition (MOCVD) and epitaxial lift-off (ELO). In ELO, AlInP was used as the sacrificial layer and it was removed with HCl. The thin films were transferred to methanol and collected with a quartz disc, on which the film was bonded. The polarizer structure was patterned by electron beam lithography (EBL), using PMMA as the resist and MIBK as the developer. After EBL, the structure was immersed in $\text{H}_3\text{PO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O}$ 3:1:25 solution for 1 min to etch the exposed area of the GaAs film.

6.3 Experimental Methods

The broadband THz modulation depth and switching speeds of the devices were assessed via an OPTP setup as described in chapter 4. The measurements were performed using an amplified Ti:Sapphire laser generating 35 fs pulses centred at 800 nm at a repetition rate of 5 kHz and 8 W average power. Although 8 W is the power of the laser, only 3 W have been used for this setup. Single-cycle picosecond THz transients, photoexcitation of the devices, and THz detection were achieved by splitting the main beam into three paths: (i) 0.43 mJ/pulse was used to generate THz probe pulses in a gas-plasma by combining the fundamental (800 nm) with its second harmonic (400 nm) after conversion using a 100 μm beta-barium borate (BBO) crystal, (ii) 0.03 mJ/pulse was used as the optical gate for electro-optic detection of the transmitted THz pulse using a 20 μm ZnTe crystal, and (iii) 0.143 mJ/pulse was used as the optical pump to photoexcite the sample. The energy density impinging on the sample was varied by using a neutral density filter wheel that

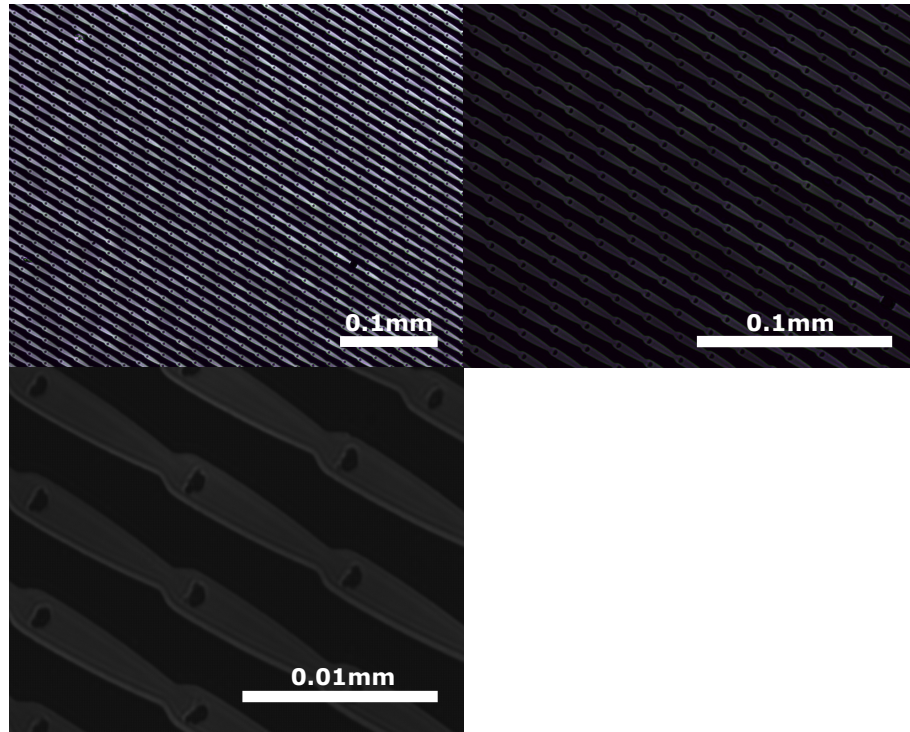


Figure 6.3: **GaAs Wire Grid Polariser:** Optical microscope image of the wiregrid polariser at different magnifications. The spacing between the nanowire columns is 0.01 mm.

allowed for photoexcitation at 100%, 75%, 50%, 25%, 10%, 5%, and 1% of the total energy. At the sample position, the optical pump beamwidth was ensured to be larger than the THz beam such that the area probed was uniformly photoexcited. The THz electric field, E , and the photoinduced change, ΔE were detected using a pair of balanced photodiode in a heterodyne fashion. Spectral scans, photoconductivity decay scans and modulation scans were measured by varying stage positions accordingly. All the measurements were performed at room temperature under a dry nitrogen-purged atmosphere to minimise water vapor absorption by the THz pulses.

By varying the THz delay stage while keeping the pump delay fixed, the transmission of the electric field of the THz probe pulse through the NWs can then be measured in the time domain, $E(t)$, and then Fourier transformed to the frequency domain, $E(\omega)$. The electric field transmitted through the sample without photoexcitation (at equilibrium) is given by E_{off} . Upon photoexcitation, free charge carriers are pumped into the conduction band in the NWs and these carriers interact with the THz wave to reduce the transmission to E_{on} . The photoinduced change in THz transmission through the NWs is denoted by $\Delta E = E_{\text{on}} - E_{\text{off}}$. The value of $-\Delta E/E_{\text{off}}$ is then proportional to the photoinduced conductivity of the NWs and directly related to the photoexcited free carrier concentration. $t = 0\text{ps}$ is defined to be the pump-probe delay at which $-\Delta E/E_{\text{off}}$ is maximum, i.e. the

peak photoconductivity.

In this OPTP system, there are two ways of achieving the polarization modulation of the THz radiation: (i) the polarization of the photoexcitation beam is selected via a halfwave plate (HWP) or (ii) the device is mounted onto a rotation stage whilst the polarization of the photoexcitation beam is kept fixed. This is depicted schematically in Figure 6.4. Two cases are shown with θ denoting the angle of the wave plate, $\theta = 0^\circ$ and $\theta = 45^\circ$. A rotation of θ for a HWP induces a polarization change of the optical pump beam by an angle of 2θ . Thus, by rotating the HWP by 45° , the optical pump beam was rotated from vertical polarization to horizontal polarization with respect to the NW long axis. A full 360° scan was achieved by varying θ from 0 to 180. The devices were placed in an orientation corresponding to a maximum photoinduced change, i.e. the case for the photoexcitation pulse being parallel to the NW axis.

6.4 Results & Discussion

Nanowires have high anisotropic THz absorption along their long axis in the conductive state. Therefore we investigated how the rotation of the NWs can modulate the THz intensity. The NWs are oriented vertically and the incident THz electric field is also vertically polarized. The THz polarization is established by having the magnetic field vector through the spintronic emitter in the horizontal direction as explained in Chapter 2. A HWP ensures the rotation of the polarization state of the 800 nm photoexcitation pump beam by 2θ , where θ is the angle between the vertical and the waveplate axis. As such, when $2\theta = 0^\circ$, the NWs are aligned with the polarization of the pump beam, so are photoexcited and rendered conductive through the filling of the conduction band, leading to maximum THz absorption. When $2\theta = 90^\circ$, the polarization of the pump beam is flipped by 90° and the NWs are orthogonal to the polarization of the pump beam. The incident pump pulse does not photoexcite the NWs effectively and consequently leads to minimum THz absorption.

THz transmission, $E_{\text{on}}/E_{\text{off}}$, through a photoexcited single-layer NW polariser as a function of polarization angle (2θ) of the photoexcitation pulse. Photoexcitation was performed with pump fluences at 5.98, 29.88, 59.76, 149.4, 298.8, 448.2, 597.6 $\mu\text{J cm}^{-2}$ (corresponding to 1, 5, 10, 25, 50, 75, and 100% fluence) and data in (b) were measured with the pump-probe delay at $t = 0$ ps at which $-\Delta E/E_{\text{off}}$ is maximum. Malus's cosine squared law was fitted to the data and showed very good agreement as previously demonstrated. The experiment was repeated for the 8 layered device, 16 layered device and 32 layered device and the modulation depth for all of them are shown below.

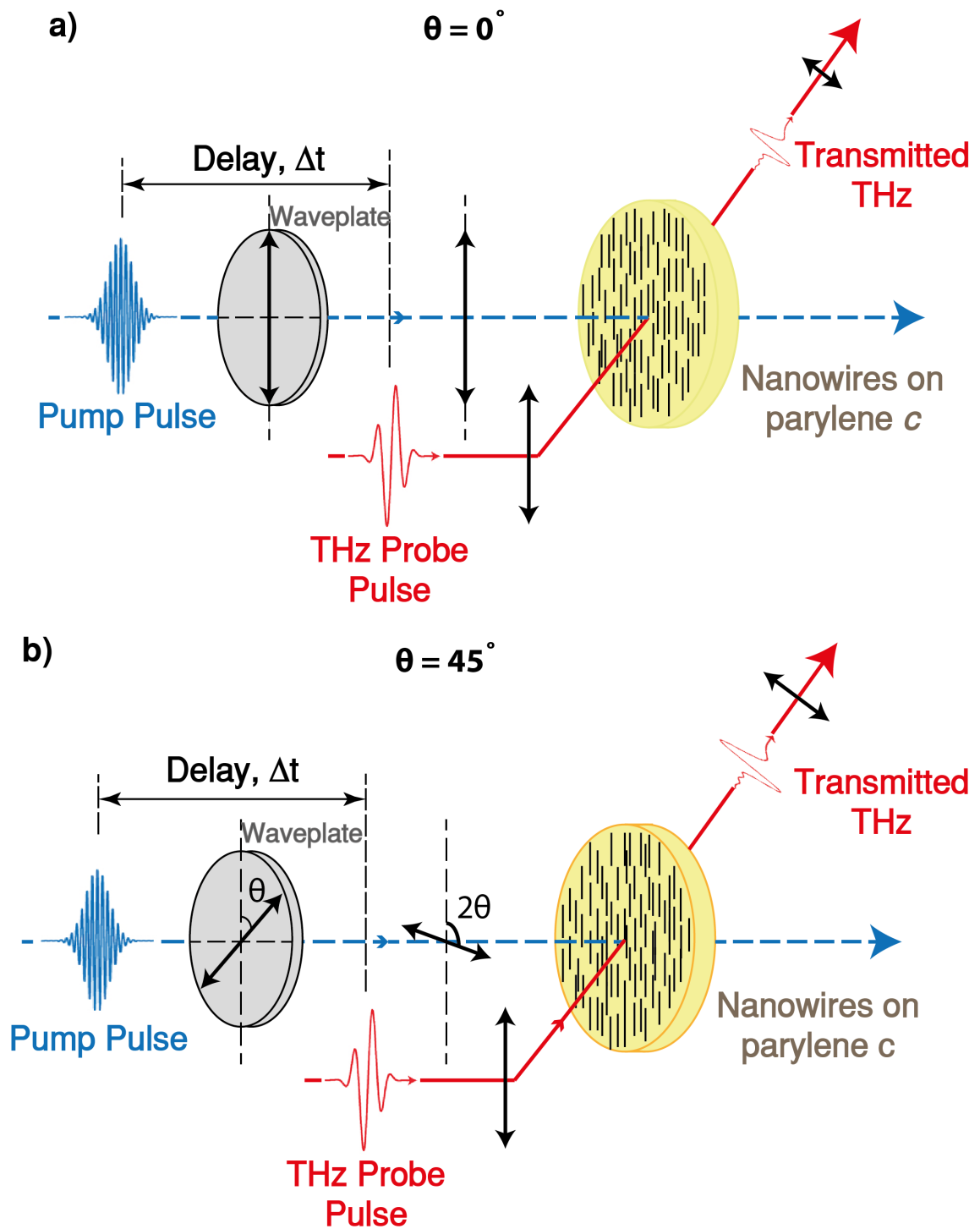


Figure 6.4: **THz Modulation Experiment:** Schematic diagram showing how the experiment was performed.

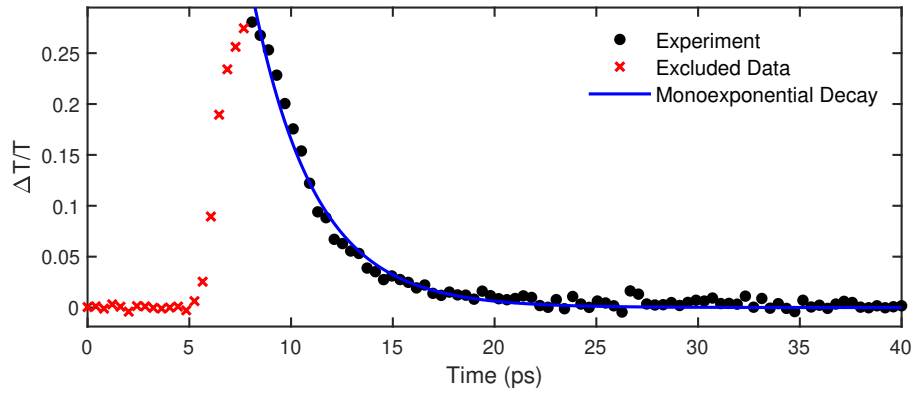


Figure 6.5: **Photoconductive Decay:** Plot of the photoconductive decay of the 16 layer device with the pump pulse polarized parallel to the NWs. A monoexponential decay was fitted to the experimental data and a lifetime of ≈ 3 ps was extracted. This indicates that the parylene coating did not introduce any effects for carrier-carrier recombination paths and is an ideal substrate for this device.

Characterization of the Devices: As mentioned earlier, the inherent geometry of semi-conducting NWs allows them to modulate the THz radiation. By photoexciting charge carriers with light polarized parallel and perpendicular to the NW long axis, maximum and minimum modulation depths are achieved respectively. This is mainly due to the dielectric mismatch between the NW and the parylene-*c* medium that enables the parallel and perpendicular components of the electric field to penetrate or being suppressed. Additionally, NWs exhibit strong THz absorption along their long axis. Surface plasmon modes (SPM) at terahertz frequencies ($0.1 < \text{SPM}(\omega) < 4$ THz) propagate longitudinally along the NW axis and are responsible for the signature plasmonic absorption. Therefore, throughout all the experiments, THz polarization along the NW long axis is maintained.

We start by characterizing the photoconductivity response of the devices by photoexciting the devices in two main directions: parallel and perpendicular. Figures 6.5 and 6.6 show the photoconductive decay response and the time-domain THz waveforms of the devices. The monoexponential decay fit within the first few picoseconds gives a lifetime of around 3.3 ps which is consistent with our previous work for which a 14 layer sample gave a lifetime of around 3.5 ps. It is clear that the embedded NWs show no significant deviation from the lifetime of normal unpassivated GaAs NW ensembles which suggests that the parylene coating is perfect for such devices where very fast switching speeds are sought.

Figure 6.6 shows how the polarization of the photoexcitation pulse, $2\theta = 0^\circ$ (parallel) and $2\theta = 90^\circ$ (perpendicular), affects the device. When $2\theta = 0^\circ$, the NWs are oriented along the polarization direction of both the THz and photoexcitation pulses. The device succumbs a large increase in photoconductivity as a maximum density of electron-hole plasma is formed. This leads to a maximum absorption of the THz and change in ΔT as

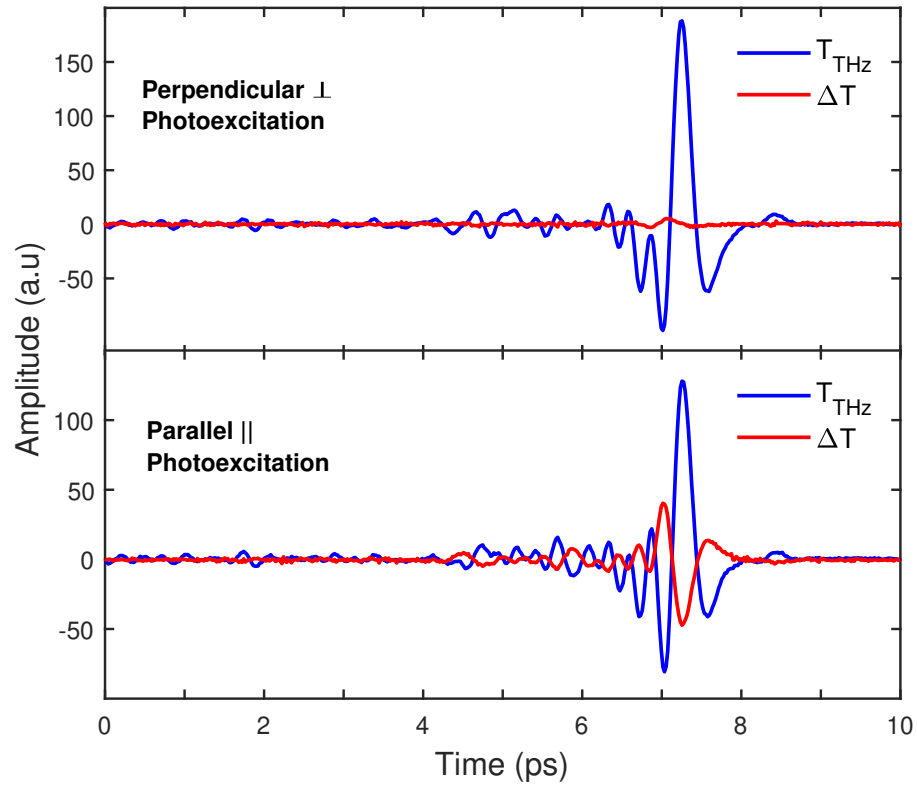


Figure 6.6: $\parallel$ and $\perp$ Photoexcitation: Plots of the THz intensities and change in THz intensities upon photoexcitation of the 16 layer device (champion device). The top plot shows the effect of photodoping the nanowires perpendicular to the NW long axis and the bottom plot parallel to the NW long axis. For the latter case, a high ΔT is observed while for the former case, minimum change is observed.

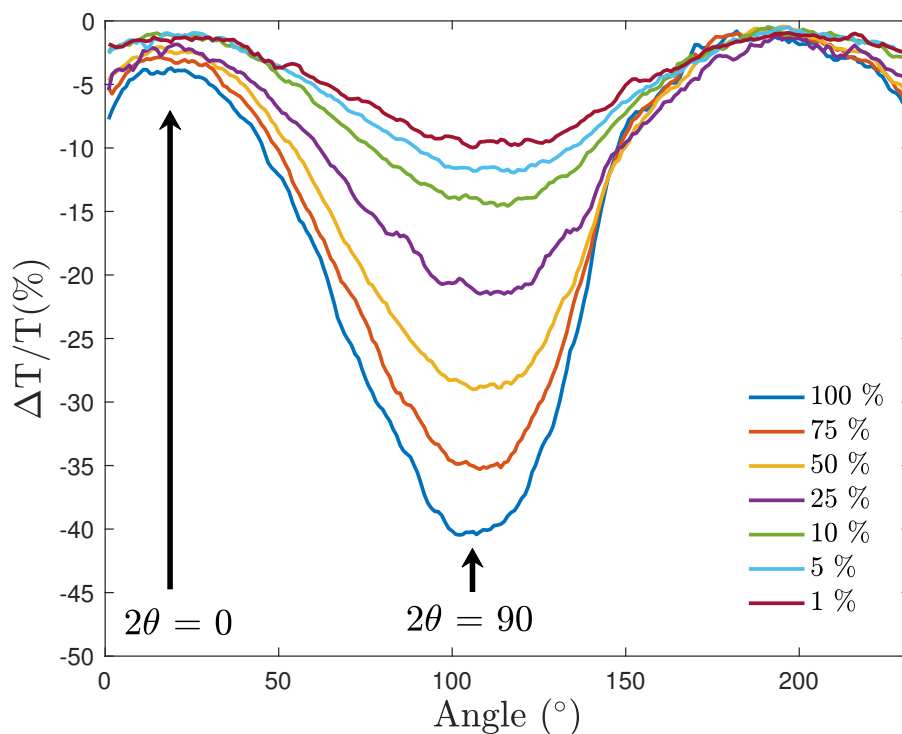


Figure 6.7: 16 Layer THz Modulation: The above plot showcases the THz transmission $\Delta T/T(\%)$ through the photoexcited device at 7 different fluences. The x -axis depicts the angle of the photoexcitation pulse polarization makes with the NW long axis. As the waveplate is rotated from $\theta = 0$ to $\theta = 45$, the polarization changed from 0 to 90. A maximum modulation depth of 40% is seen at the highest fluence. The asymmetry in the data is due to the device not being centred onto the substrate which made it difficult to achieve perfect modulation at all angles.

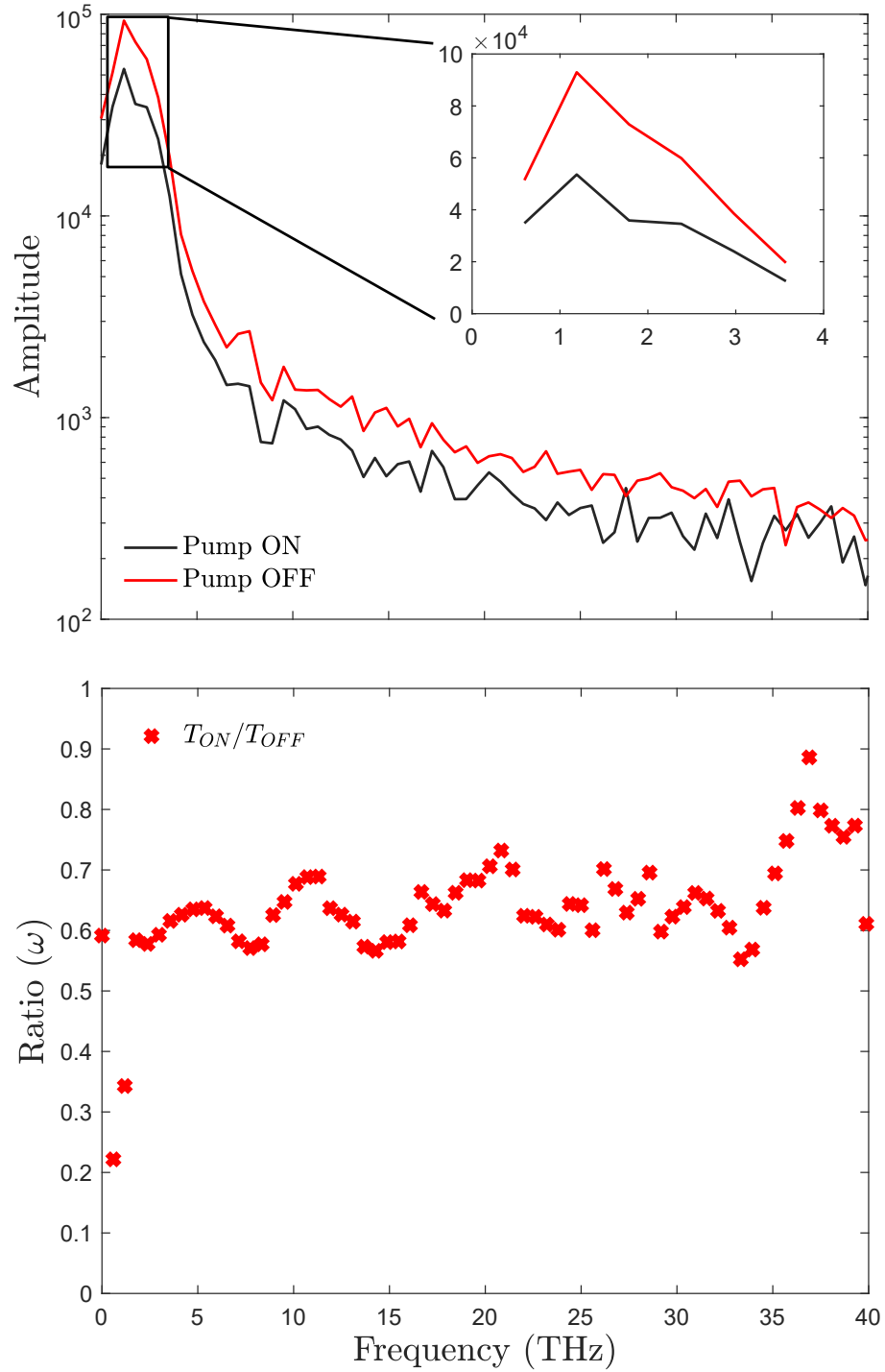


Figure 6.8: 16 Layer Spectrum Comparison and Ratio: Plots of the spectra for the 16 layered device illustrating the effect of photoexcitation at maximum fluence on the amplitude transmission spectrum. The top figure shows a downshift of the spectrum up to around 35 THz indicating that the device is active over this broad range. The bottom figure is a ratio of the 'Pump ON' to 'Pump OFF' which is nearly constant at 0.6 up to 35 THz.

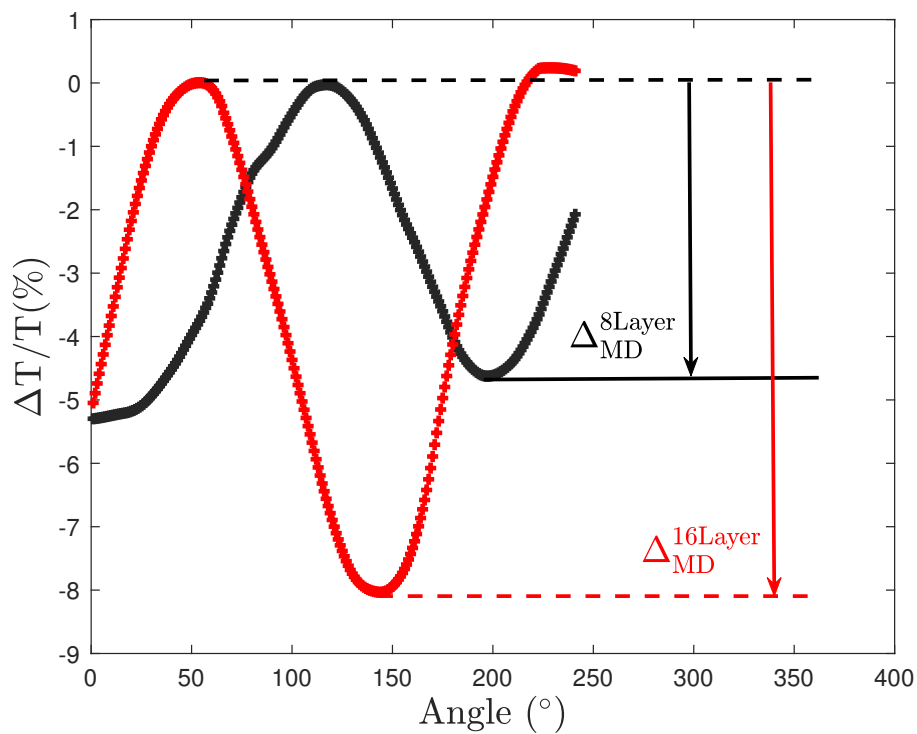


Figure 6.9: 16 and 8 Layer Device Modulation Depth Comparison: The plot shown illustrates the effect of stacking layers onto the device which was photoexcited at a fluence of 1%. It is evident that the 16 layer has a modulation depth of roughly twice that of the 8 layer sample. This is due to the fact that the NW density has increased by two-fold, therefore generating more photocarriers which will absorb a higher portion of the THz radiation.

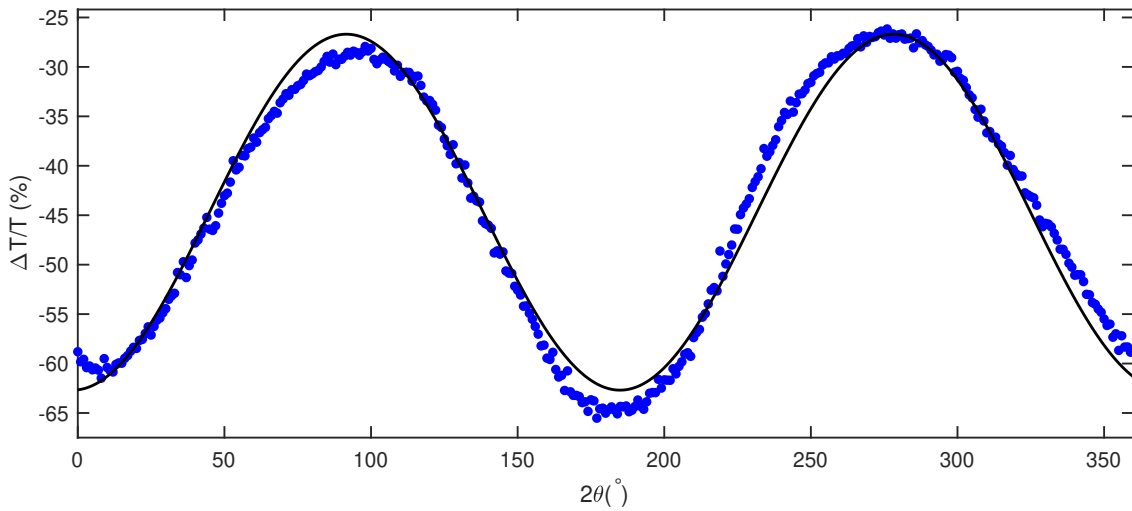


Figure 6.10: 32 Layer Device Modulation Depth: Plot showing the THz modulation of the 32 layered device at 100% fluence (597.6 J cm^{-2}). The maximum modulation depth achieved by this device is around 30% which is less than twice that of the 16 layered device and also lower. This decrease can be attributed to the fact that with a thick device, the transmission of the photoexcitation pulse becomes weaker and not all the layers are photoexcited resulting in lower charge carrier density and thus lower THz absorption.

indicated by the red curve. When $2\theta = 90^\circ$, the NWs are now oriented perpendicular to the photoexcitation pulse resulting in minimal generation of electron-hole plasma density. Therefore, minimum THz absorption is seen.

Layered Devices: In 2017, we showed that increasing the number of layers stacked on top of each other increases the modulation depth of the devices. This is due to an increase in the NW density, resulting in more charge carrier generation. A higher modulation depth of up to 50% was seen for the new 16 layer device for several reasons: (1) higher NW density within the individual layers, (2) better encapsulation of the NWs by the parylene coating, and (3) the new devices are uniform across the surface suggesting that there are no curvatures within the individual layers and therefore internal reflections or losses are minimised.

A 32 layered device was also made by laminating the 16 and two 8 layer devices together. Figure 6.10 depicts its THz modulation performance. Despite the increasing number of stacked layers, the performance was lower than what we expected, with a modulation depth of around 30%. This is attributed to a low number of photoexcited carriers given the low absorption depth of the photoexcitation beam. This is in agreement with the results we obtained in 2017 where a device with 26 layers had a modulation depth less than the champion device which consisted only of 14 layers. This suggests that there is an optimal number of layers that will give the maximum modulation of THz which is in between 16 and 32.

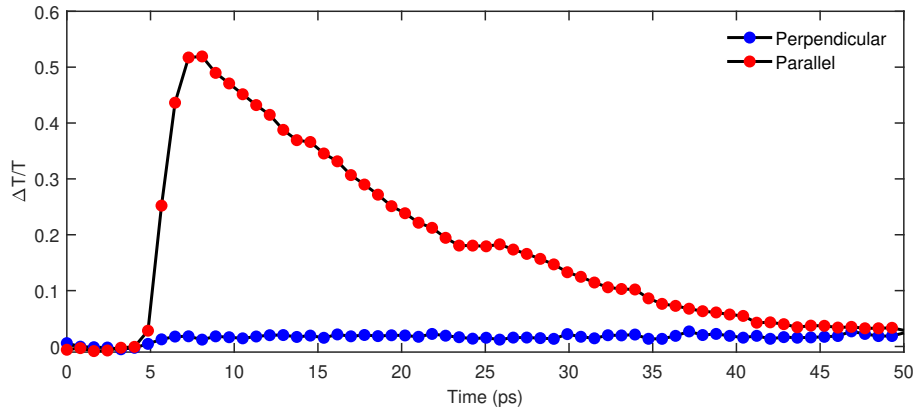


Figure 6.11: **Wire Grid Pump Scans:** Plots of the pump scans for the wire grid polarizer with the excitation beam polarized parallel and perpendicular to the patterned design. A carrier lifetime of around 11 ps was extracted for this device which is still very fast.

Fluence Dependence Modulation: Figure 6.7 shows a clear dependence of the modulation depth of the devices on the energy density impinging on the sample. This is due to the increase of charge carriers being promoted into the conduction band thereby increasing the absorption density of the THz radiation. However, due to Moss-Burstein effect, the increasing fluence has a threshold value above which no further increase in modulation depth is seen. The effect occurs when the electron carrier concentration exceeds the conduction band edge density of states, which corresponds to degenerate doping in semiconductors. Thus, as we hit maximum fluence, we observe an increase in the apparent band gap at which higher energy radiation is needed to pump the electrons into the conduction band. At this point, no more THz will be absorbed.

Wire Grid GaAs Polariser: Figure 6.3 shows microscope images of the GaAs wire grid polariser. The stripes shown as “tear drops” are the etched areas and the darker regions are the GaAs. The stripes are $\approx 5\mu\text{m}$ thick with $\approx 5\mu\text{m}$ spacing and the film is 400 nm thick GaAs. A thin film was used since thicker ones had more issues with droplets remaining under the film, which expanded during the curing of the EBL resist. The pattern (i.e. the sidewalls) can be improved by tuning the EBL parameters. During the EBL fabrication, the pattern was shifted by 0.6 mm in the x and y directions upon exposure, and therefore the pattern is not exactly in the centre of the quartz disc which made it a bit difficult to achieve perfect modulation with rotation angle during the experiment. Additionally, there is also the resist (PMMA, $\approx 350\text{ nm}$) still on the sample which should otherwise not affect the performance of the device over a broad range.

We tested our wire grid polariser on the ultrawide bandwidth system. For preliminary data, we checked whether the lifetime of the photocarriers was not significantly altered. Figure 6.11 shows the photoconductivity response of the device when photoexcited

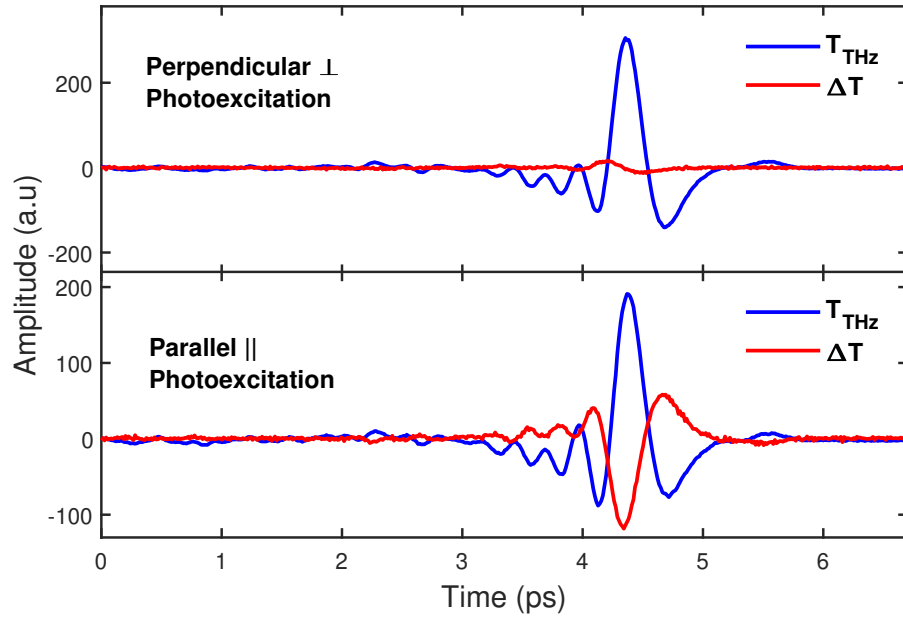


Figure 6.12: **Wire Grid Polarizer THz Waveform:** Plots illustrating the change in T when the device is photoexcited with light polarized parallel and perpendicular to the wire grid.

parallel and perpendicular to the wire grid configuration. For the latter case, barely any rise in photoconductivity is seen while for the former, a maximum change of around 50% is seen decaying over a few picoseconds. A monoexponential fit gives a carrier lifetime of around 11 ps which is ten times higher than that of the NW devices. Despite this change, the carrier lifetime is still on the order of picoseconds offering the potential for ultrafast switching speeds.

Next, to get an idea of the modulation depth, we analyzed how the THz peak changes with the rotation of the polarization of the pump beam. The corresponding waveforms for parallel and perpendicular photoexcitations are given in Figure 6.12. This is similar to the NW devices indicating that polarisation modulation is indeed possible. To assess how the modulation varies with the pump polarisation, we went on to perform exactly the same experimental procedures we implemented for the NW devices. Figure 6.13 shows the plots for the THz transmission as a function of the optical pump polarization angle at 7 different fluences (100%, 75%, 50%, 25%, 10%, 5% and 1%). A clear dependence of the modulation depth on the pump fluence is seen with the modulation depth reaching a plateau at high fluences due to the Burstein-Moss effect. Also plotted in Figure 6.14 are two plots of the modulation for both the highest and lowest fluences together with their respective fits, all obeying Malus's cosine-squared law. Although the device fabrication was not refined for better quality, the modulation depth of the device as is was around 40% and better quality can be made. For instance, the droplets under the film could

be avoided by using a patterned sapphire substrate. That should make it easier to use thicker films and reduce defects in the pattern.

6.5 Conclusion

In summary, broadband ultrafast THz modulation using III-V semiconductor NW materials has been demonstrated and is an improvement on the previous devices. [76] Moreover, a significantly higher modulation depth has been achieved owing to the higher densities of NWs coupled with more efficient parylene encapsulation and lamination. THz polarizers from GaAs NWs embedded in parylene thin films have been fabricated and a carrier lifetime of approximately 1ps demonstrated, allowing for picosecond switching speeds. A broad bandwidth between 0.1 THz and 40 THz for THz transmission is observed: the highest bandwidth recorded to date for THz modulation. A high extinction ratio of over $\sim 45\%$ can be obtained by stacking GaAs NWs embedded in thin parylene films. These values are comparable to those observed for graphene-based THz modulators and surpass those for any previous modulators based on nanostructures, such as unaligned CNTs. Thus, semiconductor NW-based THz polarizers are highlighted as ideal candidates for ultrafast THz modulation, as not only do they give a large modulation depth, broad bandwidth and picosecond switching speeds, but also are cheap and simple to manufacture.

Additionally, the wire grid polarizer has demonstrated exceptional performance with a modulation depth of around 40% for just a single layer epitaxial GaAs film. The device maintained picosecond carrier lifetime offering the opportunity for high speed telecommunication devices.

There is also much scope for further development and improvement of these polarizers. For example, by changing the NW electronic characteristics via doping, shell-coating, or wrapping in π -conjugated polymers, [304] the carrier lifetimes and therefore switching speeds can be controlled. Furthermore, the modulation depth and extinction could be further increased by adding more NW layers to the THz polariser. Even more interestingly, by utilising two NW polarisers orientated perpendicular to each other, and increasing the number of layers, a modulation depth close 100% could also be achieved, with THz radiation attenuated in both polarization directions. Thus, semiconductor NW polarisers are presented as a way of realizing THz intensity and polarization modulation on picosecond timescales, thereby enabling ultrafast THz communication.

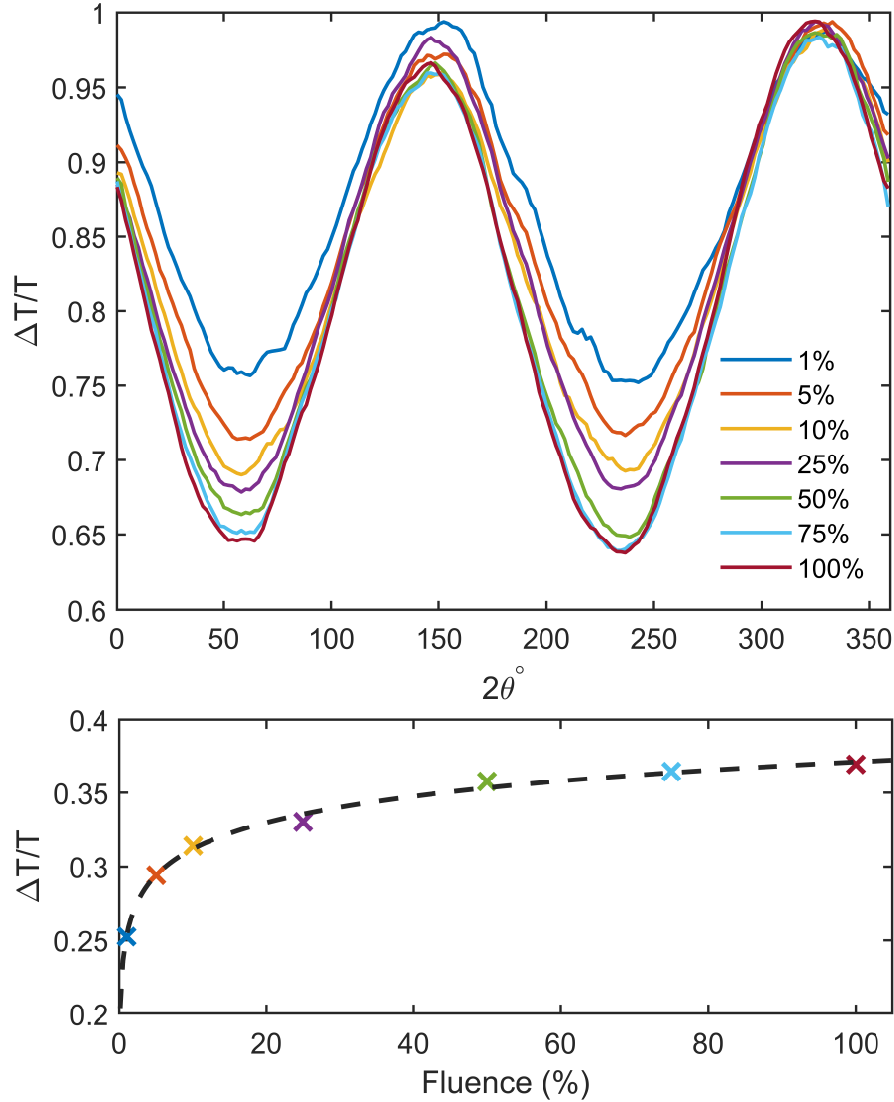


Figure 6.13: **Wire Grid Fluence Dependence Modulation Depth:** The top plot shows the modulation of the wire grid polarizer at various fluences. The bottom plot illustrates the effect of the pump fluence on the modulation depth. As the fluence is increased from 1% to 100% fluence (corresponding to $597.6 \mu\text{J cm}^{-2}$), the Burstein-Moss effect comes into play and the change in THz absorption plateaus as beyond a certain threshold, the conduction band is filled up and no more electrons can be photoexcited.

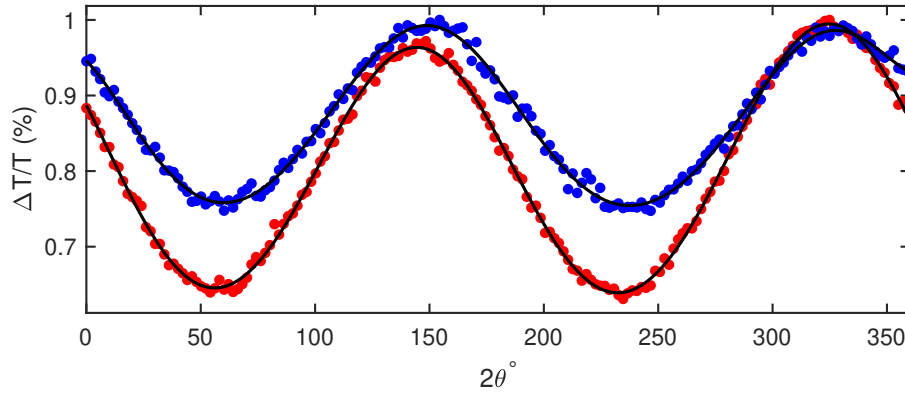


Figure 6.14: **Malus's Law:** Plots showing the data (dots) and fits (black lines) for the highest and lowest fluences. The modulation of the device follows Malus's law.

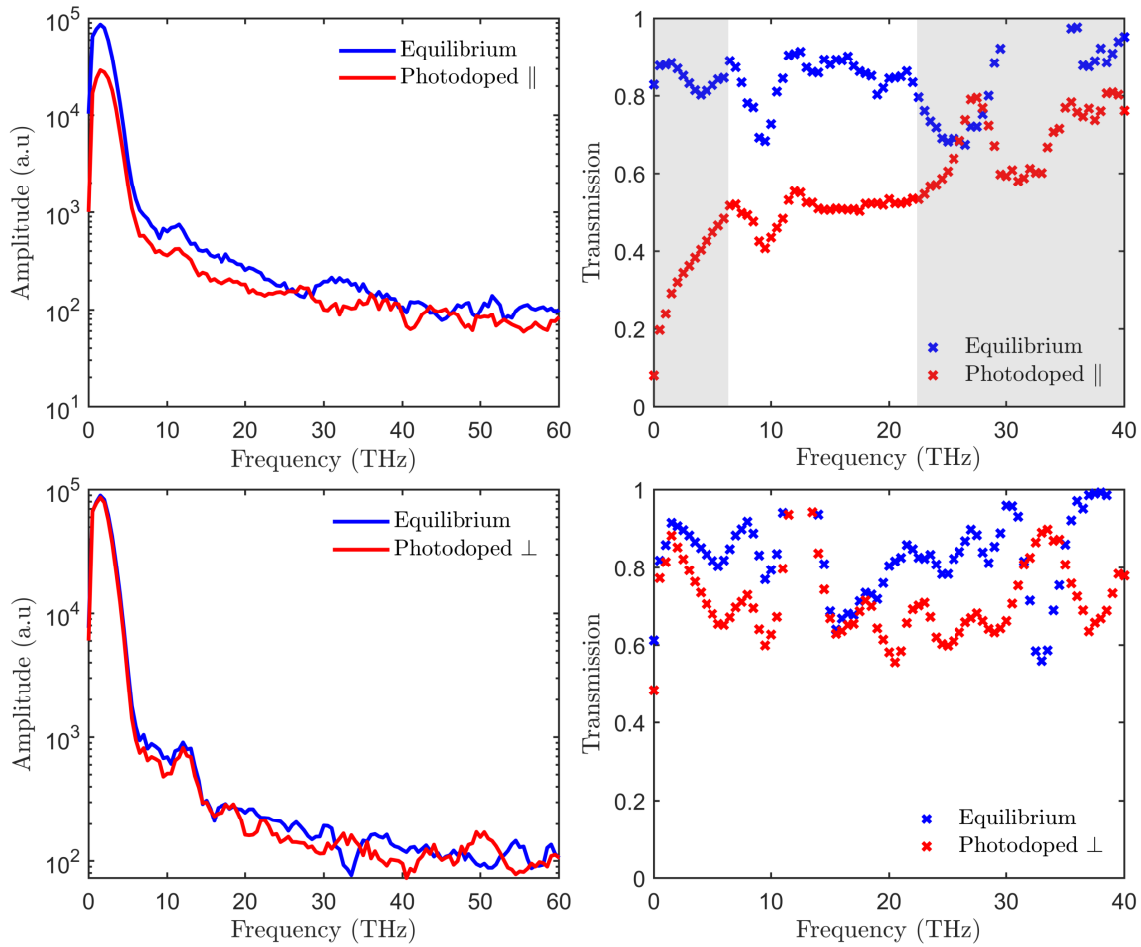


Figure 6.15: **Device Spectra and Ratio:** Two sets of plots showcasing the spectra of THz transmission and their ratios. For photoexcitation parallel to the wire grid, a maximum absorption of THz happens for frequencies below 5 THz as the GaAs has strong plasmonic effects in that range. Thereafter, a constant decrease of around 45% is seen for up to 20 THz after which the device does not show no longer operates as expected. The bottom plot shows the device being photoexcited perpendicularly for which minimum THz is absorbed.

Optoelectronic Properties of Hexagonal Boron Nitride

Hexagonal boron nitride (hBN), or otherwise most commonly referred to as ceramic, has been widely used for decades as a chemically inert/robust and thermodynamically stable substrate and materials for the engineering of nanoscale optoelectronic devices. hBN resembles graphene in many forms on the atomic scale, possessing layers of covalently bonded boron and nitrogen atoms stacked on top of each other and held via weak Van der Waals forces. Recently, further research into this material has revealed a distinctive combination of exciting optical properties that could enable previously unavailable photonic functionalities. This work looks at unveiling charge dynamics in both hexagonal boron nitride nanotubes and thin films. Although photoexcitation of the materials was not possible owing to the wide bandgap, this study investigates chiefly the dark conductivity in the terahertz range using an ultrawide bandwidth air-plasma terahertz spectroscopy setup.

7.1 Introduction

The discovery of 2D graphene [365,367,380] revolutionised the field of atomically layered quantum materials, offering great avenues for interesting research owing their unique combination of optoelectronic and mechanical properties. More recently, *hBN*, also a 2D material, has emerged as an interesting material in its own right, offering novel material properties enabling vast possibilities in a broad range of optical, electro-optical, and quantum optics functionalities. [380–387] *hBN* consists of sp^2 hybridized boron and nitrogen atoms covalently bonded to each other forming an extended network in 2D as shown in Figure 7.1. Although *hBN* is the polymorph of choice, there are in total four

known different modifications, cubic boron nitride (*c*BN), wurtzite boron nitride (*w*BN), hexagonal boron nitride (*h*BN), and rhombohedral boron nitride (*r*BN). The *h*BN and *r*BN have layered structures with lower density than *c*BN and *w*BN

The characteristic features of *h*BN including its highly anisotropic crystal structure, properties and polar chemical bonds can be exploited in device applications in IR nanophotonics through the formation of hyperbolic phonon polaritons in a natural material. [381] Owing to its point defects, the material exhibits single-photon emission properties, providing quantum emitters from the visible to the near-IR range, even at room temperature. Moreover, even though *h*BN is an indirect, wide-bandgap semiconductor (bandgap 6 eV), offering very high internal quantum efficiency for deep UV emission. Finally, it exhibits strong, thickness-dependent optical nonlinearities, and novel optical and electrical properties have been realized within *h*BN-based moiré heterostructures as a function of the rotation angle between the constituent layers. [381]

To realize the potential of *h*BN for device applications, materials synthesis and processing techniques must be advanced, including bulk crystal growth, thin-film deposition, etching, metallization and device integration. Significant advancements in the synthesis of bulk, high-quality, isotopically enriched materials improved the prospects for some of these nascent applications. These efforts are still in their infancy, but progress in bulk growth, chemical vapour deposition (CVD) and molecular beam epitaxy (MBE) have been demonstrated in several reports. [388–391] In addition to growth, several other scientific and engineering challenges must be addressed. Reference [381] provides an overview of the cutting-edge *h*BN research in photonics, including quantum optics, UV photoelectronics, IR nanophotonics, and nonlinear optics, and in sample growth and moiré heterostructures should the reader be interested to learn more about the recent advances in the field.

Hexagonal boron nitride is a highly anisotropic crystal, consisting of boron and nitrogen atoms strongly bonded in the in-plane direction. The difference in electronegativity between boron and nitrogen is larger than 0.4 eV, making the B-N bond polar covalent. Out of plane, there are only van der Waals bonds between adjacent sheets, as is the case with graphite layers enabling the sheets to slide on top of each other. Although *h*BN is an indirect bandgap semiconductor (with an energy gap of ≈ 6 eV), it exhibits an exceptionally high internal quantum efficiency for deep UV emission (up to 40%). Owing to the highly anisotropic crystal structure of *h*BN, the frequencies of the normal lattice vibrational modes (optic phonons) are also highly anisotropic, with two distinct optic phonon branches. These are designated as the upper (FS $\approx 6.2 - 7.3 \mu\text{m}$) and lower (FS $\approx 12.2 - 13.1 \mu\text{m}$) bands, derived from in-plane and out-of-plane phonons, respectively,

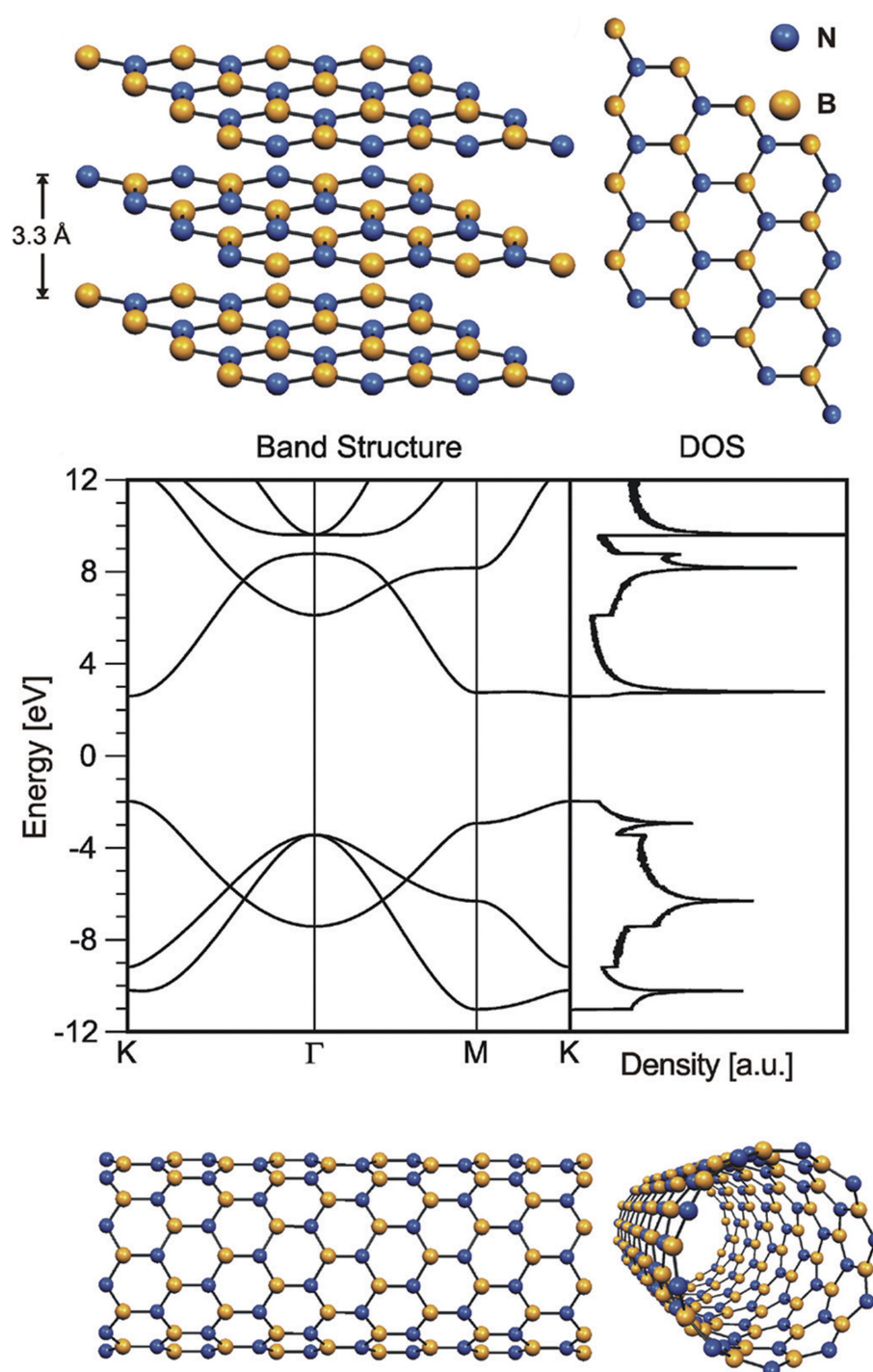


Figure 7.1: hBN Molecular Model: Hexagonal boron nitride (*h*BN) is a layered material with a structure very similar to graphite. They both exhibit a hexagonal crystal structure (lattice parameters: $a = 2.50 \text{ \AA}$, $c = 6.66 \text{ \AA}$; In this material, the hexagonal layers eclipse one another ($aA, aA, \dots$ stacking) and the B_3N_3 hexagons overlap and alternate with N_3B_3 hexagons. From the electronic perspective, *h*BN is an insulator with a very wide bandgap of $\approx 5.8 \text{ eV}$. The middle figure shows the calculated band structure and density of states for a single sheet of *h*BN showing that this material is an insulator with a bandgap of $\approx 4.5 \text{ eV}$ (E_f located at zero). Note that this local density approximation calculation underestimates the band gap; other studies considering the GW approximation reveal a bandgap of 5.4 eV for bulk *h*BN and 6.0 eV for a single *h*BN layer; and (d) molecular model of a BNNT exhibiting a (10,0) zigzag chirality (two views are depicted). Reproduced with permission from [392]

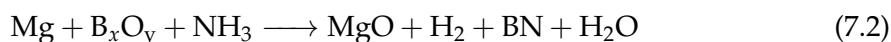
where λ represents the wavelength in free space. Owing to the polar nature of the bond, the transverse optic and longitudinal optic phonons of each branch are spectrally separated, forming a highly reflective 'Reststrahlen band'. Within this band, surface phonon polaritons can be supported; with the optic phonons, along with the acoustic phonons, forming phonon sidebands in the UV luminescence spectrum.

Motivation: The aim of this study is to improve the synthesis procedures of BNNT films from a material scientist's point of view and also enhance our understanding of their electronic and optoelectronic behaviour in order to demonstrate the feasibility of using material in next-generation UV emitting/sensing device applications. The initial goal is to synthesise the BNNTs using chemical vapour deposition, where the diameter of the nanotube, nucleation density and nanotube morphology can be controlled through control of the catalyst particle size, directed deposition of the catalyst and flow dynamics respectively. Patterned growth is important for device applications where the active material must be accurately deposited, so this too will be investigated.

The next step of the project then focuses on chemical doping of the surface of the nanotubes, either by integration of heteroatoms into the surface of the tube or by surface functionalisation by nanoparticles and then investigate the successive modification of the physical, optical, and electrical properties. Finally, device fabrication will be carried out, implementing the materials synthesised and tested previously.

7.2 Synthesis & Fabrication process

***h*-BN Nanotubes:** Boron nitride nanotubes were synthesised at the University of Oxford by Eoin O'Sullivan via a one step reaction where the catalyst and reactant precursors were present in the CVD furnace. A mixture of amorphous boron and MgO powders were placed in an alumina combustion boat with the substrate on top, facing down towards the precursors. The reaction proceeds as follows:



Substrates were initially cleaned with a protocol of sonicating in EtOH, acetone and isopropanol, each for 10 minutes before a final UV treatment. Substrates were then loaded into the reactor and the chamber purged with Ar for 30 minutes before beginning each experiment. Then, the furnace was heated up to 1200C under the flow of 300 sccm of Ar and once the desired temperature had been reached, NH_3 introduced. An ammonia flow

of 100-300 sccm was used in the experiments with the total gas flow being kept at 300 sccm through mixing with Ar where necessary. The reaction time for each experiment was 1 hour. Subsequently, the NH_3 was shut down and the reactor allowed to cool under the flow of Ar once more. Samples could be removed from the furnace once temperatures lower than 500°C had been reached and the risk of oxidation unlikely.

***h*-BN Thin Films:** All *h*BN films were grown at the Australian National University (ANU) by Dipankar Chugh using MOCVD on 2" sapphire substrates with Triethylboron (TEB, for Boron) and Ammonia (Nitrogen) as growth precursors. The thickness of all films are 45 nm (± 5 nm). The samples received are *h*BN films which have been transferred on to the round z-cut quartz discs with a diameter of 13 mm and thickness of 2 mm. Three sets of samples were fabricated based on the amount of TEB:

1. 135 – (TEB 10 sccm)
2. 064 – (TEB 20 sccm)
3. 063 – (TEB 30 sccm)

For these sample, the TEB flux has been changed as indicated above by the sccm. *h*BN films grown with higher TEB have more carbon incorporated in them as impurity. Hence 063 has highest amount of carbon and also a slight yellowish appearance, due to impurity based absorption of light. As you may already know that *h*BN is a wide bandgap semiconductor. Recently it has been reported to have an indirect bandgap of just under 6 eV. Impurity incorporation such as carbon or magnesium used during the fabrication process will modify its optical properties. We have noticed a significant sub-bandgap luminescence from *h*BN in the visible range, which increased with TEB flux. Carbon in the film was measured using XPS, and we found a direct link between TEB flux and % C in the film (incorporated as B-C).

The *h*BN coverage on the quartz disks can be identified with naked eye as the *h*BN films offer some optical contrast. The samples were mounted in SEM stubs using double sided Cu tape and ensured to be at the centre of the quartz discs for THz measurements. This is important as the THz is focused on the surface of the sample with a diameter of around 1 mm and any misalignment would give unreliable results. The substrate surface with *h*BN film were facing up with the films delaminating very easily if brought in contact with any solvent (water, ethanol, acetone etc) due to the differential wetting between *h*BN and quartz substrates, as *h*BN is hydrophobic while quartz maybe more wetting. Water is the worst, while delamination with low surface tension liquids (acetone, ethanol) is slower.

7.3 Experimental Methods

The broadband THz modulation depth and switching speeds of the devices were assessed via an OPTP setup. The measurements were done using an amplified Ti:Sapphire laser generating 35 fs pulses centred at 800 nm at a repetition rate of 5 kHz and 8 W average power. Although 8 W is the power of the laser, only 3 W have been used for this setup. Single-cycle picosecond THz transients, photoexcitation of the devices, and THz detection were achieved by splitting the main beam into three paths: (i) 0.43 mJ/pulse was used to generate THz probe pulses in a gas-plasma by combining the fundamental (800 nm) with its second harmonic (400 nm) after conversion using a 100 μm beta-barium borate (BBO) crystal, (ii) 0.03 mJ/pulse was used as the optical gate for electro-optic detection of the transmitted THz pulse using a 20 μm ZnTe crystal, and (iii) 0.143 mJ/pulse was used as the optical pump to photoexcite the sample. The energy density impinging on the sample was varied by using a neutral density filter wheel that allowed for photoexcitation at 100%, 75%, 50%, 25%, 10%, 5%, and 1% of the total energy. At the sample position, the optical pump beamwidth was ensured to be larger than the THz beam such that the area probed was uniformly photoexcited. The THz electric field, E , and the photoinduced change, ΔE were detected using a pair of balanced photodiode in a heterodyne fashion via free-space electro-optic sampling using a gallium phosphide (GaP) crystal. Spectral scans, photoconductivity decay scans and modulation scans were measured by varying stage positions accordingly. All the measurements were performed at room temperature under a dry nitrogen-purged atmosphere to minimise water vapor absorption by the THz radiation.

By varying the THz delay stage (with no photoexcitation pulse), the transmission of the electric field of the THz probe pulse through the *h*BN can then be measured in the time domain, $E(t)$, and then Fourier transformed to the frequency domain, $E(\omega)$. The electric field transmitted through the sample without photoexcitation (at equilibrium) is given by E_{off} . Two reference samples were also measured by looking at the THz transmission through them: *z*-cut quartz and *c*-cut sapphire. Additionally, all the material characterizations were done in the Department of Material Science by Eoin O'Sullivan.

7.4 Results & Discussion

The nanotube samples were first characterised via Raman spectroscopy. Figure 7.2 shows the spectrum collected on sample BNNT013. The analysis showed the presence of *h*BN with a definite peak at 1367cm^{-1} and a small peak at 780cm^{-1} . This is in accordance with what has been obtained previously, both theoretically and experimentally. *h*BN has

two phonon modes in the mid-infrared region: the low frequency out-of-plane (780cm^{-1}) mode and the high-frequency in-plane (1367cm^{-1}) mode, both of which have negative real parts of the dielectric function.

For the transmission electron microscopy (TEM), the sample was prepared by sonicating the substrate in ethanol (EtOH) to get a suspension. The latter was then centrifuged at 3000 rpm for 15 minutes to remove any of the larger particles or aggregates from the suspension before dropping onto a TEM grid for analysis.

The tubes here showed two distinct distributions of diameter; the large tubes were $590 \pm 40\text{ nm}$ and the smaller tubes in the region of $110 \pm 10\text{ nm}$. A closer look at the SEM images revealed that the tubes display a narrowing of their diameters as growth continues. This suggests that the size of the tubes is controlled by the concentration of reactant species available at the reaction interface. As the reaction proceeds and the concentration of reactive species decreases, the formation of large diameter nanotubes is reduced as they require more BN species to form, and smaller diameter tubes form instead.

As for the *h*BN thin films, SEM (HV 2.00kV, Spot 2.0, HFW $14\mu\text{m}$, WD 4.2 mm and Mag $\times 18293$) images were obtained as shown in Figure 7.4. A fairly uniform surface is seen with small specks of either dust or residuals from the growth process. SEMs from other parts of the sample revealed some scratches, possibly due to chaotic movement in the sample box during transportation and handling.

Owing to the material's wide band gap of 5.9 eV, THz photoconductivity was not possible. Instead we opted for measuring the dark conductivity which would be caused by the dopants such as magnesium and carbon. The results extracted from the measurements (method detailed in Chapter 3) was fitted to a Drude sheet conductivity given by:

$$\sigma_{\text{drude}} = \frac{\sigma_{\text{DC}}}{1 - i\omega\tau}.$$

Figures 7.3 and 7.4 show the conductivity responses. A Drude response for both the nanotubes and the thin films is seen. Compared to the NW semiconductors, there are no localisation of charges in the nanotubes owing to the vast percolation pathways and the 2D geometry of the films. As for the nanotubes, samples were synthesised on both quartz and sapphire substrates. The references used were coated with the dopants used in order to eliminate any effects that will otherwise make the data hard to interpret. For both substrates, similar responses and fits were obtained and an equilibrium charge density on the order of 10^{23} m^{-1} and scattering rate of 10^{13} s^{-1} were extracted. The frequency range

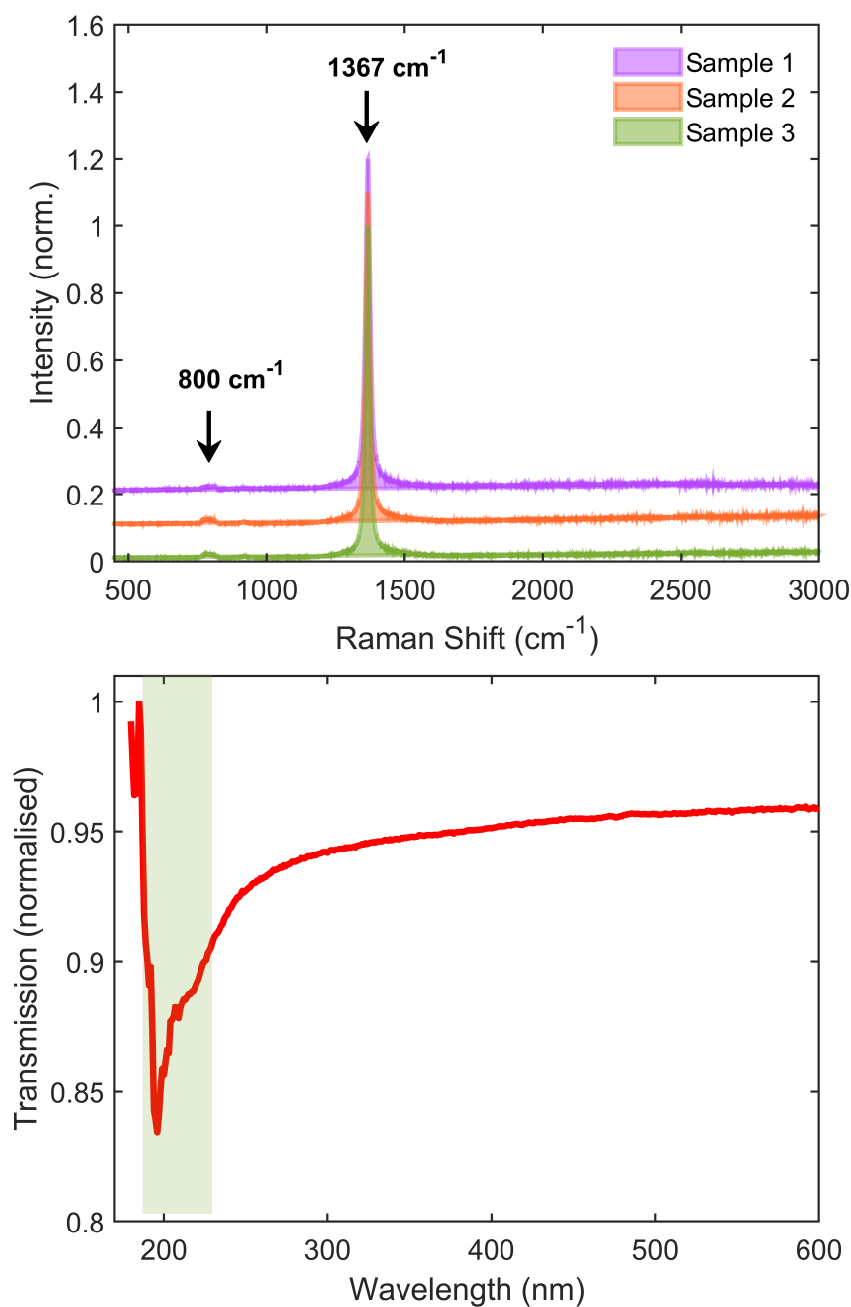


Figure 7.2: **Raman Shift and Absorbance of BNNT:** The top image depicts the Raman Shift Spectra of 3 samples of BNNT. They all displayed a strong response for the high frequency in-plane mode at 1367 cm^{-1} and a low intensity peak for the low frequency out-of-plane mode at 800 cm^{-1} . The bottom image is a plot of the absorbance of the BNNT sample with wavelength. It is evident that doubling (@400 nm) and tripling (@266 nm) would not show any dynamics.

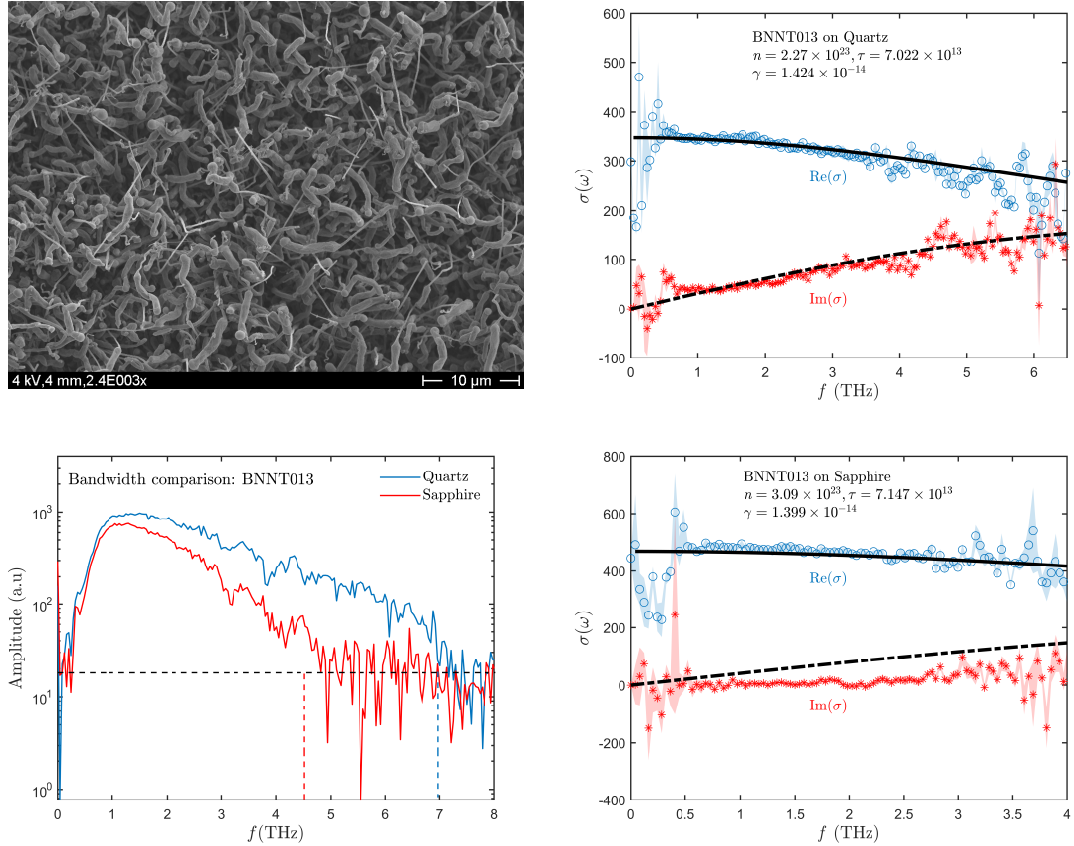


Figure 7.3: Dark Conductivity of *h*BN nanotubes: The top left image is an SEM of the BNNT samples. It is clear that there is a vast network of interconnected nanotubes. As such, one would expect the charge carriers would move freely around. The dark conductivity spectra of the samples are shown for both on a z-cut quartz and *c*-cut sapphire substrates. A Drude response is seen for both of them with roughly the same density of carriers due to the dopant (Magnesium in this case used as precursor). Also plotted are the spectra of the *h*BN on quartz and sapphire substrates. *c*-Sapphire at room temperature has limited bandwidth transmission of up to around 4 THz whilst z-Quartz transmits beyond with a phonon mode at around 3.5-4 THz.

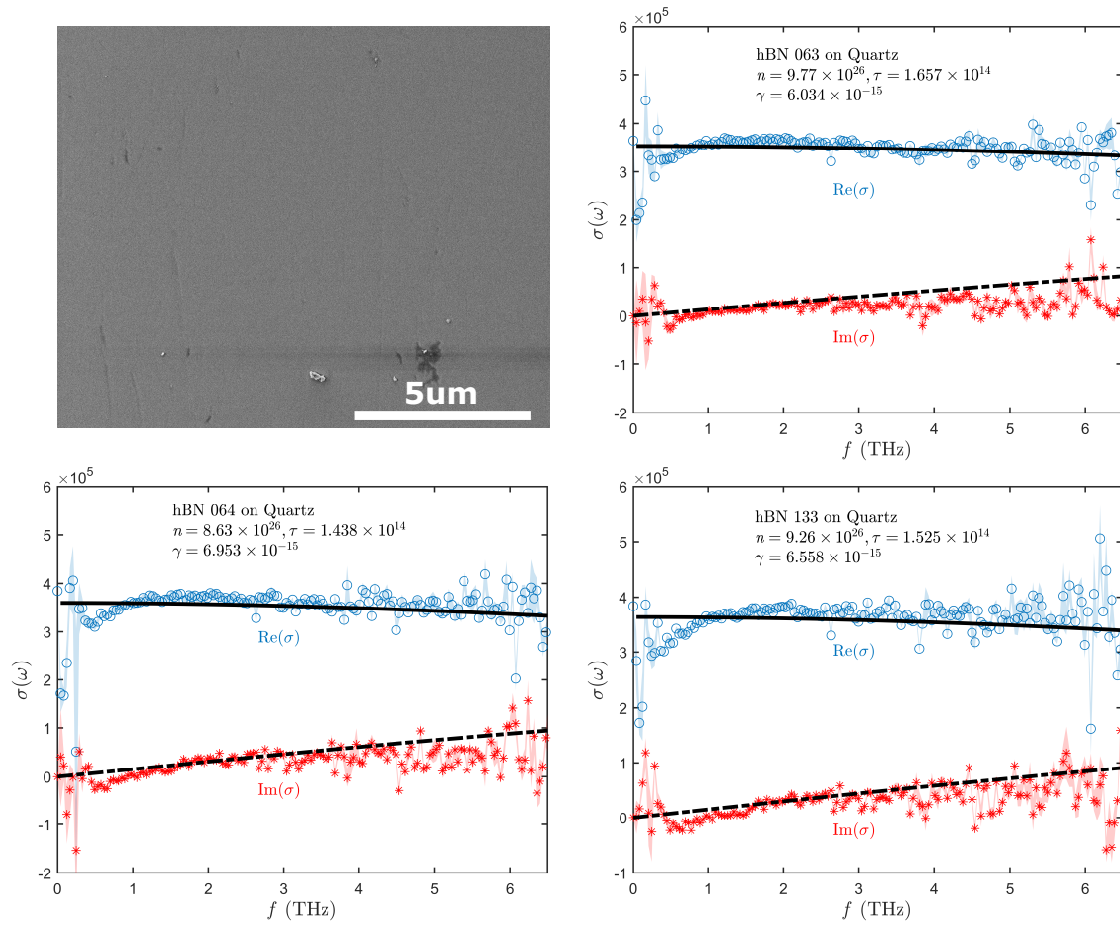


Figure 7.4: **Dark Conductivity of hBN thin films:** The top left image is an SEM of the hBN films. The sample looks very uniform across and very flat with a speck of impurity. The other images show a Drude response for the dark conductivity with very similar equilibrium carrier densities and scattering rates.

probed for the on-sapphire substrate was lower as has been shown in Chapter 3. This is due to the high extinction coefficient of the material above 4 THz at room temperature.

For the thin films, a Drude response was also seen for all the three samples as was expected for such material geometry. An equilibrium charge density on the order of 10^{26} m^{-3} and scattering rate of 10^{14} s^{-1} were extracted. These results suggest that the charge carrier dynamics in these types of materials are dominated by the free-electron motion with no localisation of charges. The carriers are mostly due to dopants and even though no photoexcitation of more carriers into the conduction band was not possible, the dark conductivity offered insights into primarily the effects of the synthesis precursors.

7.5 Conclusion

So far, BNNT films of various morphologies, diameter and impurity levels have been synthesised. Control over the tube diameter has been achieved with improvements of the synthesis method. Results of increased alignment have been shown with the latest method.

Both the *h*BN nanotubes and thin films displayed similar response for their dark conductivity. Unfortunately, photoexcitation of charge carriers in the conduction band was not possible given the wide bandgap. Frequency doubling and frequency tripling would not have given enough energy to photodope the samples. The crystal required for frequency quadrupling was too expensive and has a conversion efficiency of less than 8%. Nevertheless, the dark conductivity provided important insights into how the fabrication process of these materials can result in doping which would need to be taken into account when engineering optoelectronic devices.

EDS and XPS methods have been used to study the composition of the nanotubes and also determine impurity levels. This will also play an important role when systematic doping of the nanotubes is achieved. Additionally, TEM analysis of more recent samples are yet to be completed. Photoluminescence studies will need to be carried out to examine the emission properties of the various films synthesised and to investigate the effect of doping on the band structure. Even though OPTP measurements were not carried out, the dark conductivity offered valuable insights into the synthesis process of these materials where dopants are often introduced. This significantly impacts the optoelectronic properties of the material which can eventually either be exploited or discarded according to the device usage.

Conclusion

Although a lot has been covered, in conclusion, we have highlighted the importance of THz spectroscopy and semiconductor nanowires. As we move towards a more sophisticated world, the demand for nanoscale devices is ever increasing. More effort is being put into understanding the optoelectronic properties of semiconductor nanowires in order to probe their functionalities. This will in turn help in tailoring their use in devices. Additionally, as sources and detectors have been widely studied now in the THz regime, there is a demand for ultrawide bandwidth systems that are capable to probe the dynamics of charge carriers beyond 3/4 THz. The state-of-the-art THz air plasma generation setup will allow future avenues for collaborations and hopefully help elucidate various exciting properties at high THz frequencies.

In summary, chapter 3 and 4 dealt in great detail about the various aspects of THz spectroscopy: from THz emission from a PC antenna to detection via a gas plasma, these two chapters hopefully offer a comprehensive explanation of what the system can offer. Of particular interest is Chapter 4 which describes the newly-built state-of-the-art air plasma THz system. We showed that by using an ultrathin electro-optic crystal (20 μm ZnTe), it is possible to extract frequencies of up to 40 THz. We also presented how the phonon modes of EO crystals can be accounted for theoretically and use the full response function to eliminate these modes and extract missing frequencies. Although the physics behind THz generation from an air plasma is still subjected to debates, we provided two dominant theories presented in literature that accounts for physical phenomena happening during the THz emission. More work can be done on that side in the future. Chapter 5 discussed the length-dependence of plasmonic resonance in both GaAs and InP

NWs. Numerical simulations initially showed an inverse relationship between the surface plasmon frequency and the NW length. Varying lengths of MOCVD grown and SAE grown GaAs and InP respectively were then used as samples: from $2\text{ }\mu\text{m}$ to $12\text{ }\mu\text{m}$ long. The photoconductivity spectra validated the theoretical simulations. The reported values of mobility however were smaller than the ones extracted through the data analysis as detailed in Chapter 3. We went back to using the Drude dielectric function to simulate a series of plots with varying mobilities at different lengths and try to fit the experimental data.

Chapter 6 was built upon a previous paper we published in 2017. Here we looked at the polarization modulation of THz radiation using unpassivated GaAs NWs as the active component. The devices were very small, offering the opportunity to integrate with small electronics and a significant improvement was seen in the modulation depth owing to better stacking of layers and higher density of NWs. Moreover, we tested the device on the air-plasma setup to see whether the devices were still active beyond 4 THz. The modulation depth persisted even beyond 10 THz which was a huge improvement from the previous study. Furthermore, a novel GaAs wiregrid polariser was fabricated which showed an impressive modulation depth of around 40-45%.

Chapter 3 looked at the temperature-dependent complex refractive index of *c*-sapphire. Quartz is usually the material of choice as a substrate when it comes to THz measurement. However it possesses a strong phonon mode at 4 THz which becomes more pronounced at low temperatures. The study showed that sapphire has no phonon modes in the terahertz region between 0.1 THz and 7 THz. The transmission through the substrate however varied significantly with temperature being almost 100% transparent at cryogenic temperatures but becoming highly absorbing/reflecting as it heats up with a cut off frequency at around 2 THz beyond room temperature. This will allow us to choose carefully the substrate one would need to deposit samples onto.

Chapter 7 finally looked at the optoelectronic properties of hexagonal boron nitride nanotubes and thin film. This novel material has been highly sought owing to the various physical and chemical properties it possesses. However, not much has been done to elucidate its properties in the terahertz region and this study revealed the equilibrium properties of *h*BN .

8.1 Future Works

The projects undertaken for this thesis have many additional avenues to be explored that will set the path for future works. Chapters 4, 5, 6, and 7 can be further expanded

with more studies. The generation of THz radiation via air-plasma filamentation is not well understood owing to the various complex processes happening inside the plasma. For instance, modelling of this effect in a relativistic approach will help in giving a broader background to the subject. Previous works have been performed on magnetized plasmas and this same route can be taken to investigate the effect of magnetic fields on the emission of THz pulses. As for the III-V semiconducting nanowire THz modulator, alternating layers of the device can be stacked together, providing a better way to modulate the THz intensity. Instead of parylene-C being used as a host, the effect of other polymers can be looked at such as pi-conjugated molecules which may or may not modify the electronic behaviour of the nanowires. The wiregrid polariser fabrication is still yet to be optimised and this will undoubtedly produce better devices and possibly higher modulation depths.

As for the hexagonal boron nitride, photoexcitation of charge carriers into the conduction band would give a better insight behind the optoelectronic behaviour of these novel materials. The synthesis process can be tailored such that a range of absorption is possible, for instance an absorption in the frequency range of 400 – 800 nm.

The work performed on *h*BN films and nanotubes is still in its infancy. More work is currently being done on doping vertically aligned CNT with nitrogen and boron. Eoin O'Sullivan has successfully synthesised them directly on quartz with alignment perpendicular to the quartz face. The electronic properties could be compared (increase/decrease in photocurrent, promotion/reduction of the charge recombination rate) with the photocatalytic activity of devices made up of the various CNT films and tested on their group. The N-CNTs have a broad absorption spectrum over 800 – 300 nm and gets quite noisy after 240 nm. This will definitely enable photoductivity to be measured in the THz regime. 2D *h*BN is yet another possible route to undertake although the growth methods need to be well controlled first.

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