

Insulating, Semiconducting and Metallic 2D Materials for Flexible Electronics



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A thesis submitted for the degree of
Doctor of Philosophy
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Thesis submitted for the degree of Doctor of Philosophy

Two-dimensional (2D) materials have enjoyed significant attention in recent years as new materials for use in flexible electronics. Combining unique electronic properties with unparalleled strain resilience and transparency, they represent ideal candidates in a broad range of different applications. However, though significant progress has been made this field is still in its relative infancy and there is still much to discover. This project details aspects of the synthesis, fabrication, and physical processes and mechanisms that are pertinent to flexible electronics, with a focus on a subset of three materials: metallic graphene, semiconducting tungsten disulphide, and insulating boron nitride. All materials were synthesised by chemical vapour deposition.

‘Bulk’ heterostructures of the above materials in several different permutations were fabricated on flexible polymer substrates and studied during repeated strain cycling. A mechanism by which strain is accommodated by inhomogeneous debonding from the substrate and a time dependent relaxation effect were identified and studied. With repeated strain cycling the response of the heterostructures was found to stabilise—an encouraging result for future device work.

Subsequent work explores two disparate flexible devices based on 2D materials. The first of these is an array of flexible photodetectors. Polymer substrates impose severe limitations on processing conditions and necessitated significant modification to existing fabrication techniques. Functional devices were demonstrated and their response to strain studied, revealing a transient enhancement of sensitivity followed by permanent failure. The mechanism behind this effect was explored.

The second device is a MRI and CT compatible cardio-respiratory monitor for use in preclinical imaging—a device which represents a significant improvement over existing technology. Its properties were studied in detail and its functionality confirmed through extensive *in vivo* testing, and a patent has since been filed. Several prototypes are already in use at the Oxford Institute for Radiation Oncology.

To my Parents.

Acknowledgements

This research would not have been possible without the guidance and support of a number of people, namely my supervisor, colleagues, family, and friends. Their support throughout the course of my DPhil has been instrumental in a great many ways, not least the successful completion of this work.

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All of my colleagues in the Nanostructured Materials Group have likewise been invaluable in this project, providing a great many insightful discussions and sharing knowledge freely. Special thanks go to Dr Viktoriya Shautshova, Dr Haijie Tan, and Dr Chit Siong Lau for their assistance with the multifarious difficulties associated with 2D device fabrication; and Dr Yuewen Sheng, Mr Xiaochen Wang, Miss Linlin Hou, and Miss Wenshuo Xu for providing raw 2D materials, as well as insights into their synthesis.

Beyond the NSM, there are several figures who have played important roles. Mr Reuben Harding provided numerous deft insights into the electronic measurements used herein. Mr Ilija Rašović has served in a great many capacities as a valuable touchstone throughout. Last but not least, my latter-day collaborator Dr Sean Smart provided me with an opportunity that in many ways reinvigorated my interest in

scientific research.

Additional thanks go to the EPSRC for supporting this research, and to Oriel College, the Department of Materials, and the University of Oxford for their understanding and assistance during a vital additional six months beyond the initial 3.5 year period. This support enabled me to resolve some personal difficulties and properly complete this work, and without it this thesis would not have been possible.

Lastly, my family. My parents Stephen and Ruth Tweedie have been supportive from the very beginning, providing no end of encouragement and advice, spending long hours proof reading, and helping me to navigate the complicated world of academia. Their passion for learning is the reason I am in this position today. I am eternally indebted to my wonderful cousin Jessica Tweedie, and her family, for providing refuge and welcoming me into their home in Oxford; and to my Aunt and Uncle, Monica and Ian Newberry, for allowing me to fulfil a long-standing Victorian dream by providing me with a solitudinous cottage in the foothills of the Cotswolds in which to complete my thesis. And finally, endless gratitude to my girlfriend Libby Lamb—for support, care, and above all showing me the meaning of occupational balance.

Publications

Below is a list of publications associated with this work. First author publications form the basis of Chapters 4–6, and co-author publications in related areas are cited when relevant. Chapters 5 & 6 are based on as-yet unpublished work; in the case of Chapter 6, this was to allow time for protection of the intellectual property demonstrated herein.

First Author:

Chapter 4

M. E. P. Tweedie, Y. Sheng, S. Sarwat, W. Xu, H. Bhaskaran, J. H. Warner, “Inhomogeneous Strain Release during Bending of WS₂ on Flexible Substrates”, *ACS Applied Materials and Interfaces* **2018**, *10*, 39177–39186.

Chapter 5 (unpublished)

M. E. P. Tweedie, C. S. Lau, L. Hou, X. Wang, Y. Sheng, J. H. Warner, “All-2D Transparent Photodetector Arrays on Flexible Substrates”, *Manuscript under preparation* **2019**.

Chapter 6 (unpublished)

M. E. P. Tweedie, V. Kersemans, S. Gilchrist, S. Smart, J. H. Warner, “Piezoelectric Sensors with Graphene Electrodes for Pre-Clinical Cardio-Respiratory Monitoring”, *Manuscript under preparation* **2019**.

Co-author:

2018

S. G. Sarwat, **M. E. P. Tweedie**, B. F. Porter, Y. Zhou, Y. Sheng, J. Mol, J. Warner, H. Bhaskaran, “Revealing Strain-Induced Effects in Ultrathin Heterostructures at the Nanoscale”, *Nano Letters* **2018**, *18*, 2467–2474.

2017

H. Tan, W. Xu, Y. Sheng, C. S. Lau, Y. Fan, Q. Chen, **M. E. P. Tweedie**, X. Wang, Y. Zhou, J. H. Warner, “Lateral Graphene-Contacted Vertically Stacked WS₂/MoS₂ Hybrid Photodetectors with Large Gain”, *Advanced Materials* **2017**, 1702917.

2016

Y. Fan, A. W. Robertson, X. Zhang, **M. E. P. Tweedie**, Y. Zhou, M. H. Rummeli, H. Zheng, J. H. Warner, “Negative Electro-Conductance in Suspended 2D WS₂ Nanoscale Devices”, *ACS Applied Materials and Interfaces* **2016**, 32963–32970.

Foreword

Unless explicitly stated, the work presented in this thesis is the exclusive work of the author. The first person plural pronoun *we* is used throughout by convention and for consistency, though it is the opinion of the author that this encapsulates the nature of collaboration in which research is undertaken across the various spheres of the university, and indeed throughout academia as a whole and beyond. In addition to the acknowledgments above, specific contributions are detailed at the end of each chapter.

“The truth will set you free. But not until it is finished with you.”

— **David Foster Wallace**, *Infinite Jest*

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List of Abbreviations

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
3Rs	(of animal research) Replacement, Reduction, and Refinement
AFM	Atomic force microscopy
Aq.	Aqueous
CCD	Charge-coupled device
CNT	Carbon nanotube
CT	Computed tomography
CVD	Chemical vapour deposition
DC	Direct current
DOS	Density of states
ECG	Electrocardiogram
EDLT	Electric double-layer transistor
EQE	External quantum efficiency
FET	Field-effect transistor
FWHM	Full-width half-maximum
Gr	Graphene
hBN	Hexagonal boron nitride
IPA	Isopropyl alcohol
IR	Infrared
ITO	Indium tin oxide
I-V	Current-voltage

KPM	Kelvin probe (force) microscopy
LED	Light-emitting diode
LPE	Liquid phase exfoliated
MRI	Magnetic resonance imaging
MSM	Metal–semiconductor–metal
Non-aq.	Non-aqueous
OLED	Organic light-emitting diode
PCE	Power conversion efficiency
PDMS	Polydimethylsiloxane (<i>silicone</i>)
PEN	Poly(ethylene naphthalate)
PES	Poly(ether sulphone)
PET	Poly(ethylene terephthalate) (<i>polyester</i>)
PI	Polyimide
PL	Photoluminescence
PMMA	Poly(methyl methacrylate) (<i>acrylic</i>)
PP	Polypropylene
PVDF	Poly(vinylidene fluoride)
QW	Quantum well
rGO	Reduced graphene oxide
SEM	Scanning electron microscopy
SWCNT	Single-walled carbon nanotube
TFET	Tunnelling field-effect transistor
TMD	Transition metal dichalcogenide
UV	Ultraviolet

Chapter 1

Introduction

The aim of this project was the systematic study of how 2D materials may be employed in flexible electronics through an investigation of the interfacial dynamics of heterostructures, and the demonstration of flexible sensor technology, utilising 2D materials that are insulating, semiconducting, and metallic. The work that follows brings together all aspects of their production, starting with the synthesis of each material, through an exploration of a range of fabrication techniques tailored for the increased challenges associated with soft-matter substrates, and culminating in the creation of functioning flexible and transparent devices. One of these is now patent pending, and several prototype devices have been provided to collaborators at the Oxford Institute for Radiation Oncology for use in pre-clinical medical imaging.

Thesis Overview

This DPhil thesis marks the completion of four years of research, and eight total years of study, in the Department of Materials, University of Oxford. Herein we explore a range of 2D materials as components of flexible electronic devices, utilising diverse materials and fabrication and characterisation techniques, in three distinct studies within this topic. All materials were grown by chemical vapour deposition (CVD), and used to fabricate a variety of heterostructures and heterostructured devices on a range of rigid and soft matter substrates, focusing primarily on poly(ethylene naphthalate) (PEN), a material commonly used as a substrate in polymer electronics.

Reports of the remarkable strain resilience of 2D materials have led to significant interest in their use in flexible electronics, but a large proportion of the literature focuses on the demonstration of a device first on a rigid substrate, followed by a simple proof of concept on a flexible substrate, without an in depth study of scalable fabrication techniques or the influence of bending on device properties. This is symptomatic of the wider field of research into 2D materials. Nevertheless, as we will explore in detail in Chapter 2, a growing number of devices with sometimes remarkable properties have already been demonstrated.

We chose a set of three 2D materials that are among the most well studied and understood, and expanded upon the existing work within the group to include the use of flexible substrates and the influence of strain. Graphene, the first 2D material, was studied as an atomically thin, chemically inert contact due to its low electrical resistance. Hexagonal boron nitride (hBN) was studied for use as an insulator or

dielectric layer. Tungsten disulphide (WS_2), a direct bandgap semiconductor when isolated as a monolayer, was studied for use as the active semiconducting component in devices. While clearly not an exhaustive set, this provides a basis for understanding the mechanisms at play and details about the fabrication techniques that are applicable to the field of 2D flexible electronics as a whole.

We begin with a detailed study of the effect of strain on ‘bulk’ heterostructures composed of the 3 chosen materials on PEN substrates, using photoluminescence (PL) spectroscopy to study the strain transfer to the WS_2 . We chose heterostructure configurations representative of device contacts, channels, and gated channels, and applied strain by bending the substrate *in situ*, leading to a tensile strain in the substrate surface. PL spectra were measured at intervals, and a mechanism by which strain is accommodated by debonding of the heterostructures from the substrate was developed to explain inconsistencies in the peak shape during the first strain cycle. Hysteresis in the measurements with repeated strain cycling was attributed to a gradual strain relaxation mechanism that was characterised in detail.

The remainder of the thesis explores two disparate flexible devices based on 2D materials. The first of these builds directly on the previous section and earlier work within the group on the fabrication of lateral graphene– WS_2 –graphene heterostructure photodetectors, previously demonstrated on silicon wafers using electron beam lithography. Here we used scalable fabrication techniques and flexible PEN substrates. With some adaptation of the fabrication techniques from those conventionally used, we were able to produce working photodetectors. However, bending was found to have a permanent deleterious effect on the devices, leading to reduction and eventual

loss of photoconductivity at relatively small strains. A further issue with the fabrication process was identified and solved, which produced minor improvements and a transient enhancement in photocurrent of up to one order of magnitude, but did not solve the problem of failure with strain. The failure was attributed to damage from the combined effect of strain, bias, and laser irradiation.

The final chapter details the fabrication and characterisation of a composite graphene piezoelectric cardio-respiratory monitor for *in vivo* preclinical MRI and CT imaging applications, making use of the electromagnetic transparency and the low atomic mass of carbon based graphene electrodes. This novel application of graphene provides a significant improvement over the existing technologies in terms of both ease of use and image quality. The properties and behaviour of the device were studied and the design refined, and several working prototypes are now in use in an all-carbon-based life support/monitoring system in the Oxford Institute for Radiation Oncology.

Chapter 2

Literature Review

2.1 Introduction

Since the first isolation of graphene in 2004 by Novoselov and Geim, the field of two dimensional (2D) materials has expanded and diversified rapidly, and now encompasses a wide range of materials exhibiting manifold properties, and spanning all classes from insulating to metallic.^[1-3] Though they had been theorised for decades, their discovery generated significant interest in the scientific community: this was the first time that a truly 2D material was directly isolated and observed, and their subsequent demonstration of the incredible properties of graphene led to their receipt of the Nobel Prize in Physics in 2010.^[4] Obtained initially by exfoliating a single layer from bulk graphite,^[1] the unique electronic properties of graphene resulted in a great deal of interest in the properties that might emerge when other layered van der Waals materials were similarly isolated as monolayers. A large and growing number of other 2D materials have since been successfully produced and studied.^[5,6]

2.1. INTRODUCTION

A common property of 2D materials is their high strength and durability, with some of the highest elastic moduli and breaking stresses ever observed, and the ability to withstand extreme strains without damage.^[7–9] Carrier mobility (μ) is also typically good in those 2D materials that are conductive, most prominently graphene, which has $\mu = 200000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ —the highest of any known material.^[7,10] These materials also typically transmit a large proportion of visible light,^[8] and as they are 2D will have a negligible contribution to device profile and weight in almost all cases. These properties compare very favourably to other transparent conducting materials.^[11] This leads to the motivation for this thesis, to wit: the production of flexible and transparent electronic devices from 2D materials.

Since its discovery, graphene has been widely investigated as a material for use in diverse electronic applications,^[12] due to its high conductivity,^[13] excellent carrier mobility,^[1] and monolayer thickness.^[14] However, in recent years attention has turned to other 2D materials that, unlike graphene, have bandgaps of a useful magnitude—an essential feature for the future implementation of 2D systems in electronics and optoelectronics.^[15–17]

Mechanical exfoliation has enabled a plethora of different 2D materials to be isolated from bulk crystals, and many of these are semiconductors with direct bandgaps that span from ultraviolet (UV) to near-infrared (IR).^[7,18,19] Synthesis techniques for producing them on a larger scale have followed close behind.^[6] One interesting family of semiconducting 2D materials is the transition metal dichalcogenides (TMDs), with many members having direct bandgaps in the visible range in monolayer form.^[3] Graphene can then be used as a contact to TMDs in devices such as transistors,

light-emitting diodes (LEDs), and photodetectors.^[20] The final component is a 2D insulator, for which a primary candidate is hexagonal boron nitride (hBN). hBN has an extremely wide bandgap (~ 6 eV)^[21] and so can be used as an insulating layer, gate dielectric, or tunnel barrier.^[22]

This review will focus on the above materials and give an overview of how they may be implemented into flexible devices, beginning with a description of their fundamental properties and the different methods for obtaining each one. Many of these properties are common to 2D materials—the extreme in-plane stiffness contrasted by the ease of out-of-plane deformations, the resistance to strain, and the high optical transparency—though an exhaustive description of their similarities and differences is beyond the scope of this review.

We then examine the advantages of 2D materials over current alternatives in flexible electronics, as well as the challenges that must be overcome for their successful implementation. Finally, an analysis of current work on producing a number of different devices from these materials is provided, with the focus being on designs that can be produced using all 2D materials and flexible substrates. Where possible, studies where flexibility has already been demonstrated are used, but examples have also been drawn from work on devices produced using rigid substrates that may be adapted for use with flexible substrates. This should provide the reader with an understanding of the many opportunities—and many challenges—afforded by the use of 2D materials in flexible electronics, several of which will then be addressed in this thesis.

2.2 Fundamentals of 2D Materials

2.2.1 Graphene

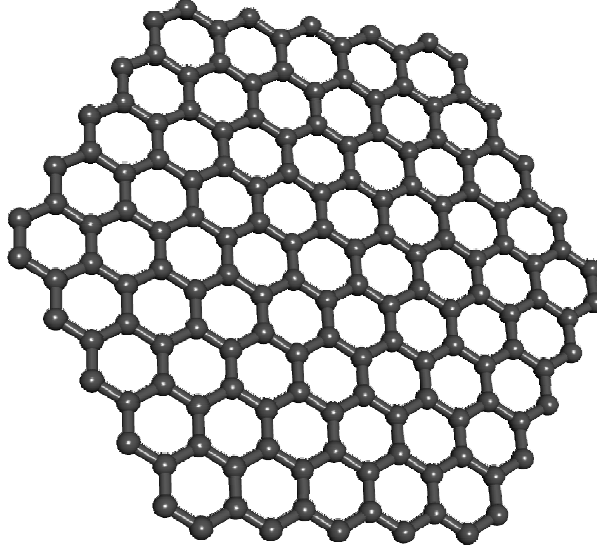


Figure 2.1: Structure of graphene.

2.2.1.1 Properties

An allotrope of carbon, graphene consists of a single layer of atoms in an sp^2 bonded hexagonal lattice (Figure 2.1).^[23] These bonds are very strong in plane, meaning that physically it boasts some of the most incredible properties of any known material. It has a Young's modulus of 1 TPa, which is among the highest ever measured, and has a breaking strength of 42 Nm^{-1} .^[24] This planar bonding leads to a significant degree of anisotropy, with easy out-of-plane deformations despite the extreme in-plane stiffness.^[23] Thermal conductivity is similarly unparalleled, with ballistic phonons in suspended monolayers supporting the highest measured value of any material.^[25]

Perhaps with more relevance to flexible electronics, it has also been shown to be able to withstand very large strains, with no damage and full recovery demonstrated up to strains of 25 %.^[26,27]

Graphene is a semimetal, meaning that like a semiconductor it has discrete valence and conduction bands, but differs in that it has no band gap. For low energies the bands are linear, leading to another of its record breaking properties: since their effective mass is proportional to the reciprocal of band curvature, carriers behave as massless Dirac fermions and so move at an effective ‘speed of light’ (0.33 % of c), resulting in mobilities up to $200000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and high electrical conductivity.^[10,28] It exhibits a strong ambipolar electric field effect, meaning that the application of an electric field can be used to introduce carriers, and this effect happens equally for both electrons and holes.^[1] In monolayer form graphene is highly transparent, with an absorption coefficient of 2.3 % for visible light and broadband transmission due to the lack of bandgap. This value decreases linearly as the number of layers increases.^[29,30] These properties have enabled the study of exotic physical phenomena in graphene, such as electron hydrodynamics—where electrons behave as a Fermi liquid, with analogous properties to classical fluids.^[31]

Raman spectroscopy is a powerful technique for the examination of 2D materials. There are two main peaks in the spectrum of pristine graphene, the G and 2D (or G’) band. The G peak arises from a first order scattering arising from an E_{2g} phonon, and is characteristic of sp^2 bonded materials. The 2D arises from a second order scattering process from two phonons, and is specific to graphitic materials.^[32,33] In monolayer graphene the ratio of 2D/G intensities is approximately 4, and as the number of

2.2. FUNDAMENTALS OF 2D MATERIALS

layers increases this ratio decreases as the 2D broadens and becomes comparatively less intense.^[33] In defected material, there is another peak (D) that also arises from a second order scattering process, this time involving a phonon and a defect. This peak will increase in intensity proportional to the density of defects, and so can be used to characterise the amount of disorder arising from e.g. processing and fabrication techniques.^[32] Example Raman spectra are provided in Figure 2.2.

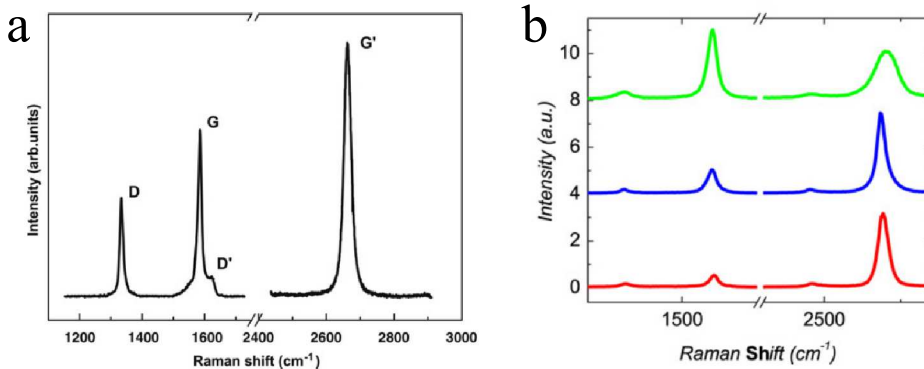


Figure 2.2: Raman of graphene. (a) “Raman spectrum of a graphene edge, showing the main Raman features, the D, G and G’ (or 2D) bands taken with a laser excitation energy of 2.41 eV.” (b) “Raman spectra of 1-LG (red), 2-LG (blue), 3-LG (green) prepared by a CVD process based on a Ni(111) precursor and then transferred to a SiO₂/Si substrate. Adapted from Malard *et al.*^[32]

2.2.1.2 Synthesis

Synthesis of graphene was initially performed by mechanical exfoliation. This is a very simple technique in which a piece of high quality graphite is repeatedly cleaved until a dispersion of flakes of mono- to few-layer graphene remain.^[1] The resultant graphene flakes will be single crystals of high quality, with excellent electronic properties since grain boundaries and defects are principle sources of carrier scattering.^[23] In the absence of such imperfections, ballistic transport has been observed over micrometer length scales.^[34] This technique has been effective for demonstrating the fundamental

properties of this material, but is critically limited to the laboratory scale because it can only produce flakes up to a maximum of millimetre dimensions.^[13]

A related process, liquid phase exfoliation (LPE), can be used to produce a suspension of graphene flakes of nanometre to micron scale.^[35] There are a number of techniques used to achieve this, but all involve breaking down flakes of graphite in solution.^[13] This overcomes the small scale limitation of mechanical exfoliation, since this solution can then be prepared into large scale polycrystalline films. However, due to the large number of defects, small grain sizes, and most damningly the high electrical resistance between grains—a result of the van der Waals bonding that connects them—these films are not suitable for high performance electronics.^[35]

To overcome the inherent issues of these ‘top-down’ processes, a number of ‘bottom-up’ methods have been developed. Epitaxial growth of graphene by the graphitisation of silicon carbide (SiC) substrates through thermal decomposition permits the production of larger areas of mono- to few-layer graphene. Growth on the crystallographic planes or terraces leads to the formation of areas of extremely flat and low-defect material. However, this technique is typically limited to the production of small scale films, and layer number is inherently difficult to control as the decomposition is not self-limiting.^[36] Although it is not always necessary since SiC is insulating and so compatible with device fabrication, transfer from the growth substrate (e.g. for flexible electronics) may also prove problematic.^[36,37]

A more viable technique for large scale manufacture that is compatible with roll-to-roll manufacture, chemical vapour deposition (CVD) is a technique that has allowed the production of large scale graphene films that, while not as high quality as those

produced by mechanical exfoliation or decomposition of SiC, are significantly better than those produced from LPE suspensions.^[37,38] This technique involves decomposing a carbon containing precursor, diluted in a flowing inert gas shield, over a catalytic substrate for graphene to grow on (Figure 2.3).^[38,39] This has been demonstrated on a number of different substrates, most commonly using the transition metals copper^[40] and nickel,^[26] though several other metallic (e.g. palladium,^[41] ruthenium,^[42] and iridium^[43]) and less commonly non metallic (e.g. SiO₂, Al₂O₃, MgO, Ga₂O₃, and ZrO)^[44] substrates are also viable. Given the overwhelming prevalence of metal substrates in the CVD of graphene, they will be the focus of this section.

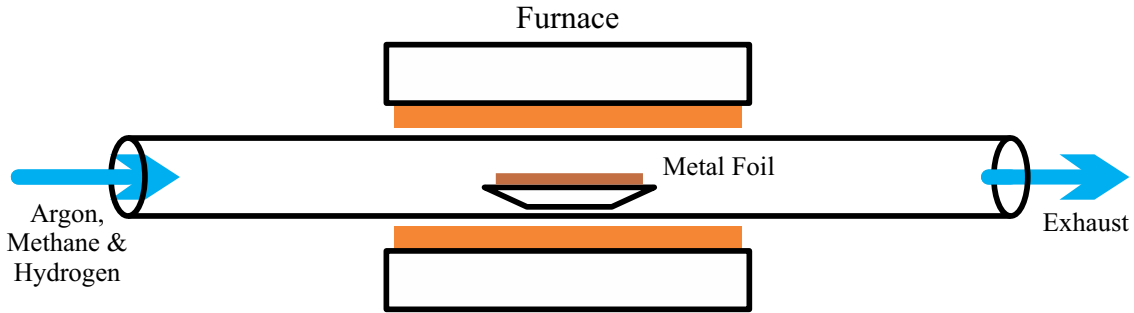


Figure 2.3: Schematic of CVD setup for graphene.

In metals where carbon can dissolve, such as nickel, growth of graphene is achieved by decomposition of a carbon containing precursor at elevated temperature such that carbon dissolves into the substrate, followed by segregation to the surface driven by the reduction in carbon solubility as the temperature is lowered. Before growth, the foil is first annealed in the presence of hydrogen to increase the grain size and reduce surface oxides.

Growth on these substrates is inherently difficult to control, as the thickness of the graphene produced depends strongly on the amount of carbon dissolved (itself

a function of precursor pressure, exposure time, and foil thickness) and the cooling rate.^[23,45] High cooling rates result in too much carbon segregating to the surface, producing thick graphitic layers; low cooling rates limit segregation to the surface since carbon diffuses into the bulk, inhibiting growth. Similarly, very high cooling rates prevent growth by quenching the substrate and preventing diffusion to the surface.^[46] Further complicating matters, carbon preferentially segregates to grain boundaries, resulting in thicker graphene in these areas.^[38]

A preferable substrate is one in which carbon has very low solubility, such as copper. In this case, growth is achieved not by segregation but by adsorption onto the substrate surface. As with nickel, the foil is annealed in the presence of hydrogen before the carbon is supplied by decomposition of a precursor. Growth occurs when there is sufficient saturation of carbon on the copper surface for nucleation to occur, which will then grow and coalesce into a polycrystalline film provided there is sufficient carbon supply.^[38] Due to its low reactivity, copper requires growth temperatures of over 1000 °C, but unlike nickel low pressure is not needed since there is no need to prevent excess carbon dissolution.^[47] Another advantage is that this process is largely surface limited and therefore monolayer films are much more readily achievable, which has meant that copper has largely superseded nickel.^[38]

Though the surface-only process simplifies growth somewhat, parameters must still be carefully controlled: insufficient supply of carbon will result in incomplete coverage; excess supply leads to a large number of nuclei and so a fine grained film, as well as producing bilayer or thicker regions at the nucleation points.^[47,48] To obtain the highest quality films a balance must be found between these two extremes.^[48]

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Another factor is the quality of the copper foil, as nucleation is favoured on surface imperfections such as roughness and grain boundaries. To limit nucleation, foils are polished to reduce roughness,^[49] and annealed prior to the precursor introduction to encourage grain growth.^[19,50]

2.2.2 Transition Metal Dichalcogenides

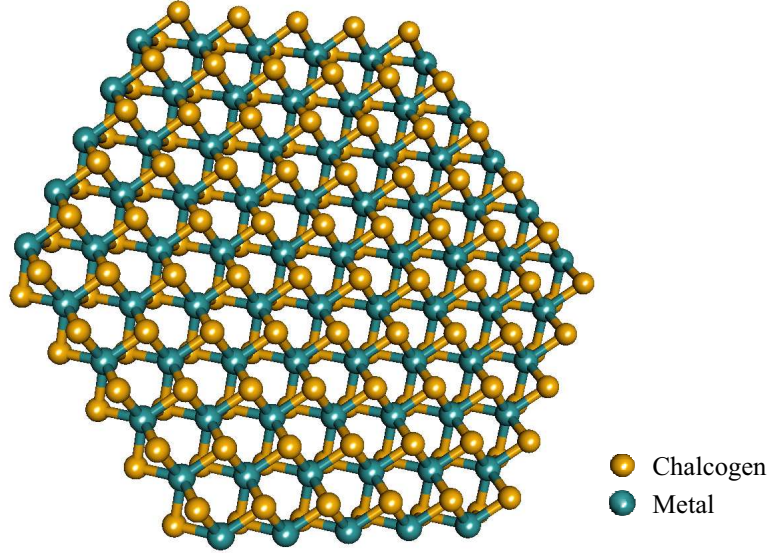


Figure 2.4: General structure of 2H-transition metal dichalcogenides.

2.2.2.1 Properties

Transition metal dichalcogenides (TMDs) are a subset of the layered metal dichalcogenides, a large family of materials consisting of one metal atom to every two chalcogen (group 16) atoms that can commonly be isolated into monolayer form.^[7] TMDs are the most extensively studied in this area, with properties ranging from metallic to semiconducting depending on the crystal structure and transition metal used.^[3] This review will focus on those that are semiconducting, since they are most pertinent to flexible electronics.

Within the study of semiconducting TMDs, the vast majority of work has been performed on those based on molybdenum and tungsten, though there is evidence that several others such as titanium, zirconium,^[51] and tin^[52] also display this behaviour.^[3]

2.2. FUNDAMENTALS OF 2D MATERIALS

All of these materials have similar physical and electronic properties, so what follows will be a general description based primarily on studies of W- and Mo-dichalcogenides.

Like graphene, TMDs are physically robust. MoS₂ has been found to have a Young's modulus of ~ 270 GPa, breaking strength of ~ 15 Nm⁻¹,^[53] and failure strains up to 25 %.^[54] As with other 2D materials they are highly transparent to visible light, with absorption varying but typically less than 5 %, but unlike graphene some wavelengths will be more strongly attenuated due to bandgap absorption.^[55,56]

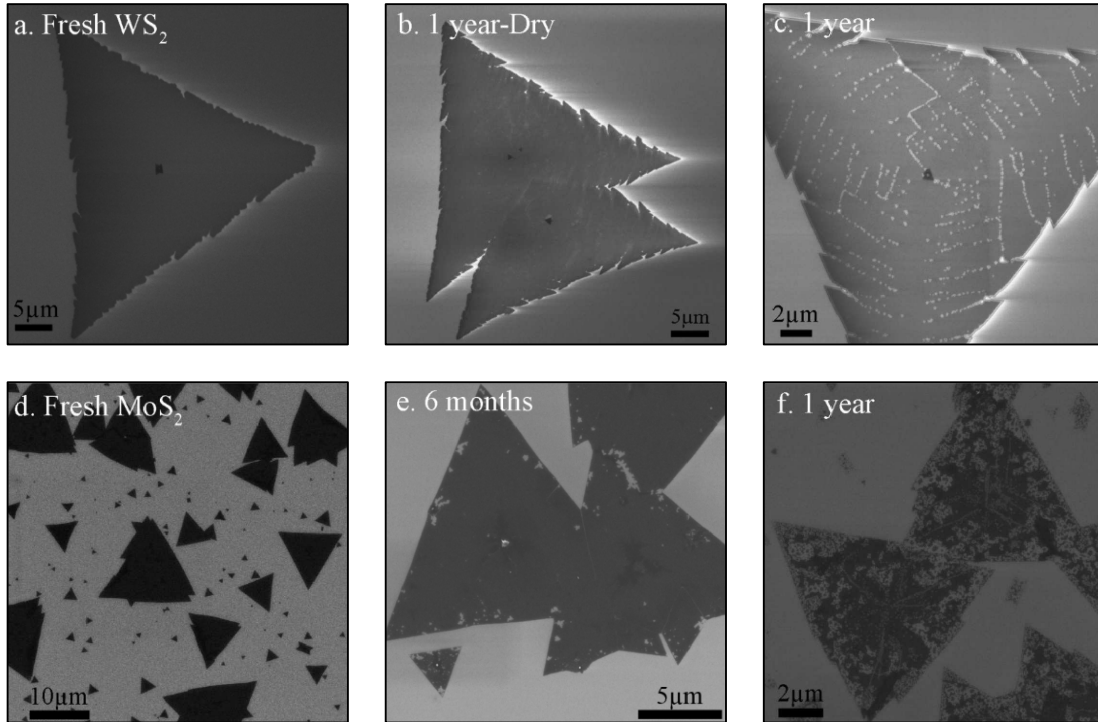


Figure 2.5: SEM images showing the degradation of WS₂ and MoS₂ over the course of one year in class 100 cleanroom conditions. (a) As grown WS₂ was stored under (b) dessicated and (c) un-dessicated conditions for one year. (d) As grown MoS₂ was stored under atmospheric conditions and imaged after (e) six months and (f) one year. In both materials fragmentation of the crystals is clearly visible. Adapted from Gao *et al.*^[57]

One problem facing the integration of TMDs into electronic devices is their tendency to degrade under ambient conditions. They are easily oxidised, beginning at existing defects and leading to a loss of chalcogen atoms over the course of several

months as they are substituted for oxygen.^[57,58] This effect can also be mediated by photoexcitation,^[59] and electronic biasing.^[60] Figure 2.5 shows the effects of such degradation on WS₂ and MoS₂. The resultant fragmentation of the crystals and breakdown of electronic properties will necessitate strategies to inhibit this effect and ensure stable device performance over long periods. Graphene had been shown to inhibit the oxidation when placed beneath WS₂, by screening the surface electric fields around the initiating defects.^[58] Encapsulation with hBN is another viable strategy to inhibit degradation.^[59]

In monolayer form, these materials are direct band gap semiconductors (in the 2H co-ordination shown in Figure 2.4; the 1T co-ordination leads to metallic behaviour but is commonly less stable^[14]) with gaps that range from visible to near-infrared, decreasing with increasing chalcogen atomic mass.^[19] This direct band gap develops from the indirect gap of the bulk due to a combination of quantum confinement and loss of interlayer coupling, raising the energy of the T_C point and lowering the energy of the Γ_V point until the gap shifts from the $\Gamma_V \rightarrow T_C$ transition of the bulk, to an intermediate $\Gamma_V \rightarrow K_C$ for 2–4 layers and finally to $K_V \rightarrow K_C$ in monolayer (Figure 2.6).^[61]

The Raman spectra of TMDs has two characteristic peaks that are also indicative of the number of layers present, the E¹_{2g} and the A_{1g}. The E¹_{2g}/A_{1g} intensity ratio is >3 in monolayer, decreasing to ~2 in bilayer and decreasing further in thicker flakes.^[62,63] An example of the Raman spectrum of monolayer of WS₂ is provided in Figure 2.7a. Due to the excitation wavelength of 532 nm used, here there is also a secondary acoustic mode (2LA(M)) centred at approximately the same shift as the E¹_{2g}—individual contributions may be revealed by Lorentzian fitting.

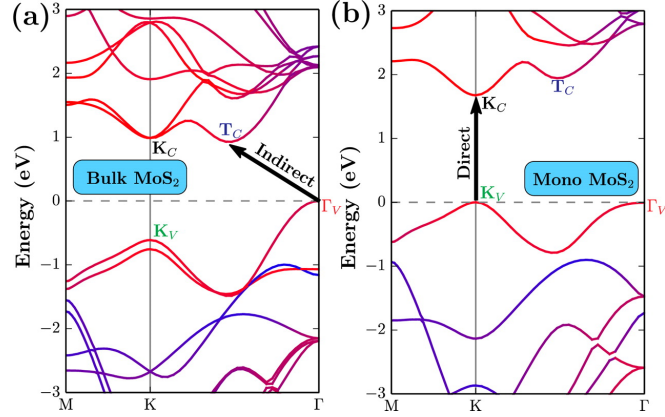


Figure 2.6: Band structure in (a) bulk and (b) monolayer MoS_2 . A similar evolution of the band structure occurs in WS_2 . Adapted from Zhang & Zunger.^[61]

Due to the direct band gap, monolayer TMDs show strong photoluminescence (PL). The room temperature spectrum consists primarily of two transitions, an exciton (A) and a trion (A^-/A^+). A trion is a charged quasiparticle consisting of an exciton bound to an electron or hole, whose population is determined by the level of doping in the material, with negative trions dominating in n-type material and positive trions dominating in p-type.^[64,65] Owing to the strong spatial confinement and reduced screening, the interaction parameter in TMDs is high, meaning that excitons are strongly bound and enabling trions to remain significant at room temperature.^[64,66] The density of trions may be tuned by adjusting the doping, for example by the application of an external electric field, to levels exceeding the density of neutral excitons and therefore dominating the emission spectrum.^[67] Another excitonic transition (B), corresponding to a higher energy transition to a lower level in the spin-orbit split valence band, is generally not observed in PL spectra since the high density of states means that most carriers can be accommodated in the higher energy level.^[68,69] An example PL spectrum from monolayer WS_2 is shown in

Figure 2.7b.

As a result of the transition to an indirect band gap, PL intensity decreases sharply with increasing layer number and is negligible in bulk TMDs. This can enable simple identification of any monolayers present in a sample.^[68] Furthermore, the application of strain can be used to modify this and has been shown to produce an indirect–direct transition and consequent giant enhancement of PL in many TMDs such as bilayer WSe₂,^[70] while conversely leading to a direct–indirect transition in monolayer crystals.^[71]

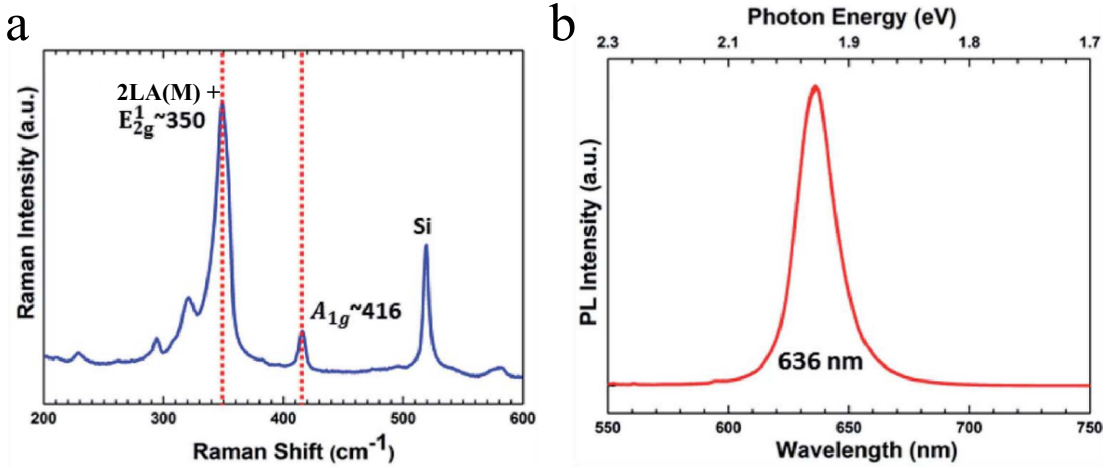


Figure 2.7: Spectroscopy of WS₂. (a) Raman and (b) PL spectra taken from a monolayer WS₂ domain. Adapted from Rong *et al.*^[62]

Though it is several orders of magnitude lower than that of graphene, the carrier mobility in TMDs is still reasonable and is comparable to that of silicon at up to $\sim 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[19] This value is very sensitive to substrate disorder and will be drastically reduced by the presence of surface roughness, trapped charges, chemical bonding etc., so substrate selection is key to ensuring high quality devices.^[72] Hexagonal boron nitride is a promising material for this application as it can provide

good surface flatness and high dielectric screening of the underlying substrate, thereby acting to increase carrier mobility.^[73,74]

2.2.2.2 Synthesis

Like graphene, synthesis of free monolayer TMDs was initially achieved by mechanical exfoliation, a process which produces high quality flakes but is severely limited in the scale of the crystals it can produce.^[75] Preparation of liquid phase solutions has been possible since the 1980s, most effectively by intercalation of lithium ions between layers in bulk TMD crystals, followed by exposure to water so that the lithium reacts and produces hydrogen gas that pushes the layers apart.^[76] This technique has the disadvantage of causing a phase change to 1T, changing the behaviour to metallic and requiring annealing to restore the 2H structure.^[77] LPE is also possible without intercalation—for example by using ultrasonication—but the yield of monolayer flakes is comparatively poor.^[78] The suspensions can then be processed into films, but their usefulness is hampered by their low quality.^[79,80] Driven by the need for higher quality films and encouraged by successes in the synthesis of graphene, there has been a large amount of research into growing TMDs by CVD.^[80,81]

CVD of these materials is complicated by the fact that they are composed of two elements, and that these elements do not typically have suitable gaseous precursors since those that exist are usually highly hazardous and require complex handling.^[82,83] The difficulties are further compounded by the fact that unlike the surface limited growth of graphene on copper where the formation of monolayers is favoured, TMDs have a propensity to form multilayers,^[84] nanoparticles, or wires.^[62,85,86] In spite of

this, techniques have been successfully demonstrated either involving evaporating a transition metal-containing precursor and chalcogen upstream of a substrate (Figure 2.8),^[62,87] or exposing a substrate coated with the metal or a containing precursor to chalcogen evaporated upstream.^[82,88,89]

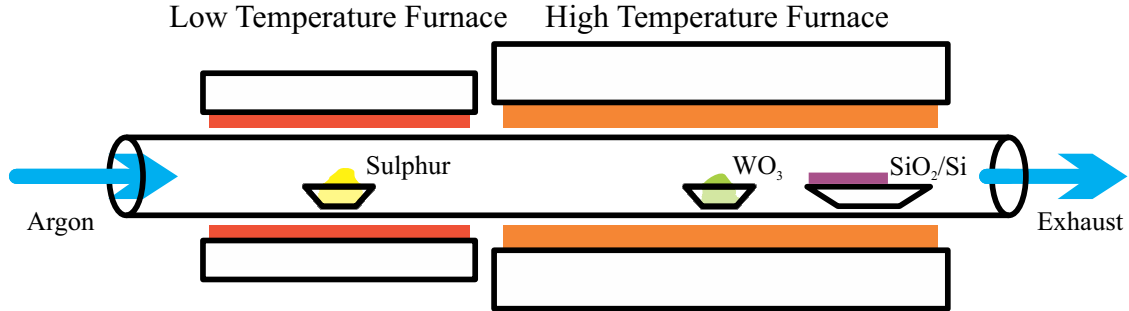


Figure 2.8: Schematic of CVD setup for WS₂. Other TMDs may be grown by this method using appropriate precursors.

The majority of TMD CVD has been performed using SiO₂/Si substrates, though other insulating substrates such as sapphire,^[88,90] fused silica,^[82] and hexagonal boron nitride,^[91] as well as gold foils^[83] have also been demonstrated. The process is still in its infancy, and until recently the growth of spatially homogeneous monolayer films has eluded researchers.^[82] What follows will be a description of current techniques for synthesis using silicon substrates.

Two zone vapour transport, in which both precursors are evaporated separately and passed over the substrate, was first demonstrated in 2012 for MoS₂ synthesis.^[87] In this process the metal containing precursor (usually an oxide) is evaporated in a flowing inert gas shield and deposits onto the surface of a substrate at high temperature, which is then exposed to chalcogen atoms and reacts to form crystals of TMD. While this process was initially performed using a single furnace, it has been found that better control of the process can be achieved using two furnaces—one for the

chalcogen and one for the metal precursor and substrate.^[62,87] Using this technique large triangular domains have been demonstrated up to several hundred microns in size, though coverage is in general inhomogeneous, with high density toward the centre of the substrate and sparse coverage at the edges.^[62] Nucleation can be seeded, commonly using graphene derivatives such as reduced graphene oxide (rGO),^[87] but this will result in degraded electronic properties due to impurities in the final film and a finer grain structure, so is not favoured.^[83]

An alternative method involves coating the substrate with the metal precursor and sulphur/selen/tellur-ising it at elevated temperature under inert gas shield. This process is similar to the two zone vapour transport method but has the potential to more reliably provide complete coverage if a homogeneous distribution of the metal precursor can be achieved. As for two zone vapour transport it was first demonstrated in 2012 for MoS₂ synthesis, using electron beam evaporation of Mo metal^[89] or a solution of (NH₄)₂MoS₄,^[88] followed by sulphurisation at high temperature. Some monolayer regions were observed for the metal coated substrate but in general thicker material was produced, rendering this process unsuitable for large scale monolayer production.^[88,89]

Recent work has shown that it is possible to grow continuous monolayer films. Gold foils have been shown to be suitable catalysts for monolayer growth by a surface mediated process, and films have been grown with grain sizes up to 420 μm , using ammonium metatungstate and H₂S.^[83] Another technique used molybdenum or tungsten hexacarbonyl (both highly toxic gaseous precursors) and (C₂H₅)₂S at low pressure to grow 4 inch films on fused silica substrates by controlling the precursor

supply so that edge attachment was favoured, but the grain size was limited to micron scale, with a maximum size of $\sim 15\text{ }\mu\text{m}$.^[82] Larger crystals have still more recently been demonstrated using both CVD growth and decomposition growth on sapphire substrates.^[92]

2.2.3 Hexagonal Boron Nitride

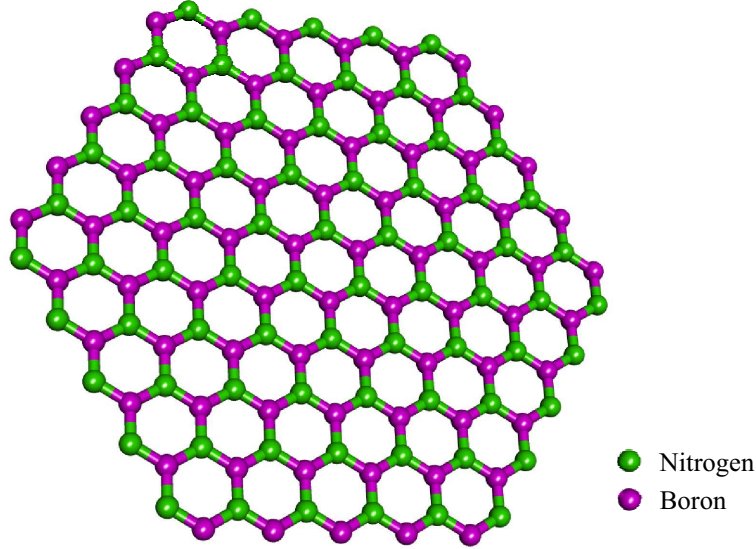


Figure 2.9: Structure of hexagonal boron nitride.

2.2.3.1 Properties

Hexagonal boron nitride (hBN) is a material that is structurally very similar to graphene, with the carbon atoms replaced alternately by boron and nitrogen atoms, as shown in Figure 2.9.^[93] Though not as impressive as those of graphene, the mechanical properties of hBN are still very good, with a measured breaking strength of 15.7 Nm^{-1} and comparable stiffness at up to 880 GPa.^[11,93,94] The lattice parameter of hBN closely matches that of graphene, differing by around 2 %.^[94] So far the fracture strain has lagged behind the theoretical value of 24 % with measured values of 3–4 %, but this may be an issue of material quality as others such as graphene and MoS_2 have both been shown to have good agreement between measurement and theory.^[11]

Despite its structural similarities, in its electronic properties hBN differs greatly

from graphene: it is an insulator with a wide band gap of 6 eV and high electrical resistance.^[95] The dielectric constant decreases as it is thinned down to monolayer but is still high at 2.31, 2.43, and 2.49 for mono-, bi-, and trilayer films respectively.^[96] This has lead to interest in its use as a complementary material for metal-insulator^[94] and other device applications in conjunction with other 2D materials.^[96]

hBN has even lower optical absorption than graphene, with broadband visible absorption at $<1\%$, and stronger absorption beginning at 202 nm due to excitation of carriers across the bandgap.^[94,97] The Raman signal of hBN shows a single characteristic peak analogous to the G peak in graphene at $\sim 1366\text{ cm}^{-1}$ for bulk material that blueshifts up to $\sim 1368\text{ cm}^{-1}$ in bilayer and $\sim 1370\text{ cm}^{-1}$ in monolayer, as shown in Figure 2.10.^[98]

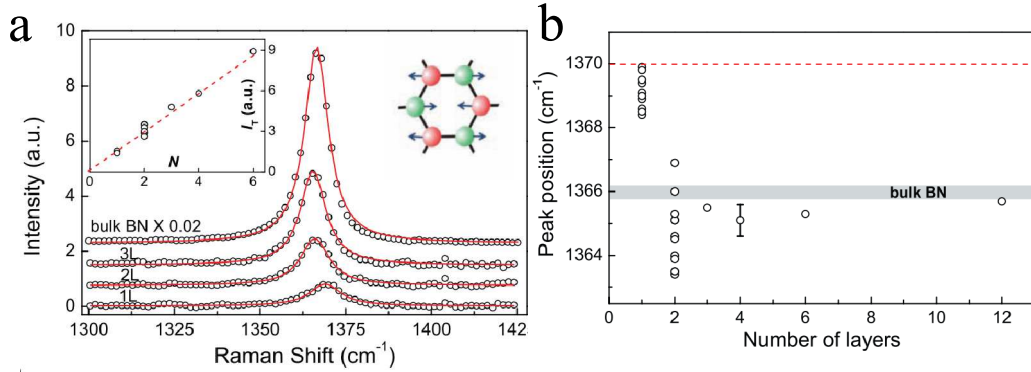


Figure 2.10: “(a) Raman spectra of atomically thin hBN. The left inset show changes in integrated intensity I_T with the number of layers N . The right picture illustrates the phonon mode responsible for the Raman peak. (b) Position of the Raman peak for different values of N . In mono- and bilayer hBN, the peak position is sample-dependent and varies by as much as $\pm 2\text{ cm}^{-1}$. The dashed line is the Raman shift predicted for monolayer hBN, compared to the bulk value (grey bar). The error bar indicates the typical accuracy of determining the peak position using our spectrometer.” Adapted from Gorbachev *et al.*^[98]

2.2.3.2 Synthesis

Once again, synthesis of monolayer hBN was first achieved by mechanical exfoliation.^[75] Liquid phase exfoliation can also be performed.^[97] Both of these techniques still suffer from the problems outlined for graphene in Section 2.2.1.2.

CVD has been demonstrated to be an effective technique for producing thin films of hBN, using a process very similar to graphene.^[94] Catalytic substrates such as copper,^[93,94] nickel,^[99] and platinum^[100] have been successfully employed to produce films with full coverage over the substrate, but control over this process is less well understood and the films produced are typically fine grained structures of mono- to few-layer material.^[94] Recent developments using electropolished copper substrates have had some success at replicating the advances in the CVD of graphene, with continuous monolayer films synthesised with grain sizes up to $\sim 35\text{ }\mu\text{m}$.^[94] A number of different precursors have been employed, in general solids such as polymeric aminoborane^[94] or ammonia borane, which are thermally decomposed to release borazine,^[100] or indeed liquids such as borazine itself.^[99] Earlier work often used high vacuum,^[101,102] but most recent work has focussed on ambient pressure synthesis.^[94,100] Chang *et al.*^[103] recently demonstrated that the growth morphology could be coarsened by limiting nucleation through controlled passivation of the copper growth substrate by means of an oxide layer. In all cases the process in general involves the decomposition of a precursor by heating in a flowing inert gas shield in the presence of hydrogen, which then passes over the substrate so that a film is deposited (cf. CVD of graphene, Section 2.2.1.2).^[94] A schematic of the typical CVD setup is shown in Figure 2.11.

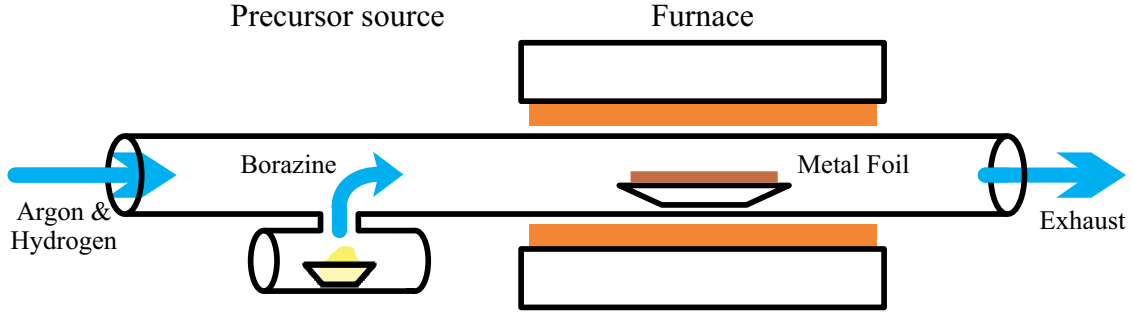


Figure 2.11: Schematic of CVD setup for hBN.

2.2.4 Friction in 2D Materials

Friction in graphene and other 2D materials is complex and the subject of ongoing research, both by simulation^[104] and experimentally—using techniques such as atomic force microscopy (AFM),^[105] and Raman and photoluminescence (PL) spectroscopy.^[106] Li *et al.*^[104] used molecular dynamics simulations to model the interaction of a silicon tip with graphene of various layer numbers, showing an increase in friction as the layer number decreases due to increased puckering around the probe tip. They further demonstrated that a previously inexplicable transient increase in the friction force over the first few atomic periods results from the formation of progressively deepening traps at the interface, with out-of-plane deformation increasing the quality of frictional contact. The material boundary condition is also important, where a loose and wrinkled sheet shows much higher friction than a tight and smooth one. This will have relevance to 2D electronics, with devices composed of stacks of different 2D materials of differing geometries, and demonstrates the importance of out-of-plane deformations.

Due to the weak van der Waals out-of-plane bonding, it is reasonable to expect in-

complete transfer of strain from the substrate to the 2D materials.^[107–110] Liu *et al.*^[106] used Raman and PL mapping to study the distribution of strain within triangular domains of monolayer MoS₂ on strained polydimethylsiloxane (PDMS) substrates, finding that at higher strains only $\sim 10\%$ of strain is transferred, and that transferred strain propagates through the triangle beginning at the point aligned most closely with the strain axis. Though incomplete strain transfer has previously been observed in 2D materials on soft substrates under tension, with the well documented impact of strain fields and inhomogeneities on 2D materials there is significant scope for improvement in the description of the mechanism and its influence on different heterostructures.^[111,112]

2.3 Devices

Although it will be difficult for heterostructured devices composed of these materials to compete with the well-established semiconductors such as silicon and III-Vs in established high-performance applications,^[11] many novel device designs have now been produced with interesting and sometimes unique properties.^[20,113–115] One area in which they compare more favourably is in flexible and/or transparent electronics, with comparable strain resilience^[3,11,19] and optical transmissivity,^[8,116] and carrier mobilities often far exceeding those of competing technologies such as conducting polymers.^[11]

The local environment can strongly influence the properties of 2D materials due to their high specific surface area;^[117,118] this typically manifests as changes to the doping level or bandgap,^[118–121] but can also lead to shifts in work function and strain.^[122] For this reason, it is necessary to have an understanding of the interactions between 2D materials in heterostructures. The field of flexible electronics provides a further complication in the form of strain, which can again cause changes to the bandgap and modify the interactions between the different materials.^[16,107,123–126]

As we have already touched upon, in recent years there has been considerable interest in the use of 2D materials in flexible electronics. There have been a great many demonstrations of devices composed of graphene, as well as heterostructure devices making use of a wide range of different 2D materials; however to date the realisation of on chip fabrication using scalable processes has typically remained outside the scope of the majority of work, which has focused instead on small scale

proofs of concept.^[14,37,92,127–130] There has also been extensive research into the deposition of liquid phase exfoliated material in the form of inkjet^[131,132] or otherwise printed devices,^[19,37,79,131–136] but limited research into devices composed of the large area, high quality materials obtainable by CVD. As such, more research is needed into the fabrication techniques for producing devices using scalable methods, and the characterisation of their properties, particularly during the application of strain.

There are significant limitations placed on the possible fabrication and processing techniques when using polymeric substrates. This is due to their typically lower thermal and chemical stabilities and, in contrast to silicon (SiO_2/Si) wafers specifically, their lack of conductivity and intrinsic back gate. For this reason, it is necessary to modify the conventional methods for truly scalable production, i.e. complete on chip fabrication, without electron beam lithography.^[137–139] The impressive properties of the materials described above can only be realised in real world applications by combining them together into devices. This section will outline current work in this area, concentrating on studies of flexible electronics, as well as technologies demonstrated on rigid substrates that may be suitable in this application.

2.3.1 Advantages of 2D Materials

There are a number of factors that make 2D materials attractive candidates for flexible electronics. Foremost, there are clear advantages in the electronic properties, especially carrier mobility. This is a parameter which has severely hampered implementation of high performance devices, since it has lagged behind conventional rigid material performance significantly.^[37] Especially in the case of graphene but also—and

more pertinently to the performance of many devices—in TMDs, mobilities several orders of magnitude above competing organic, metal-oxide, and other technologies are possible (Figure 2.12a). This parameter is important as it affects the device performance in several ways, namely maximum current density, energy efficiency, and maximum switching speed and cut-off.^[11]

From the perspective of form factor, the atomic scale of all 2D materials means they will have a smaller contribution to device profile and weight than any of the alternatives.^[37] Another advantage of the extreme thinness is that it enables highly effective electrostatic control, due to more effective penetration of electric fields. This has further implications for reductions in device scale, since e.g. in transistors the channel length must be >3 times its thickness, making a thinner channel desirable from a scaling standpoint.^[140] Flexibility will also be superior in devices built from 2D materials as the strain to failure of the raw material outperforms all other competitors by at least a factor of 2, with comparable devices built from these materials almost matching this improvement (Figure 2.12b).^[11] The extremely low optical absorbance of these materials (typically $<5\%$) enables devices with unparalleled transparency.^[8,116]

Finally, the relatively weak van der Waals interaction between layers means that heterostructure devices can be fabricated without significant interfacial strain by simple stacking of different materials, as opposed to the complicated techniques required for other materials.^[141] This greatly reduces the complexity of heterostructure device fabrication, broadens the number of possible junctions compared to other crystalline materials where deposition techniques require close matching of lattice

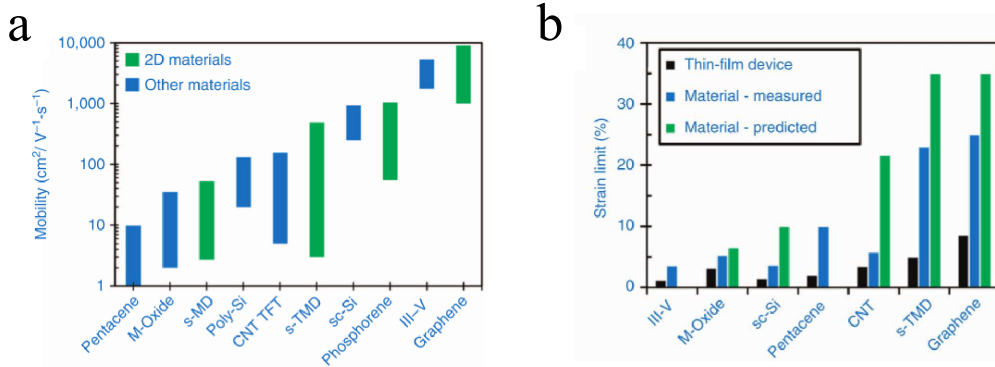


Figure 2.12: Comparison of the (a) mobilities and (b) strain limits of competing thin film materials. Adapted from Akinwande *et al.*^[11]

parameters,^[3] and completely removes the problem of interfacial mixing commonly observed in organics.^[142] In addition, the ease of out-of-plane deformations allows arbitrarily stacked layers a high degree of conformation with underlying features.^[3,23]

2.3.2 Issues & Challenges

Despite the numerous advantages outlined above, there are a number of problems which must be overcome before wide scale adoption is possible. Though it is not limited to 2D materials, heat dispersion is a challenge in thin film flexible electronics due to poor thermal conductivity and lower maximum operating temperatures of the polymer substrate materials, and is most pronounced in 2D devices due to the high current densities required.^[11] Studies of graphene show that Joule heating can lead to peak temperatures in excess of 300 °C,^[143] which is high enough to damage most substrate materials, for example exceeding the glass transition temperature of poly(ethylene terephthalate) (PET),^[144] poly(ethylene naphthalate) (PEN),^[145] and poly(ether sulphone) (PES), and above the operating temperatures of others such as polyimide (PI).^[37]

Typical thermal management strategies in conventional electronics involve the use of a metallic heat sink with large surface area to efficiently transfer heat to the air, but this is clearly not suitable in flexible electronics, and there is little research into heat management strategies in this area.^[11] Lee *et al.*^[146] suggested an elegant strategy in which the anisotropic thermal conductivity of a multilayer hBN film is exploited to form an efficient heat spreader, with the low out-of-plane conductivity limiting heat transfer into the substrate and the high in-plane conductivity dispersing the heat over a wide area. This combined with the aforementioned property of hBN to enhance carrier mobility when employed as a substrate for other 2D materials make it a very attractive material in this application.^[74,147]

A related issue to the thermal management problem is device fabrication. Many fabrication processes involve annealing steps to clean surface adsorbates^[23,148] and transfer scaffold residues,^[8,149,150] or increase conformation of stacked layers^[22] to improve device quality, using temperatures that again exceed the operating temperatures of most polymer substrates. The decreased carrier mobility and general lower quality of flexible devices as compared to their rigid-substrate counterparts can partially be explained by this limitation.^[8]

There have recently been some developments in overcoming these problems using alternative strategies. Wood *et al.*^[149] explored alternative polymer materials to replace the de rigueur poly(methyl methacrylate) (PMMA) scaffold, and found that polycarbonate scaffolds could be removed using room temperature chloroform to produce an “atomically-clean” surface. It should be noted that the use of chloroform may preclude the use of some substrates.^[151] For the removal of surface adsorbates,

Ovchinnikov *et al.*^[152] used vacuum annealing at pressures down to 5×10^{-7} mbar at a milder temperature of 115 °C to clean a WS₂ transistor and found that mobility increased by an order of magnitude, and on/off ratio increased by nearly two. This technique would be suitable for the more thermally stable substrates such as PEN and PI.^[37]

2.3.3 Device Designs

2.3.3.1 Transistors

Shortly after the discovery of graphene it was widely hoped that it could be utilised in transistors, as its high carrier mobility would enable very fast devices. However, progress has been hampered by its lack of an intrinsic band gap, and the complicated methods required to create one of useful magnitude—such as physical confinement to nanoribbons,^[17] or the application of strain^[16,153,154]—meaning that such transistors effectively cannot be switched off.^[3] TMDs are much more suitable as their large band gaps mean that a low off current is possible, increasing the on/off ratio.^[3,14,19] Another advantage is that the mobility is typically fairly similar for both electrons and holes, which has implications for simplifying combined n- and p-type devices by enabling symmetric device design.^[14] The vast majority of TMD transistors have been demonstrated using MoS₂, but the other dichalcogenides of Mo and W have also been used, among others.^[14]

Flexible thin film field-effect transistors (FETs) were first demonstrated by Pu *et al.*^[128] in 2012 using multilayer MoS₂ and ion gel dielectrics. In this work, built on successes with exfoliated material using rigid substrates and ionic liquid dielectrics,^[155]

trilayer films of MoS₂ were grown by CVD and transferred onto PI substrates, with nickel bonded gold electrodes and an ion gel gate deposited on top to produce an electric double-layer transistor (EDLT). After correcting for capacitance between the ion gel and the source and drain electrodes, the performance of this device was then compared with an identical device fabricated on an SiO₂/Si substrate (Figure 2.13a). A band structure for this device is shown in Figure 2.13b. In the absence of gate bias, current flow is blocked by the Schottky barriers. A positive gate bias will decrease the depletion region width and increase the Fermi level, leading to the formation of Ohmic contacts and increased current flow. Though performance of the device on SiO₂ was superior to the one on PI ($\mu = 12.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ vs. $\mu = 3.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, on/off ratio $\sim 10^5$ vs. $\sim 10^3$), the performance of the flexible device was encouraging. Differences were attributed to interactions with the polymer substrate lowering the quality of the MoS₂. No obvious electrical degradation was observed when the PI device was bent to a radius of curvature of 0.75 mm across the channel direction.^[128]

There have been a number of advancements in this area, with graphene source and drain contacts,^[129] and graphene gate electrodes with a hBN dielectric layer^[8] demonstrated independently, and more recently in conjunction.^[127] Various substrates have been used, but typically PET or PEN are used due to their high chemical and thermal stability.^[8,127,129] Using exfoliated bilayer WSe₂, Das *et al.*^[127] fabricated a device from all 2D materials that was $\sim 88 \%$ transparent with mobility up to $45 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and an on/off ratio 10^7 . The device characteristics were unaltered by strains of up to 2%.^[127] These properties are comparable to equivalent devices fabricated on SiO₂/Si substrates.^[22]

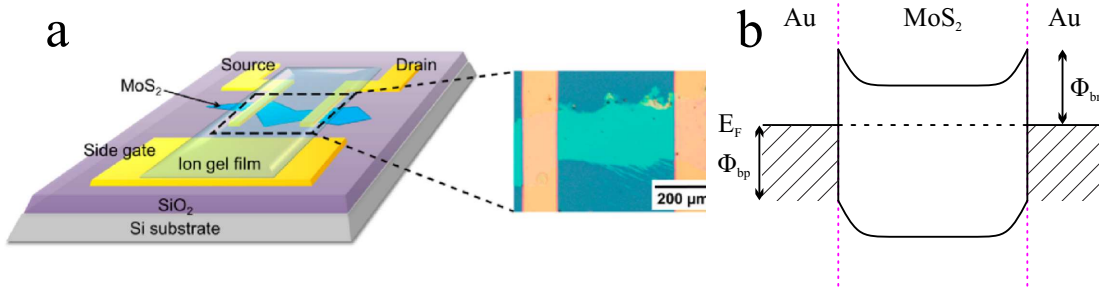


Figure 2.13: (a) Optical image and schematic of ion gel gated MoS₂ EDLT structure. Adapted from Pu *et al.*^[128] (b) Band structure for this device.

Another device design utilises the ultra thin nature of these materials to produce switching in a heterostructure by tuning the Fermi level at the heterointerface to modulate the tunnelling probability through a narrow barrier, enabling an on/off ratio up to 10^6 .^[3] Initially fabricated on an SiO₂/Si substrate that was used as the back gate electrode, this tunnelling field-effect transistor (TFET) consists of two graphene electrodes separated by an insulating layer of hBN or TMD (Figure 2.14). It exploits the low density of states (DOS) in graphene to enable a large increase in the Fermi energy (E_F) in both electrodes for a given gate voltage, decreasing the effective tunnel barrier height and increasing the tunnelling DOS.^[156] This drastically increases current flow by simultaneously increasing both the tunnelling probability and amount of thermionic emission over the barrier.^[156,157]

TFETs have since been demonstrated on PET substrates by Georgiou *et al.*,^[157] using WS₂ as the tunnel barrier, to produce devices that were insensitive to bending up to the 5 % strain tested, and demonstrating very similar behaviour to equivalent devices fabricated on silicon. One disadvantage was the use of the PET substrate as the gate dielectric, limiting the electric field due to the large separation between gate

and junction, resulting in a comparatively poor on/off ratio.^[157] Use of a thicker hBN layer as the gate dielectric, as employed in other 2D transistors, may enable more effective modulation of tunnelling current.^[8] Other, non 2D materials are unsuitable for this device architecture as they do not possess the required dimensions to allow such effective penetration of electric field,^[3] or have too high a DOS to allow adequate increase of E_F .^[156]

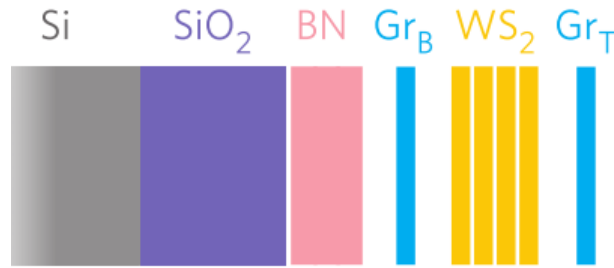


Figure 2.14: TFET structure. Adapted from Georgiou *et al.*^[157]

2.3.3.2 p–n Junction

The fabrication of p–n junctions remains a challenge for 2D materials. A number of factors contribute to this. In TMDs, there are a few intrinsically p-type materials, and very few strategies exist for doping.^[3] Charge transfer doping has seen some successes, a process in which an electron donor or acceptor is applied to the surface to produce n- or p-type doping respectively, but this technique suffers from a lack of long term stability and an increase of optical absorption.^[3,19,158] Conventional semiconductors are typically doped using ion implantation to produce substitutional doping, but—the unavoidable damage associated with this technique notwithstanding—substitutional doping in TMDs can cause unacceptable degradation of carrier mobility, as well as changes to the band structure.^[3,159]

One strategy for producing p-n junctions that has enjoyed some success is to produce a vertical heterojunction from an n-type TMD and a non 2D p-type semiconductor. Jariwala *et al.*^[160] produced such a device using MoS₂ and a film of single-walled carbon nanotubes (SWCNT) that showed strongly rectifying behaviour (forward-reverse current ratio of 10⁴) using a silicon substrate, but this design could equally be produced on flexible substrates given the resilience of CNT films to strain.^[11] Another technique involves applying an electric field to electrostatically tune the doping level in a TMD monolayer, using a split gate architecture to produce regions of n- and p-type that can be individually tuned to modify device behaviour (Figure 2.15). The main drawback of this solution is the need to continuously apply a gate bias, drastically reducing the overall power efficiency.^[161–163]

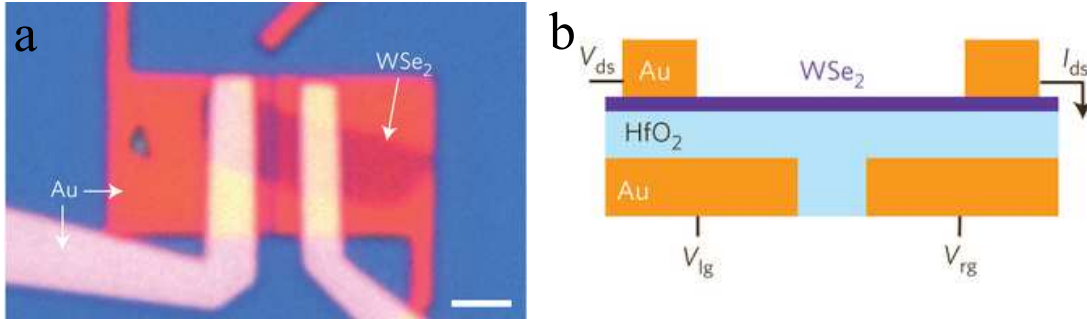


Figure 2.15: (a) Optical image and (b) schematic of split gate p-n junction structure. Adapted from Baugher *et al.*^[163]

By comparison, doping of graphene to produce either n- or p-type material is straightforward. A related structure can be produced by placing an n-type TMD over part of a graphene ribbon, leading to reduced p-type doping and so the formation of a p-p⁺ junction, though this device unfortunately lacks rectifying characteristics.^[164] Images and schematics of the TMD-doped structure are shown in Figure 2.16. Other techniques have been shown to produce sufficient doping to produce true p-n junc-

tions in graphene, using chemical doping, electrostatic gating, or optical gating via photosensitive dye molecules.^[165]

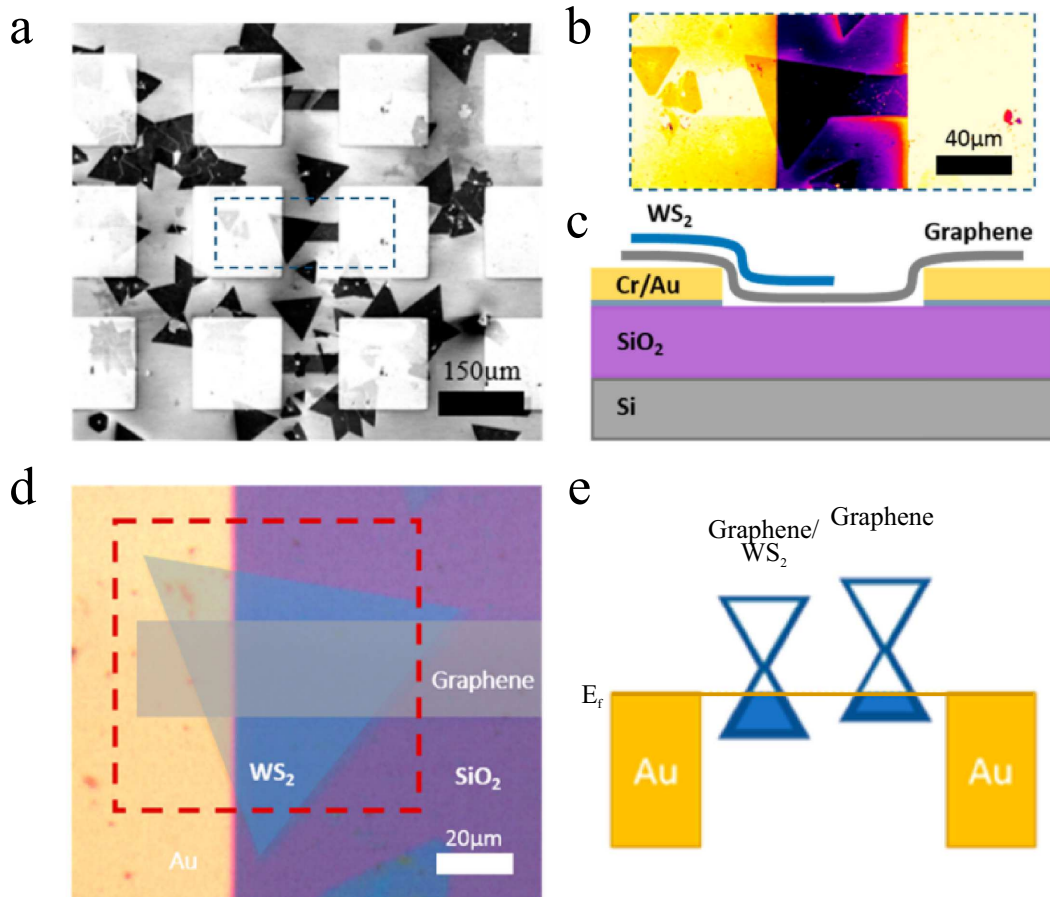


Figure 2.16: p-p+ junction produced by doping graphene using WS₂. “(a) SEM image of devices with graphene channel and vertically stacked WS₂ crystals. Bright square regions are Cr/Au electrodes, which are used as source/drain contacts of the graphene FETs. Dark triangular domains are WS₂ crystals. (b) SEM image with false color of the region indicated in the blue dashed rectangle in panel a. (c) Side view schematic of device structure. (d) Top view optical image of the graphene FET device with WS₂ partial coverage, with added color overlay to help identify the different regions.” (e) “Schematic illustration of band structure of the two distinct graphene regions.” Adapted from Tan *et al.*^[164]

2.3.3.3 Photodetectors

The operation of photodetectors depends on the excitation of carriers by incident light, producing an increase in current flow. The two main device designs exploiting

this principle are phototransistors and photodiodes, with the majority of 2D devices studied so far being phototransistors.^[3] With their direct band gaps in the visible to near-infrared range TMDs are well suited in this application, with low dark current ensured by Schottky barriers, and photogenerated excitons separated by a built in or applied electric field to produce a signal.^[3,19]

Metal–semiconductor–metal (MSM) geometries have been widely studied, with early studies reporting that the photoresponse was dominated by the photothermoelectric effect in which a temperature gradient resulting from absorbed photons generates a voltage across the metal-semiconductor junction due to differing Seebeck coefficients.^[166] However, subsequent studies concluded that while this mechanism contributes to the measured response, the dominant mechanism is still electric field induced separation of excitons,^[167] and a lowering of the Schottky barrier by the filling of trap states at the interface by photogenerated carriers.^[168] Such devices generally show internal amplification of the photocurrent, leading to good responsivity that can exceed 10^3 A W^{-1} , but unfortunately response times (determined by the speed with which carriers can be separated and collected by the source and drain electrodes) are typically poor compared to photodiodes.^[3] Hybrid devices which consist of graphene on MoS_2 have shown even greater responsivity ($R > 10^7 \text{ A W}^{-1}$), with photoexcited electrons injected into the graphene from the MoS_2 , while holes are blocked and act to produce a positive gate voltage. The combination of these effects leads to a very strong increase in conductivity.^[169]

Many of the earlier demonstrations of MSM devices that have been studied were constructed using SiO_2/Si substrates and metal contacts, but since graphene forms

Schottky junctions with TMDs there is scope for producing flexible transparent devices using the same principles.^[170,171] A study by Hu *et al.*^[172] compared the properties of Au contacted monolayer GaS (a related 2D semiconductor) on SiO₂/Si and PET substrates and found that PET increased responsivity by a factor of 4 (up to $\sim 20 \text{ A W}^{-1}$) while the response times remained similar at $\leq 30 \text{ ms}$ (limited by resolution of experimental setup). These values were found to decrease when the films were bent, though this was attributed to a corresponding decrease in the effective irradiance of the device.^[172] More recently there have been demonstrations of devices utilising graphene electrodes, such as graphene–WS₂–graphene,^[121] graphene–SnS₂–graphene,^[173] and graphene–WS₂/MoS₂–graphene.^[174] The latter device showed a significant enhancement of 1–2 orders of magnitude in responsivity over equivalent devices with isolated mono- or bilayers of either MoS₂ or WS₂, up to 1173 A W^{-1} .^[174] Fabrication processes and schematics of the different types of junction detailing the different configurations of monolayer and homo- or heterobilayers of TMDs are shown in Figure 2.17.

The introduction of larger fields to aid in exciton separation can dramatically decrease response times and boost photoresponse. Lei *et al.*^[175] demonstrated an MSM avalanche photodetector based on monolayer InSe (another related 2D semiconductor), by using Al electrodes to produce Schottky junctions and applying a large electric field to generate the avalanche effect. The high potential accelerates photo-generated carriers to energies high enough to produce impact ionisation, generating further excitons and consequent strong amplification of the signal. The response time of this device was $60 \text{ }\mu\text{s}$.^[175] Another strategy to improve response times was

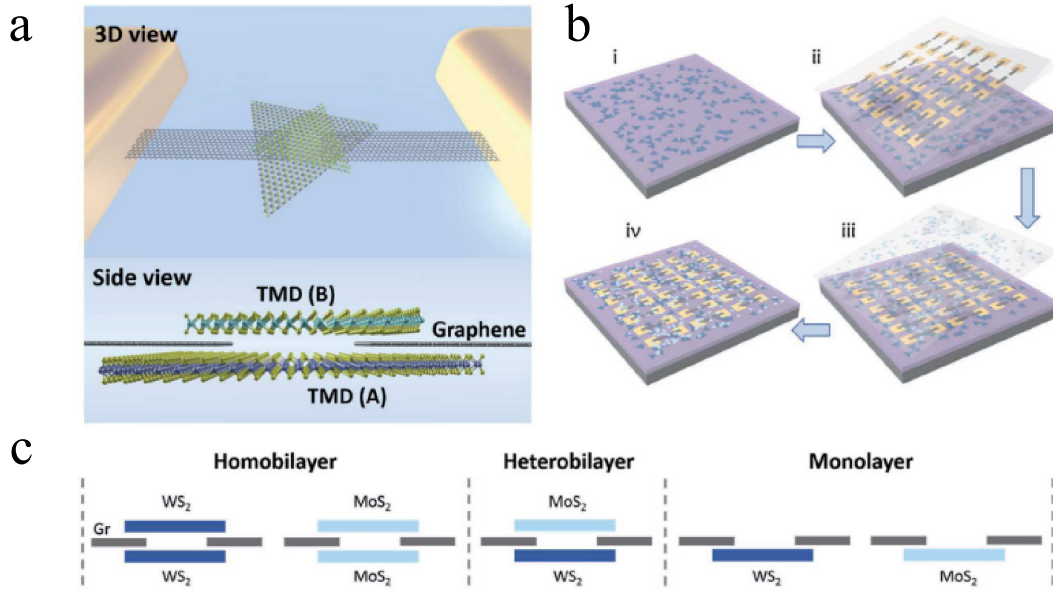


Figure 2.17: “Fabrication schematic and images of hybrid WS₂/MoS₂ photodetector array. a) Schematic 3D and side views of graphene–WS₂/MoS₂–graphene photo- detector. b) Fabrication process schematic of graphene–TMD–graphene photodetector array. Using a PMMA thin-film support, pre-patterned Au bond pads and graphene electrodes are transferred onto silicon chip with pre-transferred TMD (A) domains. For bilayer devices, an additional layer of TMD (B) crystals is subsequently transferred onto the same chip. c) Configuration schematic of the five types of photodetectors designed for this experiment, including WS₂/MoS₂ heterobilayer, homobilayer, and monolayer of WS₂ and MoS₂.” Adapted from Tan & Xu *et al.*^[174]

demonstrated by Yu *et al.*^[170] using a vertical graphene/multilayer MoS₂/graphene heterostructure, where the narrow separation of the two electrodes is significantly smaller than the depletion length and so merges the two Schottky barriers together. The combined band structure slopes upwards towards the contact on the silicon substrate since the silicon oxide increases the Schottky barrier height at this contact by producing p-doping. This sloping band structure efficiently separates photogenerated carriers to produce response times $\leq 50 \mu\text{s}$ (limited by resolution of experimental setup). Large scale arrays of such devices using CVD-derived graphene and monolayer WS₂ have since been demonstrated by Zhou *et al.*^[176] with responsivity in excess of

10^3 A W^{-1} .

Still faster response times may be achieved by using photodiodes. For example, the previously described SWCNT–MoS₂ p–n junctions show poorer responsivity of around 0.1 A W^{-1} , but have response times down to $\leq 15 \text{ }\mu\text{s}$.^[160] The structure and performance of such a device is detailed in Figure 2.18. Progress in producing all 2D devices has again been limited by the difficulty of fabricating p–n junctions due to the lack of techniques for stable doping of TMD films.^[3]

2.3.3.4 Light-Emitting Diodes

As with photodiodes, the difficulty of producing p–n junctions has hampered development of LEDs.^[3] The aforementioned electrostatically doped devices were shown to electroluminesce under bias, with WSe₂ devices showing an external quantum efficiency (EQE) up to $\sim 0.1 \text{ }\%$.^[161,162] This compares favourably to previous reports of electroluminescence in MoS₂ without an electrostatically produced p–n junction, instead arising from impact ionisation across a Schottky barrier (EQE = $0.001 \text{ }\%$),^[177] but is still far behind other flexible technologies.^[141] Moreover, these devices were only demonstrated on SiO₂/Si substrates and may be difficult to replicate on flexible substrates due to the requirement of high applied gate voltage to induce the p–n junction.^[161–163]

A more effective approach has been facilitated by recent advances in heterostructure device fabrication, with early reports of devices with EQE approaching $10 \text{ }\%$ from TMD films.^[141] This compares favourably to organic LED (OLED) technology, where EQEs are typically up to $\sim 15 \text{ }\%$, a promising result considering the rate of

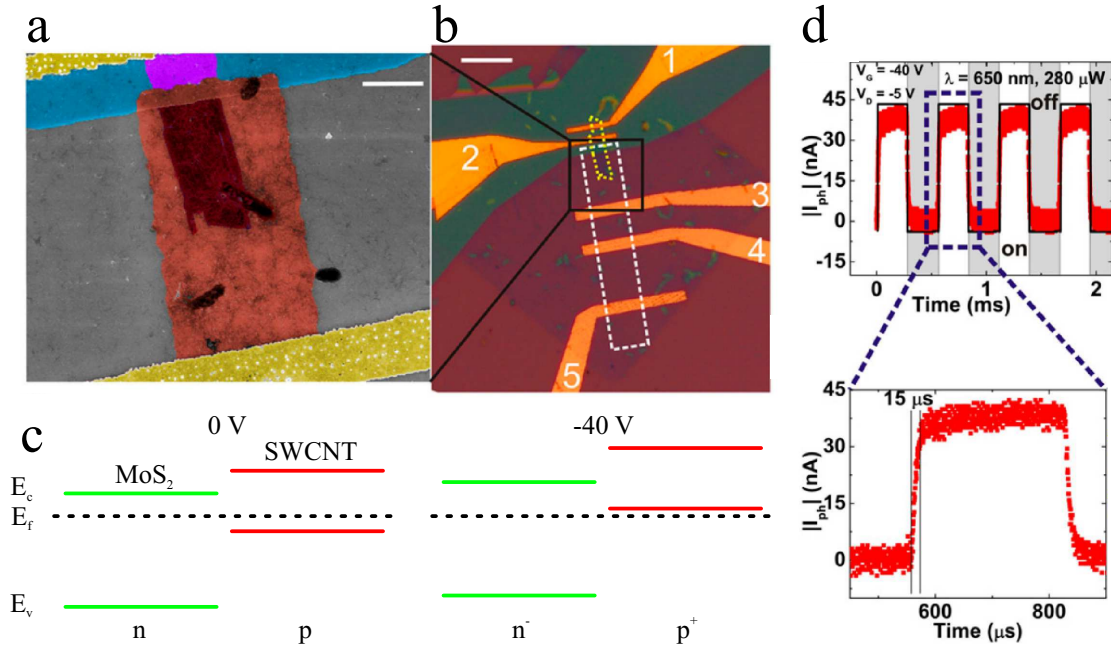


Figure 2.18: “Microscopy and fabrication of the s-SWCNTs/single layer (SL)-MoS₂ p-n heterojunction diode. (a) False coloured SEM image of the heterojunction diode. Scale bar 2.5 μm . The yellow regions at the top and bottom are the gold electrodes. The patterned alumina (blue region) serves as a mask for insulating a portion of the SL-MoS₂ flake (violet region). The pink region is the patterned random network of s-SWCNTs (p-type) in direct contact with the exposed part of the SL-MoS₂ flake (n-type) to form the p-n heterojunction diode (dark red). (b) Optical micrograph showing the device layout at a lower magnification. The dashed yellow boundary indicates the SL-MoS₂ flake, whereas the dashed white rectangle denotes the patterned s-SWCNT film. Electrodes 1 and 2 form the n-type (SL-MoS₂) FET, which is insulated by the patterned alumina film (cyan). Electrodes 2-3 form the p-n heterojunction, whereas 3-4 and 4-5 form p-type s-SWCNT FETs. Scale bar 10 μm .” (c) Band structures at a gate bias of 0 V (weakly rectifying behaviour) and -40 V (strongly rectifying behaviour). “(d) Photodetection using the p-n heterojunction diode: the time-dependent photoresponse of the p-n heterojunction showing fast rise and decay times of $\sim 15 \mu\text{s}$.” Adapted from Jariwala *et al.*^[160]

development of this nascent field, in contrast to the comparatively well developed organic semiconductor industry.^[141,178] The heterostructure devices, demonstrated by Withers *et al.*^[179] in 2015 using both SiO₂ and PET substrates, consist of a monolayer TMD film bounded on each side by bi- or tri-layer hBN to produce a quantum well (QW), which was then contacted by graphene and encapsulated in hBN (Figure 2.19a). The device luminescence arises from tunnelling of electrons and holes

through the hBN layers into the QW, producing excitons that rapidly recombine to emit light due to the direct band gap (Figure 2.19b). This single QW device showed an EQE of $\sim 1\%$.

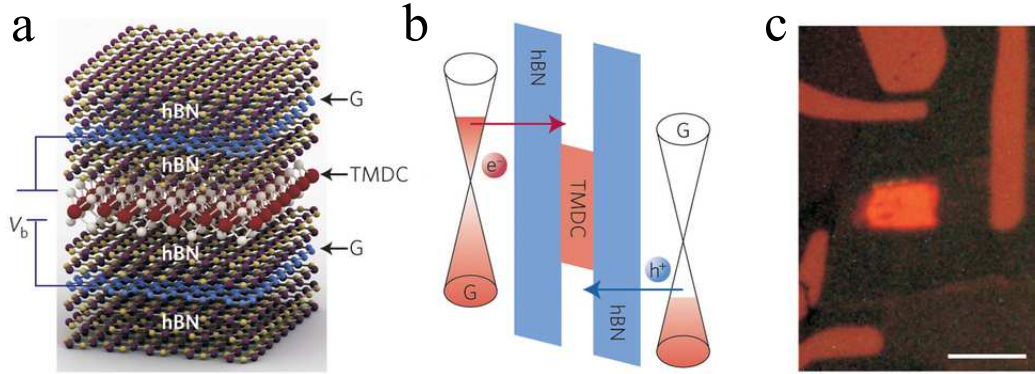


Figure 2.19: SQW LED structure and operation. (a) Ball-and-stick model. (b) Band diagram of the LED under bias showing the injection of electrons and hole through the hBN into the TMD, where they recombine to emit light. (c) Optical image of device in operation showing red light emission. Scale bar 10 μm . Adapted from Wang & Xia.^[141]

Improvements to the quantum efficiency were achieved by stacking multiple extra layers of the same hBN/TMD structure on top of one another to produce a multiple QW structure, producing a maximum EQE of 8.4 %. Also fabricated were multiple quantum wells using different TMD materials, with the combination of a WSe₂ and MoS₂ QW resulting in an increase to the EQE, up to $\sim 5\%$. In this device light originates from the WSe₂ layer because its narrower band gap means that excitons generated in the MoS₂ first transfer to it before recombining. Importantly, the same single QW devices were fabricated on PET substrates and showed equivalent luminescence properties that did not vary up to the maximum measured strain of 1 %.^[179] hBN encapsulation has also enabled the formation of a thermal light emitter using graphene, producing an ultrafast white light source with up 10 GHz bandwidth that

is stable up to electronic temperatures of 2000 K.^[180]

2.3.3.5 Photovoltaics

Photovoltaic cells rely on the ability to efficiently separate photogenerated excitons, again typically requiring the creation of a p-n junction.^[181] The difficulties posed by this aside, TMDs are good candidates in this application since the Shockley–Queisser limit calls for a high mobility semiconductor with a direct band gap of approximately 1.3 eV.^[3] The split gate architecture used to produce p-n junctions has been shown to have a power conversion efficiency up to $\sim 0.5\%$, but the gating requirements make this impractical.^[162] A more efficient device was shown using multilayer MoS₂ contacted in MSM geometry with one Au electrode and one Pd electrode (Figure 2.20a) which, if used in isolation for both contacts, produce n- and p-type transport respectively. This is due to a lowering of the Fermi energy at the Pd interface as compared to the Au interface, in spite of their near identical work functions. The resulting device shows asymmetric ambipolar transport and behaves as a diode (Figure 2.20b), with the sloping band structure bounded by Schottky contacts (Figure 2.20c) effectively separating photogenerated excitons to produce sizeable photocurrent with power conversion efficiency up to $\sim 2.5\%$.^[182]

Perovskite based photovoltaic devices have gained widespread interest as potential low cost, thin film alternatives to silicon.^[183,184] Single junction cells have developed rapidly, with an increase in power conversion efficiency (PCE) from 3.8 % to $>22\%$ over the last decade. Commonly produced with metallic thin film cathodes and transparent anodes of indium tin oxide (ITO), flexible devices have been demonstrated

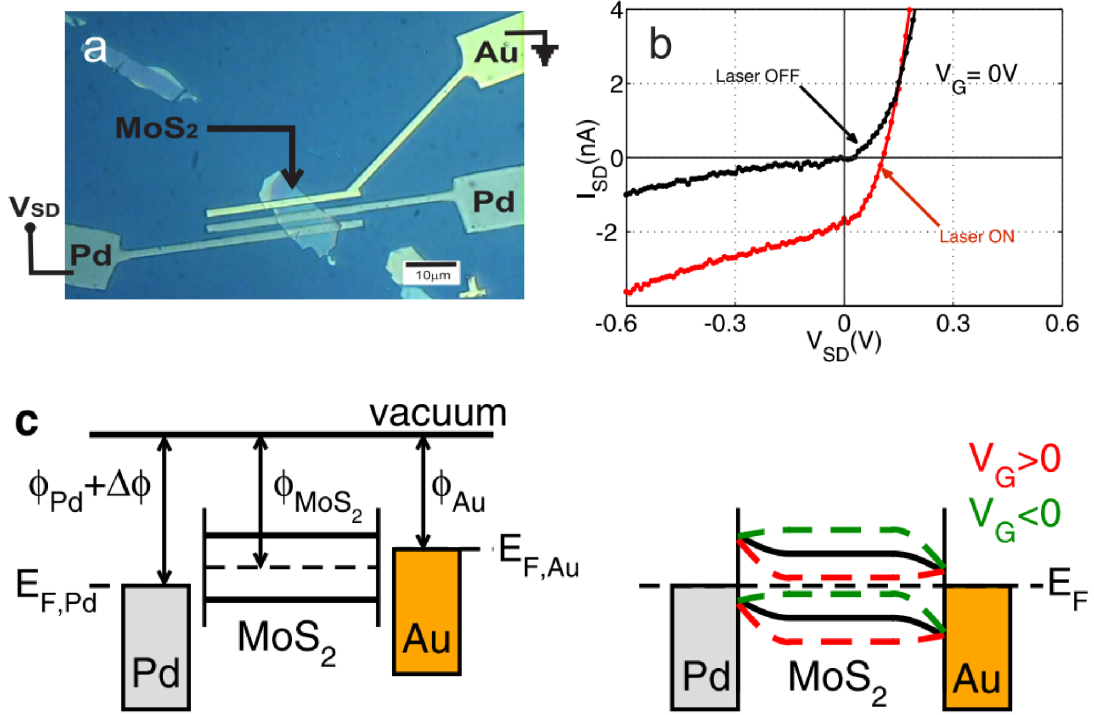


Figure 2.20: Photovoltaic device produced by asymmetric MSM geometry “(a) Optical image of the device. The spacing between the electrodes is 2 mm. (b) Current vs. source-drain voltage at $V_G = 0$ showing strong asymmetry and photoresponse with diode-like behaviour for the Pd-Au bias configuration indicated in (a).” (c) Formation of sloping band structure that leads to photovoltaic behaviour. Adapted from Fontana *et al.*^[182]

with PCEs ranging typically from 10–17 %.^[184] The recent demonstration of an all-carbon-electrode device using CNT cathodes and graphene anodes by Luo *et al.*^[184] serves to highlight the advantages of replacement of the conventional with 1D and 2D materials, with PCE up to ~12 % and enhanced stability and strain resilience compared to ITO based devices.

Vertical heterostructures have again been exploited to give drastic improvements in device efficiency. Britnell *et al.*^[181] produced a graphene/TMD/graphene stack that had a built-in electric field produced by either the use of a back gate or p-doping of the top contact using water vapour. Importantly, this field effectively separates

excitons generated in the full thickness and across the entire area of the few-layer MoS₂ used, which is an improvement over lateral devices where generation occurs only in the comparatively small depletion regions. On SiO₂/Si substrates, the devices were found to have maximum EQEs in excess of 30 % at low laser power and using a single frequency. This value declines as the laser power is increased, attributed to screening of the built-in electric field due to the increasing concentration of carriers in the MoS₂.

In this geometry the photovoltaic effect appears to depend on the layer number, with Zhou *et al.*^[176] observing a photovoltaic effect in such devices (fabricated as detailed in Figure 2.21) with bilayer WS₂ but not in those with monolayer—attributed to the longer lifetime of excitons and their smaller binding energy in bilayer material. For PET substrates performance is more modest, due in part to poorer light absorption without the enhancement provided by the silicon substrate, with quantum efficiencies approximately halved to ~ 15 %.^[98,181] Enhanced EQEs (up to 55 %) have been shown for devices using one graphene and one Ti contact, with a transparent ITO gate electrode, but this device is not suitable for production with a flexible substrate.^[170]

2.3.3.6 Gas Sensors

By virtue of their unparalleled specific surface area, the adsorption of molecules can strongly modulate the electrical conductivity by charge transfer. Using graphene, such devices have been demonstrated to have sensitivities down to parts per billion concentrations, most successfully using rGO,^[12] but also with slightly lower sensitivity

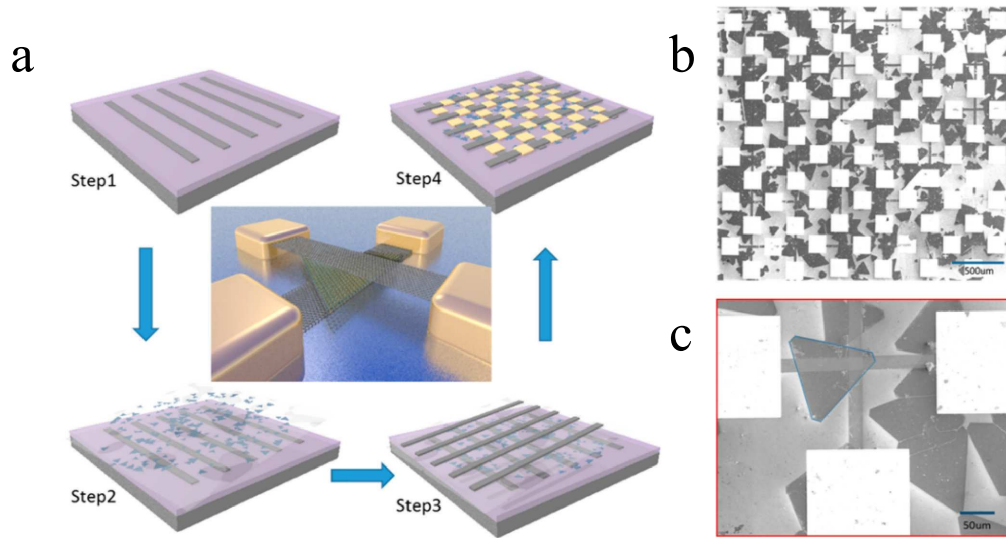


Figure 2.21: Arrays of vertical heterostructure devices. “(a) Schematic illustration showing the fabrication steps (Steps 1–4) for creating the vertically stacked graphene/WS₂/graphene devices. Step 1: Graphene nanoribbon fabrication by electron beam lithography. Step 2: Transfer of WS₂ domains onto bottom graphene nanoribbons and removal of polymer. Step 3: Transfer of top graphene nanoribbon electrodes. Step 4: Deposition of Au bond pads to graphene nanoribbons at bottom and top. Each device is isolated from all others before measurement by cutting the connecting graphene electrodes using a sharp metal tip. (b) SEM image of the fabricated device array. (c) SEM image of one of the vertical devices in (b).” Reprinted from Zhou *et al.*^[176]

using graphene foam grown on a nickel foam substrate,^[185] and CVD graphene grown on copper.^[186] Complete desorption of the adsorbed species is required in order to reuse the sensors, which is typically achieved by heating the sensor to a sufficiently high temperature to drive them off.^[186,187]

This principle was recently demonstrated on flexible and transparent substrates by Choi *et al.*,^[187] in which they used a strip of monolayer graphene as the sensing medium, surrounded on either side by strips of bilayer graphene as *in situ* heating elements, both obtained by CVD. PES was employed as the substrate due to its high thermal stability. This sensor had transparency > 90 %, and comparable sensitivity to other CVD graphene sensors, which was nearly invariant up to the maximum

measured strain of 1.4 %. Sensitivity was good at ~ 15 % for 1 part per million NO_2 , and the integrated heater enabled recovery times down to ~ 11 seconds.^[187] Another design developed by Kim *et al.*^[188] uses trilayer graphene patterned into a $5\text{ }\mu\text{m}$ ribbon that behaves as both the sensing medium and heating element, which showed similar sensitivity but had significantly longer recovery times, at a of minimum of 579 seconds. Though graphene sensors natively lack selectivity, non-covalent functionalisation has been used to specify the detection of particular molecules such as DNA, glucose, and glutamate.^[12]

TMDs have also been employed as gas sensors, in general again making use of charge transfer from the adsorbed species. Similar sensitivities have been observed, but TMDs have been shown to improve on one of the main drawbacks of graphene gas sensors as they have higher selectivity without functionalisation.^[3] For example, single layer MoS_2 has been found to be sensitive only to organic species that are electron donating, with no signal observed for electron acceptors.^[189] Guo *et al.*^[190] demonstrated a flexible humidity sensor using CVD-derived MoS_2 in a palladium contacted MSM geometry on PET. Applying tensile strain to this device by bending leads to increased sensitivity by the piezotronic effect—a result of positive polarisation charges lowering the Schottky barrier height.

Another mechanism for sensing is also possible with TMDs, making use of changes to the photoluminescence or electroluminescence efficiency, where electron acceptors increase efficiency in n-type material and decrease efficiency in p-type. Demonstration of this effect has been limited, but is promising due to the large magnitude of changes possible, and corresponding high sensitivity.^[191]

2.3.3.7 Strain Sensors

With their enormous resilience to strain, 2D materials are an obvious choice for strain sensing applications.^[27,54] A number of different device designs have been proposed to use graphene as the sensing medium, including plain films,^[192,193] rippled films,^[194] foams,^[195] and woven fabrics.^[196] For plain films, there is some dispute over the magnitude and mechanism of resistance change, with some reports of CVD films on PDMS substrates showing almost no change in resistance with strain,^[197] while others have reported gauge factors ranging from the modest (~ 0.4),^[198] to the very large (up to ~ 151), though in the latter case there was an initial region of almost no change up to 3 % strain.^[193] The reasons for these differences are not well understood, but likely result from variations in the preparation and transfer processes used, since this can cause large differences in the quality of films due to grain boundaries, defects, and damage. Another possible cause is damage during testing.^[27]

A related design relies on the creation of ripples in the graphene film by the controlled application of a tensile prestrain, that was relaxed after transfer. These ripples increase the resistance of the film by causing increased scattering of carriers, and as tensile strain is applied they relax and resistance falls (Figure 2.22). Though gauge factors were modest at ~ -2 , this has the advantage of relying on a mechanism that is more independent of film quality, as well as likely increasing the maximum strain before non-recoverable deformation occurs.^[27,194]

Graphene foams have been employed by breaking the foam down into fragments and producing a film with overlapping fragments, producing gauge factors up to 29.

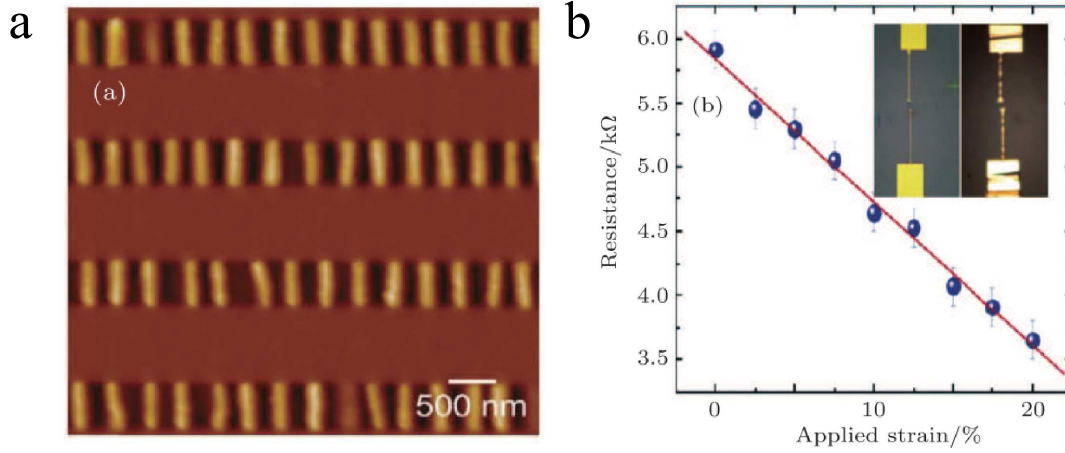


Figure 2.22: Rippled graphene strain sensor. “(a) AFM image of the rippled (monolayer) graphene ribbons. (b) Resistance response of the rippled graphene device upon different strain. The insets are optical images before and after buckling; 20 % prestrain is used to create the rippled graphene device. The resistance decreases linearly from 5.9 kΩ to 3.6 kΩ when the strain increases from 0 % to 20 %. The minimum resistance of 3.6 kΩ corresponds to the state of totally relaxed flat graphene.” Adapted from Zhao *et al.*^[27]

The strain sensitivity was attributed to changes in the overlap of the fragments. This device was shown to have excellent stability, withstanding strains up to 70 % and showing consistent performance after 10000 cycles.^[195] Graphene woven fabrics embedded in PDMS show the largest gauge factors at $\sim 10^3$ for small strains and increasing to $\sim 10^6$ for higher strains. This response is due to cracking of the fabric producing a strong increase in resistance, up to a maximum usable strain of 15–20 %, at which point no current can flow. After initial fracturing, the response stabilises and performance was found to be consistent over 100 cycles. However, due to the destructive sensing mechanism, there may be problems with long term stability and possible drift of unstrained resistance.^[196]

There has also been limited research into producing strain sensors from TMDs. Tsai *et al.*^[199] produced FETs from trilayer MoS₂ by etching channels and lithograph-

ically depositing gold contacts before transferring the devices onto PET substrates with an ITO/ Al_2O_3 back gate. Device performance was practically identical before and after transfer. The device showed a gauge factor that was strongly dependent on the magnitude of gate bias: approximately zero when it was in the off state, increasing to a maximum of ~ -40 in the subthreshold region, and decreasing again in the linear regime. See Figure 2.23 for more details. This behaviour can be explained by the piezoresistive effect, in which the strain decreases the magnitude of the bandgap, and change of the Fermi level with gate voltage. In the off state, changes to the band gap have little impact on the conductivity as the device is switched off regardless. In the subthreshold region, the amount of carriers is strongly increased by reductions in the bandgap. Finally, in the linear region the device is strongly conductive anyway, so the reduced bandgap does not have such a significant effect on the conductivity.

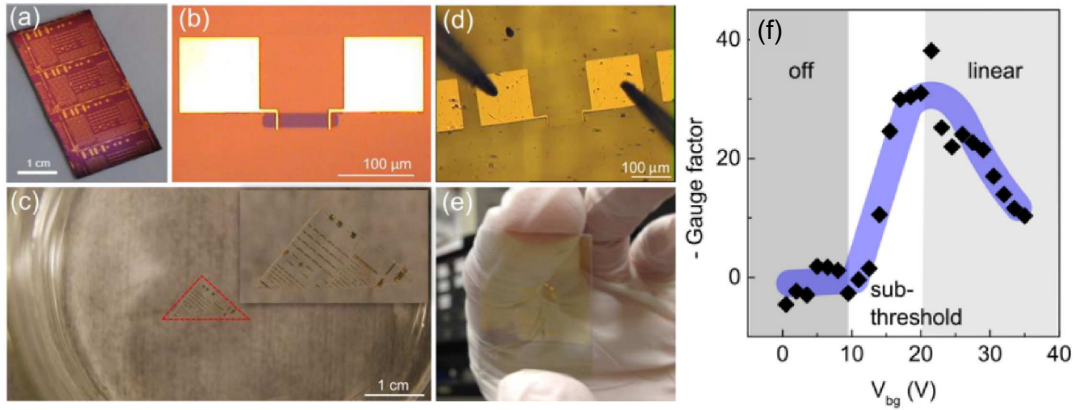


Figure 2.23: MoS₂ strain sensor with gate modulated gauge factor. “(a) A top-view optical image of MoS₂ FETs after fabrication on an SiO₂–Si wafer. (b) A typical transistor with 100 μm MoS₂ channel length from the die in (a). (c) The released MoS₂ FETs held with the PMMA layer floating on water (the inset shows a higher magnification of the same floating sample). (d) A flexible transistor on the Al₂O₃/ITO/PET substrate with probes touching the source and drain contacts during electrical measurements. (e) Flexible MoS₂ FETs on a transparent and flexible PET substrate covered with an ITO back-gate electrode and an 80 nm Al₂O₃ dielectric layer.” (f) “The relationship between $\Delta\phi_n$ and V_{bg} of a representative device.” Adapted from Tsai *et al.*^[199]

2.3.3.8 Cardio-Respiratory Monitor

To achieve stable, high resolution images in magnetic resonance imaging (MRI) and computed tomography (CT) scanning and thereby minimise artefacts that may lead to misdiagnosis or even mimic diseases, the effects of body motion must be minimised.^[200,201] This is achieved by monitoring the key sources of regular body motion—the cardiac and respiratory cycles—and gating the image acquisition accordingly, wherein image data acquired during movement is either prospectively or, less efficiently, retrospectively discarded.^[202–205]

In small animal imaging, so called *respiratory balloons* are de rigueur for respiratory monitoring.^[205–208] There are a number of variants of this device but all operate on the same principle, as described by Herrmann *et al.*^[209] and others. Respiratory motion is monitored by a device that relies on the measurement of changes to air pressure within a small pneumatic capsule, placed in contact with the the abdomen and coupled to a pressure transducer.^[205–208] Use of respiratory balloons requires careful placement and calibration, and repressurisation is required if the animal is transferred between systems—a major drawback in applications requiring co-registration between different scanning techniques, where changes to posture must be minimised.^[210] Cardiac gating is achieved by synchronisation to the electrocardiogram (ECG), commonly by invasive subdermal needles,^[205] though non-invasive means are also possible.^[211,212] Electrical measurement of the ECG can be problematic in the presence of MRI imaging gradients.^[211,213,214]

In response to issues with the respiratory balloons, piezoelectric sensors construc-

ted from poly(vinylidene fluoride) (PVDF) or a similar polymer and contacted by metallic thin films were demonstrated in pre-clinical imaging as early as 1992 by McKibben & Reo.^[215] The advantage of the piezoelectric sensors lies with their comparatively simple setup and calibration, and their insensitivity to changes in air pressure. However, they have not seen widespread adoption for the simple fact that metallic films have significant deleterious consequences for images produced by both techniques. In MRI, all objects placed in the bore of the magnet lead to distortion and detuning of the magnetic field, but metallic objects cause this effect most strongly due to their high susceptibility, and when moved within the magnetic field can cause distortions to the image.^[216,217] The radio waves used will also be strongly attenuated in metallic objects, and the induced currents may lead to local heating and cause problems such as skin burns.^[218] The presence of metal may also limit the magnitude of magnetic field possible.^[217] In CT imaging, the metal film is a strong X-ray scatterer, blocking parts of the image from view and creating bright artefacts.^[219–221]

As previously discussed, with its hexagonal lattice of sp^2 bonded carbon graphene is a material that uniquely combines high in-plane conductivity with extreme strain resilience, whilst providing a negligible contribution to device stiffness or profile.^[26,27] Unlike silver, graphene is radiolucent due to its extremely low scattering cross-section and therefore will not be observed in CT imaging.^[221] It is also suited for MRI applications for a number of reasons. Since carbon 12 (the predominant isotope of carbon) has no net spin and consequently is not detected, the graphene lattice itself will only be weakly imaged.^[222] Despite its high magnetic susceptibility, the negligible volume of graphene means it causes minimal distortion to the magnetic field.^[223–225] Further-

more, several previous studies have identified flake edges as contributing chiefly to the magnetism of graphene, and CVD derived material is a continuous film with the minimum possible edge density for a given area (cf. films composed of liquid phase exfoliated flakes of typically nm- μ m size, each with associated edges and possible consequent magnetic moments).^[132,224,226]

The above properties combine to make make graphene highly attractive for use as a planar conductor in MRI and CT imaging, since devices utilising it are likely to have little to no impact on image acquisition. It is further suited to use in piezoelectric sensors of this type as the signal is generated by deflection, so the lower stiffness could increase device sensitivity, and the high strain resilience will increase device durability.^[27]

2.4 Conclusions

In this review, we have assessed the insulating, semiconducting, and metallic 2D materials at the forefront of flexible electronics research, focusing on their relevant physical, electronic, and optical properties, as well as examining the current state of synthesis techniques. Though continuous polycrystalline films of reasonably good quality have now been demonstrated for all of these materials, there is still much scope for improvement in control over the grain size, layer number, and defect concentration, especially in the case of TMDs.

The different properties of these materials have great potential to be combined synergistically in a wide range of devices. The nature of van der Waals bonding provides the opportunity to produce heterostructured devices with atomically sharp interfaces, without any of the complicated fabrication steps required for other materials. Due to their atomic thickness and associated extreme strain resilience, they are well placed to provide alternatives in a multitude of applications. There are clear advantages to using 2D materials in flexible electronic devices, often having greater strain resilience, carrier mobility, and transparency than the existing alternatives, among other factors.

In light of the above, a survey of current progress in the fabrication of flexible electronic devices from 2D materials has been produced. The advantages and disadvantages have been outlined, along with the main device designs that have so far been demonstrated and assessed. Where possible, this has been drawn from examples where flexibility was already demonstrated, but in some cases relevant devices that

have thus far only been demonstrated on rigid substrates have also been explored. The remainder of this thesis explores several of the areas described above, with implications that reach beyond the specifics of each study to the wider field of flexible electronics as a whole.

Research into these materials is still in its infancy, with the first isolation of graphene in 2004, and other materials being discovered even more recently. Before wide scale adoption into the semiconductor industry is possible there are many aspects of synthesis, fabrication, and device design that require significant improvement. In spite of this, device designs are developing rapidly, and a huge amount of progress has been made in elucidating the nuances of this nascent field over the last decade, with new discoveries being made at an impressive rate.

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Chapter 3

Methodology

3.1 Introduction

The study of 2D electronic devices requires the use of a broad range of experimental techniques. This chapter will give an overview of many such techniques used throughout this project, beginning with the synthesis and transfer of the three chosen materials—procedures that were already established within the group but were often optimised or modified by the author, the details of which are provided here as well as in Chapters 4–6. The operation of the diverse characterisation techniques used will then be described, along with the justification for their selection within the scope of those available.

3.2 CVD Synthesis

All materials were grown by CVD. The general procedure is similar for all three materials, involving the delivery of precursor species to a substrate contained in a

quartz tube furnace, at high temperature and under an inert gas shield. Here they adsorb to the surface to nucleate and coalesce into the 2D film. The specifics of each growth process are described below.

3.2.1 Graphene

Graphene was grown by our previously demonstrated method, using a copper foil (25 μm , 99.8% purity, Alfa Aesar) substrate. Before growth, the foil was first cleaned by ultrasonication in 1 M HCl solution for 10 minutes. This was followed by rinsing in deionised (DI) water, then by ultrasonication for a further 10 minutes each in acetone followed by isopropyl alcohol (IPA). Prior to these cleaning steps the copper foil can optionally be mechanically polished, with the best results being achieved using a two stage mechanical polishing treatment, applied via cloth wheel (lustre followed by rouge, RS Pro[®], RS Components). This reduces surface roughness and so produces thinner, smoother films with a coarser grain structure due to the associated reduction in nucleation density. This is desirable in many cases but not essential. Both unpolished and polished foils were used to produce the graphene used in this project, and the development of the polishing procedure is described in Chapter 5. Once cleaned, the foil was supported by an alumina crucible and sealed in a 4" furnace tube, aligned with the centre of the furnace.

After flushing all gas lines, the system was purged with a mixture of argon (Ar; BOC) and hydrogen (H_2 ; 25 % in Ar, BOC). The furnace was ramped up to 1060 $^{\circ}\text{C}$ at a target rate of 60 $^{\circ}\text{C min}^{-1}$ and the foil annealed under a reducing atmosphere of dilute hydrogen to promote grain growth and clean the surface, resulting in increased grain

size and reduced contamination of the graphene film. Graphene growth was started by the introduction of methane (CH_4 ; 1 % in Ar, BOC) and allowed to proceed for 1 hour before switching off the methane flow and moving the furnace away to facilitate fast cooling. These parameters are summarised in Table 3.1. Once the furnace had cooled, the graphene/copper was removed from the furnace and either immediately spin coated with poly(methyl methacrylate) (PMMA) as described in Section 3.3.1.1, or stored in an airtight container to prevent surface contamination.

Step	Flow Rate (sccm)			Temperature ($^{\circ}\text{C}$)	Time (min.)
	Ar	H_2	CH_4		
Purge	2000	500	100	RT	5
	2000	500	0		30
Anneal	500	100	0	RT $\rightarrow$ 1060	90
	500	100	0	1060	60
Growth	500	100	5–10		60
Cooling	500	100	0	1060 $\rightarrow$ RT	120

Table 3.1: Parameters for CVD of graphene.

3.2.2 Boron Nitride

Owing to their very similar structures, growth of boron nitride (hBN) films was again achieved using copper foil as the substrate, following a very similar procedure to graphene. Preparation of the foils followed the same procedure described above. The foils were placed in a 1" quartz tube and centred in the furnace, and 8–15 mg of ammonia borane precursor (technical grade, 90 %, Sigma-Aldrich) was placed in an alumina crucible in a separately heated chamber upstream of the main furnace. The sealed system was then purged with Ar (BOC). Once purging was complete, the precursor chamber was isolated by means of a butterfly valve, and a mixture of Ar and H_2 (25 % in Ar, BOC) introduced to the rest of the system. At the same time, the

3.2. CVD SYNTHESIS

furnace temperature was increased to 1000 °C at a target rate of 60 °C min⁻¹. Once at temperature, the foils were annealed for one hour. Growth was initiated by heating the ammonia borane precursor to 120 °C, resulting in the evolution of borazine gas. Once at temperature, the butterfly valve was opened to introduce the borazine into the reactor, and growth was allowed to proceed for 20 minutes. After growth, the precursor chamber was again isolated by closing the butterfly valve, and the samples were fast cooled and stored as described for graphene in Section 3.2.1. See Table 3.2 for details of the growth parameters.

	Flow Rate (sccm)		Temperature (°C)			
Step	Ar	H ₂	Precursor	Furnace	Time (m)	Valve open?
Purge	500	0	RT	RT	30	✓
Anneal	425	75		RT → 1000	30	✗
				1000	60	
Growth	0	120	RT → 120	1000 → 1040	5	
			120	1040	60	✓
Cooling	425	75	120 → RT	1040 → RT	120	✗

Table 3.2: Parameters for CVD of hBN.

It was observed during this project that precursor residues accumulated over time in the precursor heater assembly, leading to significant contamination of the hBN surface with nanoparticles. In response a cleaning procedure was developed, in which the system was purged with diluted H₂ (425 sccm Ar/75 sccm H₂) with all heaters set to 150 °C for at least 8 hours. Periodically performing this procedure helped to limit the amount of contamination on the film surface. See Figure 3.1 for a comparison of SEM images of the hBN films grown before and after this cleaning procedure was performed.

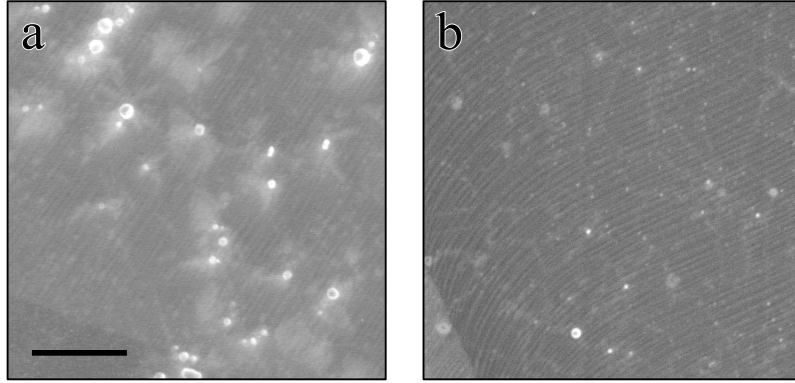


Figure 3.1: hBN films grown (a) before and (b) after the system had been cleaned of precursor residues. Note reduction in the appearance of particles in (b). Scale bar is 2.5 μm .

3.2.3 Tungsten Disulphide

Tungsten disulphide (WS_2) domains were grown on the surface of silicon wafers (most metallic substrates including copper are precluded by the high reactivity of sulphur) with 300 nm oxide layer (University Wafer), diced into 2×2 cm substrates. Substrates were cleaned by ultrasonication in DI water, acetone and IPA for 15 minutes each. This was followed by cleaning in a 90 W oxygen plasma for 15 minutes. Growth was performed by two zone vapour transport in a 1" quartz tube in which two different precursors are evaporated in separate furnaces upstream of the substrate. The first (low-temperature; LT) furnace was used to evaporate sulphur powder, while the second (high-temperature; HT) furnace was used to evaporate WO_3 powder and heat the substrate. 350 mg of sulphur (purum grade, >99.5 %, Sigma-Aldrich) was placed directly in the furnace tube and centred in the LT furnace. 200 mg of WO_3 powder (puriss. grade, 99.9 %, Sigma-Aldrich) was placed in a 1 cm quartz tube that was placed inside the 1" tube, placed on top of the sulphur powder such that the end was at the upstream edge of the LT furnace, and the WO_3 was centred in the HT furnace.

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The clean silicon substrate was placed in the 1" tube, close to the downstream edge of the HT furnace and supported by an alumina crucible. The system was then sealed and purged with Ar. The HT furnace was ramped to 470 °C, and once at this point the LT furnace was ramped to 180 °C, and the HT furnace was increased to 1145 °C, such that the target temperatures were reached simultaneously. The flow rate of Ar was reduced once the LT furnace had reached 100 °C. Growth was then allowed to proceed for around 4 minutes—a shorter time producing smaller isolated domains, and a longer time leading to larger domains and regions of continuous film. Further extensions to growth time were found to be detrimental to the material quality, by producing multilayer and non-2D crystals, and so were avoided. After this time, growth was arrested by reducing the Ar flow to 10 sccm, and the HT furnace switched off. The low temperature furnace was ramped to 400 °C, and once the HT furnace cooled to 900 °C, the Ar flow was returned to 500 sccm to purge the remaining sulphur from the system. The LT furnace was subsequently switched off, and the furnaces separated to enable fast cooling of the substrate. See Table 3.3 for a summary of this procedure. Typical domains grown by this procedure are shown in Figure 3.2a.

To achieve the continuous films used in our production of suspended devices,^[1] we incubated the growth with the HT furnace at 470 °C for ~5 minutes, while the LT furnace was increased to 100 °C. Growth was then continued as normal. This incubation period leads to more nucleation on the surface, without the associated degradation in quality observed when simply extending the growth time. An example image of the continuous region is shown in Figure 3.2b. The lines of brighter points

		Temperature (°C)		
Step	Ar	LT Furnace	HT Furnace	Time (m)
Purge	500	RT	RT	40
Ramp			RT → 470	15
		RT → 100	470 → 1145	10
		100 → 180		15
Growth	250	180	1145	3–5
Purging	10	180 → 400	1145 → 900	10
	500	400	900 → 800	5
Cooling			400 → RT	800 → RT

Table 3.3: Parameters for CVD of WS₂.

visible here are regions of multilayer or non-2D growth which nucleate at the grain boundaries.

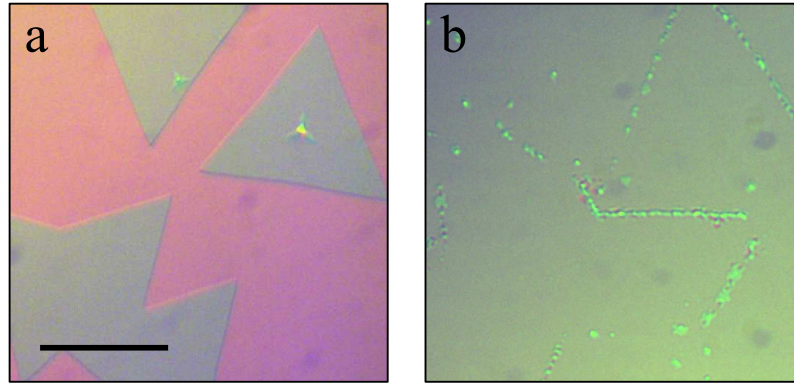


Figure 3.2: Optical images of WS₂ grown (a) without and (b) with incubation period to encourage the growth of a region of continuous film. Scale bar is 100 μ m.

3.3 Fabrication Methods

3.3.1 Transfer of Materials

Transfer of the 2D materials to target substrates was achieved using two variants of the well established wet chemical etching process. Both procedures involve supporting the materials with a sacrificial polymer scaffold that was removed before further

processing steps and characterisation.

3.3.1.1 Aqueous Transfer

A 500 nm PMMA (MicropositTM A8 495 K, DOW) scaffold was spin coated at 4000 rpm for 60 seconds onto the surface of the chosen 2D material. The coated samples were then baked at 180 °C for 90 seconds—evaporating any remaining solvent, and ensuring good adhesion between the scaffold and 2D material. The substrate was etched away by placing the sample on the surface of an etchant solution. For copper substrates, a 0.1 M solution of ammonium persulphate ((NH₄)₂S₂O₈) was used (Figure 3.3a). For WS₂, before etching was performed the area(s) with best coverage of domains was determined by mapping with optical microscopy. These regions were then diced from the larger substrate using a diamond scribe, the edges chamfered using a diamond file to ensure they were free of PMMA, and the oxide layer etched to detach the silicon chip using a 1 M solution of KOH (Figure 3.3b). One improvement was made during this project by etching the WS₂ substrate in KOH solution that was shallower than the smallest lateral dimension of the substrate, preventing a common failure of this procedure where the chip sinks during etching and destroys the partially detached film. Once the growth substrate was completely removed, the floating films were washed by transfer into clean DI water 3–4 times.

Substrates were prepared by ultrasonication for 10 minutes each in acetone and IPA, followed due to surface porosity in the case of polymer substrates by baking at 100 °C for 10 minutes for PEN, and 30 minutes of vacuum desiccation for PVDF, to remove solvent residues. The washed floating films were picked up using the substrate

and left to dry overnight (Figure 3.3c). To ensure good conformation and adhesion to the substrate, the samples were baked at 120 °C for 25 minutes, and the PMMA scaffold was removed by immersing the samples in acetone at 45 °C for at least 3 hours. Subsequent layers were transferred immediately after removal of the PMMA, minimising the contamination between layers. Due to its low working temperature, for the transfer of graphene to PVDF conformation was ensured instead by the redeposition of a layer of diluted PMMA (A1 495 K), and PMMA removal accomplished in room temperature acetone for 48 hours.

Since acetone was precluded in the transfer onto PMMA used in Chapter 4, a procedure using a 2 µm film of negative photoresist (ma-N 1420, Micro Resist) was developed instead, due to its solubility in IPA. The transfer was performed as normal, with a reduced baking temperature of 100 °C (the softbake temperature of ma-N 1420). Removal was performed in IPA at 45 °C for 3 hours.

3.3.1.2 Non-Aqueous Transfer

To reduce contamination with water and facilitate better alignment of the layers, the non-aqueous technique demonstrated by Sheng *et al.*^[2] was also used. All preparation was the same up to the point of transfer to the target substrate. At this point, the floating film was picked up onto a custom piece of apparatus developed for this project consisting of a small frame holding a hinged piece of glass. This was then placed such that the free end was on top of one edge of the substrate. IPA was used to carry the film down the ramped cover glass and onto the substrate, which could then be aligned much more precisely than in the case of aqueous transfer by means of an underlying

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grid. A schematic of this procedure is shown in Figure 3.3d. Baking and PMMA removal then followed the same procedure as before.

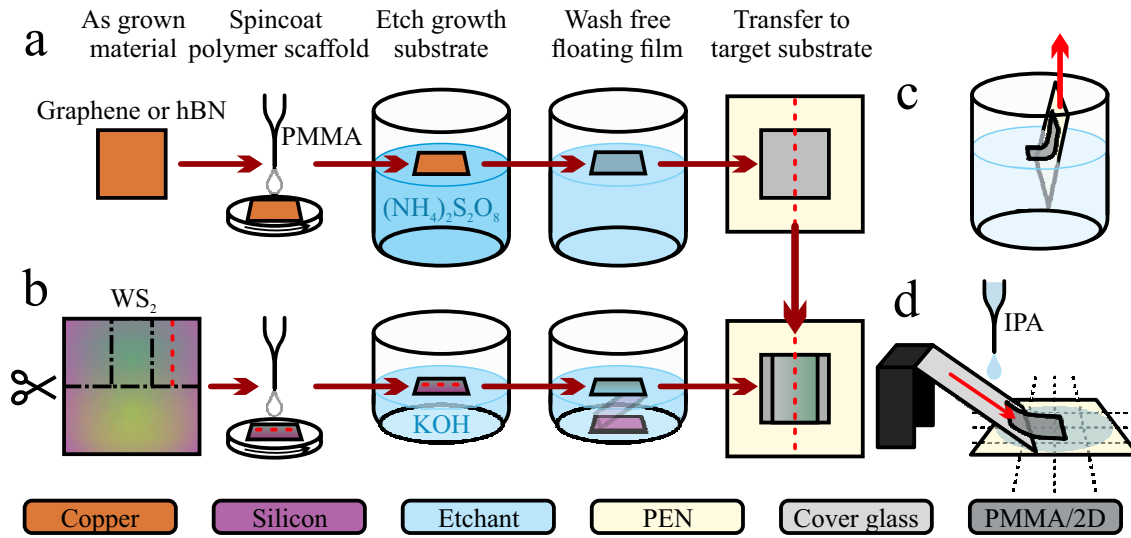


Figure 3.3: Schematics detailing the different transfer processes. (a) Etching of copper foil for graphene or hBN transfer. (b) Etching of silicon oxide for WS_2 transfer. (c) Aqueous transfer and (d) non-aqueous transfer.

3.3.2 Photolithography

Photolithography, performed using a mask aligner, was used in several different patterning processes. This technique uses UV light to pattern a polymer film, and was favoured over electron-beam lithography for its compatibility with insulating substrates, and its scalability. PEN substrates were first cut to size by means of a laser cutter to ensure proper squareness without damaging the surface finish. Contaminants and residues from the laser cutting process were then removed by sonication in acetone and IPA for 10 minutes each before baking at 100 °C for 10 minutes to remove solvent residues. Once cooled, they were immediately spin coated with appropriate photoresist and softbaked to remove solvent residues. The majority of devices were produced using only the positive resist S1813 (MicropositTM S1813 G2, DOW). A 1 µm film was produced by spinning at 4500 rpm, followed by a 115 °C softbake for 1 minute. Preparation of silicon substrates followed a similar procedure, without laser cutting. The substrates were loaded into the mask aligner, aligned to the photomask (by means of the substrate corners in the case of gold, and deposited gold alignment marks for subsequent layers), and exposed in hard contact mode.

Once exposed, the photoresist was developed by gentle agitation in the appropriate developer (MicropositTM 351, DOW, diluted 1:5 in DI water). Increased cleanliness and removal of resist scum was achieved by dipping the sample in clean developer following development. Development was completed by rinsing in DI water and drying by nitrogen gun. Samples were stored under class 1000 cleanroom conditions to avoid contamination and further UV light exposure. This was especially important when

graphene was to be transferred on top of the pattern, since all traditional substrate cleaning methods were precluded. Exposure and developer times for the various procedures using S1813 are summarised in Table 3.4 below.

3.3.3 Metallization

3.3.3.1 Thermal Evaporation

Thermal evaporation, a process that uses Joule heating under high vacuum to evaporate a layer of the chosen metal onto the target substrate, was used to metallize contacts defined by photolithography. The patterned substrates were attached to the sample plate by means of Kapton tape and loaded into the evaporator (Edwards 360). Evaporation was typically performed once the chamber was pumped down to 2×10^{-6} mbar. Electrodes were deposited in gold to a typical thickness of 100 nm, with the deposition kept at a low rate of 0.1–0.2 nm s⁻¹ to reduce the flux of heat into the substrate, thereby minimising thermal damage.

Chromium is commonly used as an adhesion layer for gold films but was not used for the flexible devices fabricated here as it has been shown to cause embrittlement of deposited metal films.^[3] Without chromium it was found that the adhesion of gold to PEN was very poor, resulting in destruction of the deposited contacts when lift-off was attempted. As a result, another means of improving adhesion was required. A post lithography treatment in 90 W oxygen plasma for 2 minutes was used to functionalise the PEN surface and increase the roughness in the exposed parts, with the remaining substrate area protected from damage by the photoresist. Once metal deposition was complete, the samples were heated on a hotplate at 120 °C (T_g of

PEN) to increase the conformation between the gold and PEN. Further details are available in Chapter 5.

3.3.3.2 Lift-off

Lift-off of the gold electrodes was performed by immersing the samples in acetone at 45 °C for at least 3 hours, and the majority of the loosened gold removed by agitation using a pipette. Any remaining gold was removed using ultrasonication for approximately 1 minute, performed in 15 second intervals until lift-off was complete.

3.3.4 Graphene Patterning

3.3.4.1 Oxygen Plasma Etching

Conventionally, graphene is patterned using oxygen plasma. This is performed by first transferring a layer of graphene onto the desired substrate, and photolithographically producing a positive image of the desired structures on its surface. The exposed graphene is subsequently etched away using oxygen plasma, with typical parameters being 60 W for 2 minutes. This process is very effective for hard substrates like silicon and quartz, but is inappropriate for soft matter such as the polymers used throughout this work, as detailed in Chapter 5. For this reason, the majority of devices were instead patterned using the method described below.

3.3.4.2 Lift-off

Based on the work of Trung *et al.*,^[4] a modified lift-off procedure was developed to pattern the graphene without etching. The desired structures were photolithographically defined in negative using a positive photoresist (S1813) on a clean substrate surface.

3.4. IMAGING TECHNIQUES

An increased development time compared to that used for metal patterning was used, producing more rounded edges to enable better conformation of the graphene film. A graphene film with a PMMA scaffold of significantly reduced thickness (100 nm, to further facilitate conformation to the pattern; cf. the 500 nm films used conventionally) was transferred on top of this pattern, dried, and baked for 6 hours at 80 °C to ensure conformation between the graphene and substrate surface. This lower baking temperature enabled the film to relax slowly and avoided outgassing from the S1813. To produce the thinner scaffold, the spin coating procedure described in Section 3.3.1 was repeated twice using A1 495 K PMMA (A8 495 K diluted 1:7 in anisole).

The excess graphene was then removed by dissolving the resist and scaffold in acetone at 45 °C for 3 hours, followed by 30 seconds of ultrasonic treatment to scission the free floating film. The patterned structure was then washed of any remaining residues using IPA, and dried by nitrogen gun. The development of this procedure is described in greater detail in Chapter 5.

Process		Dose (mJ cm ⁻²)	Development (s)
Metal electrode deposition		45	50
Graphene patterning	Plasma	45	60
	Lift-off	25	70

Table 3.4: Exposure and development times for S1813 based photolithographic processes.

3.4 Imaging Techniques

3.4.1 Optical Microscopy

Optical microscopy was used to examine and characterise many of the samples—predominantly the as grown WS₂ and fabricated heterostructures and devices. Cus-

tom built microscopes with objective lenses ranging from 4–50 $\times$ magnification were used for preliminary characterisation, with higher resolution images taken using a system with 100 $\times$ magnification. The main purpose of this was to assess the quality of the samples, as well as to map the WS₂ prior to dicing and transfer, before proceeding with subsequent fabrication and characterisation steps. Due to the poor contrast of graphene on PEN high resolution imaging was important during the characterisation of patterned graphene in Chapter 5, where the small scale features and defects required high quality images and significant enhancement to be resolved. Image enhancement and analysis was performed using the ImageJ software package.

3.4.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used extensively to study each of the 2D materials before and after transfer, as well as after microfabrication techniques and after optoelectronic measurements had been performed. A Hitachi S-4300 SEM was used, with a typical accelerating voltage of 3 kV and a beam current of 11 μ A . This low accelerating voltage enables good contrast of the 2D materials, without significant over-penetration of the electrons into the underlying substrate, which can hamper image quality. Conductive substrates were grounded by using carbon tape to affix the substrate to the SEM stub, and insulating substrates were only imaged where graphene was present to prevent substrate charging, with the graphene connected to the specimen stub by first depositing a gold or silver paint (RS Components) electrode, and grounding this with carbon tape. Cross-sectional SEM was performed by first cleaving the substrate using a diamond scribe, and fixing the sample perpendicular

to the stage by means of a cross-section stub. Image enhancement and analysis was performed using the ImageJ software package. For measuring the average spacing of two lines (e.g. the measurement of film thickness in Chapter 4 and electrode spacing in Chapter 5), the *Distance Between Lines* plug-in for ImageJ was used.

3.4.3 Atomic Force Microscopy

Atomic force microscopy (AFM) was used to provide topographic information inaccessible by other methods. Two systems were used in tapping mode under ambient conditions: an Asylum Research MFP-3D with silicon AC160TS cantilever tips, and an Agilent 5400 with Mikromasch NSC35/ALBS tips. Scan rates of 0.5 lines per second were used to produce maps of the surface. These were analysed to produce line profiles and surface roughness measurements using the Gwyddion software package.

3.4.4 Magnetic Resonance Imaging

Magnetic resonance imaging (MRI) was performed using a 7 T, 210 VNMRS horizontal bore preclinical imaging system with 120 mm bore gradient insert (Varian Inc.). A 25 mm ID quadrature birdcage coil with 35 mm RF window length (Rapid Biomedical GmbH) was used for transmission and reception of RF signals. A constant TR, steady-state respiration gated gradient echo imaging procedure was used for *in vivo* imaging. Typical parameters were TR = 16.8 ms, TE = 12 ms, FA = 10°, THK = 2 mm, in plane resolution = 250 μm and image matrix = 128×128 . Adapted from Gilchrist *et al.*^[5]

3.4.5 Computed Tomography Imaging

For computed tomography (CT) imaging, the following settings were used: X-ray tube operated at 50 kV and 500 μA , a 300 ms exposure time per projection, 540 projections, and 360° continuous rotation, a binning factor of 4 and a matrix size of 3072×2048 . Images were reconstructed using the Feldkamp algorithm. Adapted from Kersemans *et al.*^[6]

3.5 Optical Spectroscopy

3.5.1 Raman Spectroscopy

Raman spectroscopy was performed using an imaging confocal Raman spectrometer (JY Horiba Labram Aramis) coupled to a 532 nm frequency doubled Nd:YAG laser. Rapid profiling was performed using a 600 slits mm^{-1} grating, and when fine resolution was required a 1800 slits mm^{-1} grating was used. Owing to their differing Raman shifts and signal intensities, different parameters were required for each material. Typical values are summarised in Table 3.5. In some cases, individual points were examined at pertinent locations on the sample, while at others the mapping function of the spectrometer was used to gain insight into the distribution over an area.

Material	Laser Power (μW)	Acq. Time (s)	Accumulations	Range (cm^{-1})
Graphene	587	5	5	1200–3000
hBN	587	10	30	1300–1500
WS ₂	1600	5	3	200–550

Table 3.5: Summary of typical Raman parameters.

3.5.2 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy was performed using a custom built spectrometer, equipped with a diode-pumped solid-state 532 nm laser (Thorlabs DJ532-40), and coupled to a charge-coupled device (CCD) spectrometer (Princeton Instruments Acton SP-2300 spectrometer with Princeton Instruments PIXIS 100 CCD). The typical acquisition parameters were 1.1 mW or $\sim 4 \text{ kW cm}^{-2}$ laser power, and 1 second acquisition time. The measured spectra were corrected for the PEN background prior to analysis using Matlab, and the peak properties determined by Lorentzian or Gaussian fitting.

PL spectra are generally captured in units of wavelength, but (due to non-linearity and resultant distortion of fitted peak shapes) must be converted into units of energy before analysis. This is performed using the Planck–Einstein relation (Equation 3.1):^[7]

$$E = h\nu = \frac{hc}{\lambda} \quad (3.1)$$

Where E is energy, h is the Planck constant, c is the speed of light, ν is frequency, and λ is wavelength. In addition, the intensity (I) must be rescaled by the Jacobian transformation (Equation 3.2):^[7]

$$I_E = \frac{I_\lambda hc}{E^2} \quad (3.2)$$

Once this has been performed, the spectra can in principle be decomposed into

their various contributions.

3.6 Strained Measurements

In many of the spectroscopic and optoelectronic measurements in Chapters 4 & 5, a method to apply strain *in situ* was required. This was achieved using a custom built holder, by *collapsing radius test*—where the substrate is controllably bent, and the strain in the surface calculated from elasticity theory. The holder was mounted directly to the sample stage and could be moved in half-mm increments, enabling a maximum strain $>2.5\%$ to be applied in the case of the $250\text{ }\mu\text{m}$ substrates used here. The strain in the substrate surface was calculated as outlined by McCreary *et al.*^[8] and others,^[9–12] using Equation 3.3:

$$\epsilon = \frac{t \sin \theta}{d} \quad (3.3)$$

Here, ϵ is the strain in the substrate surface, θ is the angle of the tangent of the substrate at the point of contact, d is the grip separation of the holder as measured by the scale, and t is the substrate thickness. See Figure 3.4 for more details.

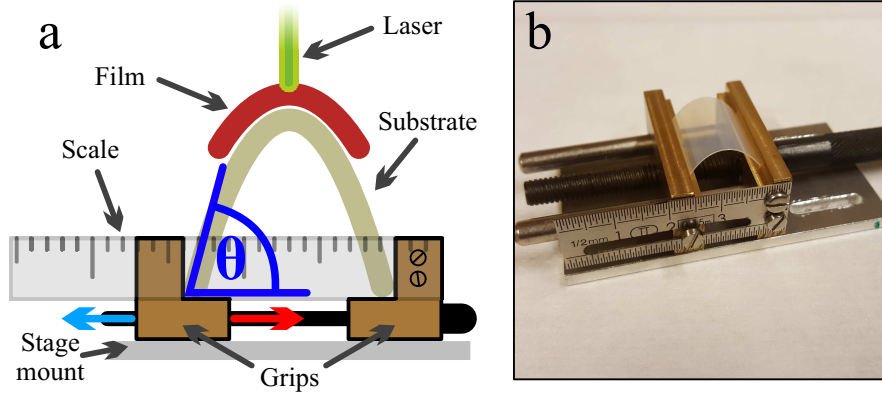


Figure 3.4: Details of the holder used to apply strain *in situ*. (a) Schematic of the strain holder detailing key components. (b) Image of the strain holder with blank substrate in place.

In this measurement geometry, when force is applied to the substrate the stress at the film edge will be lower than at its centre, with load transferred through shear forces. This leads to a distribution of strain across a stress transfer length L_t (i.e. when $x < L_t$, with $x = 0$ at the film edge), beyond which the stress may simply be calculated from the Young's modulus by:

$$\sigma_f = \varepsilon E_f \quad (3.4)$$

Where σ_f is the stress in the film and E_f is its Young's modulus. Prior to yield of the interface the magnitude of stress transferred from the substrate to the film depends on the differing dimensions and stiffness values of the two materials—the stiffer film experiencing a smaller stress and strain than the more compliant substrate. This situation is shown schematically in a cross section of the film and substrate in Figure 3.5a.

When the interface begins to yield, the depiction in Figure 3.5a is no longer valid.

Instead, the magnitude of interfacial shear τ_f is assumed to be constant within the stress transfer length (i.e. when $x < L_t$) and can be calculated by considering a thin segment perpendicular to the load axis of length δx and at a distance x from the film edge (of width w and thickness t), as shown in Figure 3.5b.

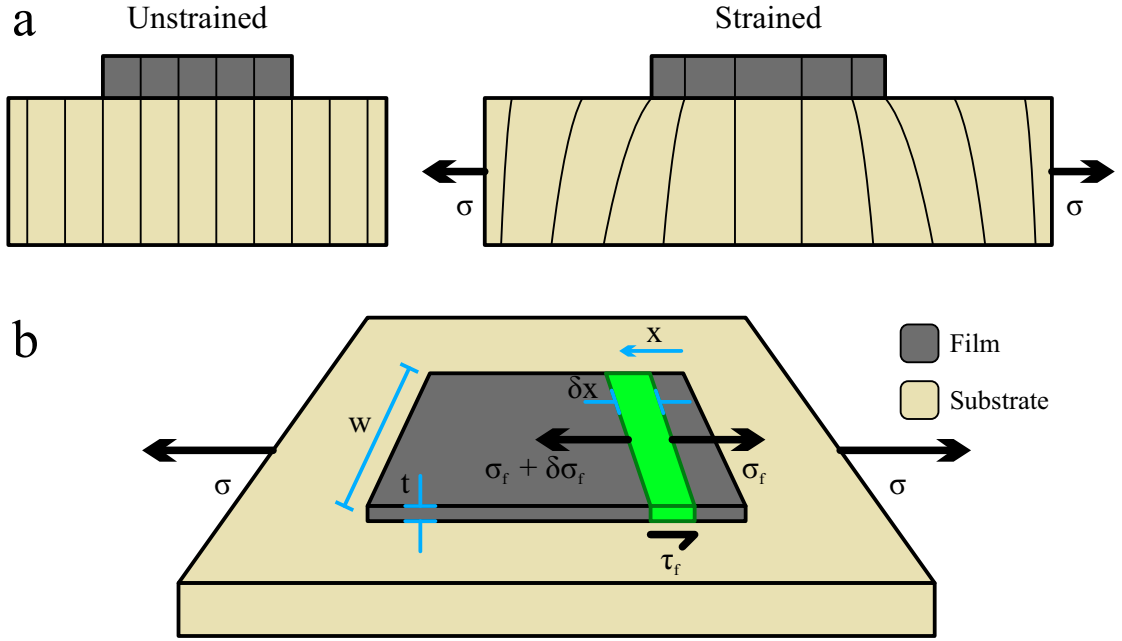


Figure 3.5: Stresses acting on a thin film where (a) the interface does not yield and (b) where it does. The vertical lines in (a) are plotted to display the displacements when the film is stressed.

The total force on the element shown in Figure 3.5b must be zero to maintain equilibrium, therefore:

$$(\sigma_f + \delta\sigma_f)wt - \sigma_f wt - \tau_f w \delta x = 0 \quad (3.5)$$

Collecting terms and simplifying leads to:

$$\frac{\delta\sigma_f}{\delta x} = \frac{\tau_f}{t} \quad (3.6)$$

Integrating under the assumption that $\sigma_f = 0$ when $x = 0$ gives the equation:

$$\sigma_f = \frac{\tau_f x}{t} \quad (3.7)$$

Inserting Equation 3.4 with a measured value for the strain in the film (ϵ_f) enables estimation of the interfacial shear stress:

$$\tau_f = \frac{\epsilon_f E_f t}{x} \quad (3.8)$$

This description is based on the work of Hull & Clyne.^[13]

3.7 Electrical Measurements

Electrical measurements were performed using two separate pieces of equipment: a Keithley 2400 SourceMeter[®] for I-V and sheet resistance measurements; and a Biopac[®] MP150 with attached DA100C amplifier, modified to further increase amplification by a factor of 10, for high speed potential measurements.

3.7.1 Keithley 2400 SourceMeter

3.7.1.1 I-V

I-V measurements were used to characterise the all-2D photodetector devices described in Chapter 5. The devices were mounted to a microscope stage, using the strain holder described in Section 3.6 in the case of flexible devices, and contacted by two tungsten probes (Sel-Tek Signatone[®] SE-T). The probes were connected to the unit by shielded BNC cables to mitigate electrical noise. A bias was applied in both directions, and the current measured at incremental points. The measurements were automated using Python with the PyMeasure package. Laser irradiation was provided by means of a diode-pumped solid-state 532 nm Thorlabs DJ532-40 laser.

3.7.1.2 Sheet resistance

Sheet resistance (R_s —measured in Ohms, but denoted as $\Omega/\square$ to avoid confusion with the bulk resistance R , also in Ohms) is a measurement used to characterise thin films of uniform thickness that is useful because it removes the influence of geometric factors and contact resistance from the measurement. This measurement can be made using a number of different techniques. Here the van der Pauw method was used, where ideally point but in practice small, Ohmic contacts are made to the four corners of a square specimen, and numbered 1–4. A current is then applied between two contacts on the same edge (e.g. 1 & 2), and the resulting potential measured across the other two corners (3 & 4). The resistance (here $R_{1\,2,\,3\,4}$) is then calculated using Ohm’s Law. This measurement is repeated at 90° to produce $R_{2\,3,\,4\,1}$. R_s can then be calculated iteratively using Equation 3.9:^[14]

$$e^{-\pi \frac{R_{12,34}}{R_s}} + e^{-\pi \frac{R_{23,41}}{R_s}} = 1 \quad (3.9)$$

To improve the precision of the measurement it was repeated in all possible permutations, viz.: reversed along each side ($R_{1\,2,\,3\,4}$ & $R_{2\,1,\,4\,3}$), flipped across the centre ($R_{3\,4,\,1\,2}$ & $R_{4\,3,\,2\,1}$), and similar for $R_{2\,3,\,4\,1}$. The sheet resistance equation then becomes Equation 3.10:^[14]

$$e^{-\pi \frac{R_H}{R_s}} + e^{-\pi \frac{R_V}{R_s}} = 1 \quad (3.10)$$

In which:

$$R_H = \frac{R_{12,34} + R_{34,12} + R_{21,43} + R_{43,21}}{4}$$

And similar for R_V .

The measurements and calculation of R_s were automated using a Python script written by Dr. Zhengyu He (modified from original by Dr Chris Allen).

3.7.2 Biopac MP150 & DA100C

The respiratory monitors described in Chapter 6 produce short, transient signals that require measurement rates exceeding the capabilities of the Keithley 2400 SourceMeter[®].

The MP150 provides high measurement rates and signal to noise ratio, with adjustable signal amplification provided by the DA100C unit, enabling accurate measurement of the generated potential. The devices were connected to a shielded potential divider to reduce electrical noise and enable adjustable control of the input signal intensity, and the potential between the two sides as a result of small mechanical deformations measured at a rate of 1 kHz. The reduction of electrical noise was critical here due to the high amplification used. By enclosing all components up to the sensor in a shield, and using twisted pair leads, the noise was reduced by several orders of magnitude. Measurements were recorded using the AcqKnowledge[®] software package.

3.8 Animal Handling

Animals were handled in accordance with the UK Animals Scientific Procedure Act of 1986, under licences approved by the UK Home Office, and with the approval of the University of Oxford ethical review committee, under PPL 30/3266. All *in vivo* work (animal handling, and MRI and CT imaging) was carried out by Dr Veerle Kersemans, under PIL IC45C45D9. Details of animal preparation and handling are

adapted from Gilchrist *et al.*^[5]

3.8.1 Animal Preparation

CBA mice (Charles River) were housed in individual ventilated cages, maintained at 22 °C and 50 % humidity, with a 12 hour dark/light cycle. Animals were provided with autoclaved bedding material, cage enrichment, filtered water *ad libitum*, and a certified rodent diet. Every practical effort was made to minimise suffering, in accordance with the *3Rs* of animal handling, though one animal had to be euthanised on welfare grounds. 1–4 % isoflurane in air was used to induce anaesthesia, the condition of which was typically monitored using our piezoelectric sensor as described in Chapter 6, and maintained at 40–80 breaths per minute.

3.8.2 Homeothermic Maintenance

Rectal temperature was measured using a fibre-optic thermometer. This temperature was continuously monitored and body temperature maintained at ~35 °C by means of the carbon-fibre heating system demonstrated previously by Gilchrist *et al.*^[5]

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Chapter 4

Heterolayer-Independent

Inhomogeneous Strain Release in

Strained WS₂-Containing

Heterostructures

4.1 Introduction

Before the full potential of 2D materials can be achieved in flexible electronics, a more comprehensive understanding is needed of the influence of strain on the various heterostructures likely to be found in these devices. As discussed in Chapter 2, there are numerous ways in which the local environment can modify the properties of 2D materials.^[1,2] Like other materials, strain can also influence their properties significantly.^[3-5]

As described in Section 2.2.4, friction in 2D materials is complex. The van der Waals forces that hold the layers together are comparatively weak, and so incomplete strain transfer and sliding are likely to be a factor in their response to strain.^[6,7] Furthermore, the unique ease of out-of-plane deformation can lead to distortion and folding of the film at the nanoscale in response to mechanical stimuli.^[8]

In an effort to understand the influence these effects may have in vertically stacked 2D layered systems of different materials, herein we examine the changes in the photoluminescence (PL) spectra of the direct bandgap TMD tungsten disulphide (WS_2) in several different heterostructure configurations involving graphene and boron nitride (hBN), in response to strain. Poly(ethylene naphthalate) (PEN), a material commonly employed in flexible electronics, was used as the substrate due to its high chemical, thermal and hydrolytic resistance.^[9] The chosen heterostructures were (stacked vertically from top to bottom): WS_2/PEN , $\text{WS}_2/\text{hBN}/\text{PEN}$, $\text{WS}_2/\text{graphene}/\text{PEN}$, and $\text{WS}_2/\text{hBN}/\text{graphene}/\text{PEN}$, representing two possible device channels, contacts and gated channels respectively. Chemical vapour deposition (CVD) was used to grow the 2D materials, to demonstrate the reproducibility of these findings and their applicability to materials suitable for large scale manufacture.

4.2 Results and Discussion

All materials were grown via CVD, as described in Section 3.2, producing large domains of WS₂ (Figure 4.1a), and continuous films of typically bilayer graphene and hBN (Figure 4.1b & 4.1c). Quality and coverage were determined by optical microscopy and scanning electron microscopy (SEM). Raman spectroscopy was performed to characterise the films and determine the layer number (Figure 4.1d–4.1f). These represent typical spectra taken from each material, though the position of the Raman peaks can deviate due to doping and strain. The ripples visible in Figure 4.1b & 4.1c will lead to local variations of strain, though as we similarly observe later in the PL measurements the size of the laser spot exceeds the size of these ripples and so the Raman signal represents an average across the resulting strain distribution. Despite its sensitivity to strain, Raman was not used for measurements of the heterostructures on PEN as the large background signals produced by this polymer were found to obscure the signals from the 2D materials.^[10]

We used the well-established wet chemical etching technique to remove the growth substrate, with transfer predominantly achieved using wet/aqueous transfer (aq.). This was compared with our previously reported non-aqueous transfer technique (non-aq.), in which isopropyl alcohol is used to displace water, as this can modulate interlayer interactions by reducing trapped interfacial contamination.^[11] Further information and schematics of the two processes are provided in Section 3.3.1. The heterostructures were stacked layer-by-layer from 1×1 cm films of graphene and hBN, and domains of WS₂ typically 100–200 μm in size.

4.2. RESULTS AND DISCUSSION

PL measurements were performed on the different heterostructures (shown schematically in Figure 4.1g) before, during and after the application and relaxation of strain by bending. The maximum strain was 2.5 %, which was deemed to easily accommodate the maximum strain that real devices will experience.^[12] Application and relaxation of strain was repeated for a further 2–3 cycles, after which point the PL changes were observed to stabilise.

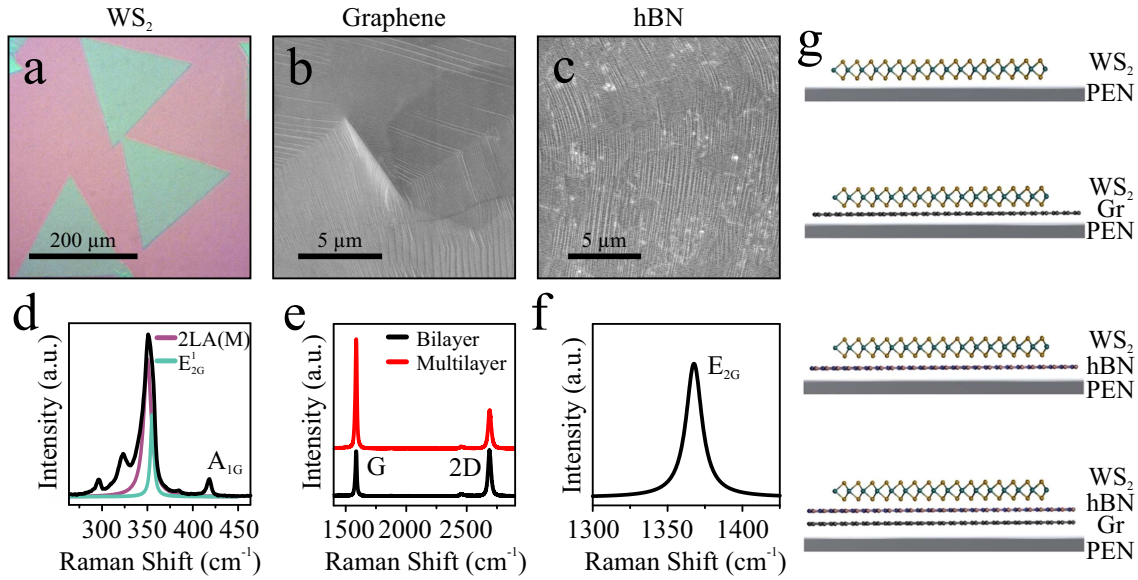


Figure 4.1: Characterisation of the studied 2D materials and schematics of their configurations in heterostructures. (a) Optical (200 μm scale bar) and (b,c) SEM (5 μm scale bar) images of the as grown WS_2 , graphene and boron nitride, respectively. (d–f) Raman spectra from the same, showing: (d) the combined 2LA(M)/ $\text{E}_{2\text{G}}^1$ (second order LA/in-plane, individual contributions revealed by Lorentzian fitting, other peaks omitted) and $\text{A}_{1\text{G}}$ (out-of-plane);^[13] (e) the G (sp^2 specific) and 2D (second order, specific to graphitic materials);^[14] and (f) the $\text{E}_{2\text{G}}$ (sp^2 specific, analogous to the G peak in graphene)^[15] characteristic Raman modes, respectively. The ratio of the peak intensities indicates that WS_2 is monolayer (d) and that graphene is bilayer with small multilayer islands (e), and the position of the peak indicates that the hBN in (f) is bilayer. (g) Schematic illustrations showing the layer ordering of the four heterostructures.

All measurements were carried out using a spectrometer and 532 nm laser, with strain applied *in situ* by collapsing radius test using a custom built holder mounted to

the sample stage. See Sections 3.5.2 & 3.6 for more details. The thickness of the 2D materials can be neglected from the calculation of strain since it is at least 5 orders of magnitude less than the substrate (~ 0.8 nm for bilayer graphene^[16] and hBN^[15] and 0.6 nm for WS₂^[17]).

Due to the convex shape of the substrate as strain is applied, it was only possible to measure the central region of the specimen under tension. The number of measurable WS₂ domains was optimised by mapping their positions on the growth substrate to determine the area with the best coverage of high quality domains, and aligning this to the centre of the PEN substrate (see Figure 3.3 in Section 3.3.1 for more details). This had the advantage of confining our measurements to a region of approximately uniform strain.

The position and intensity of the PL peak is strongly dependent on the laser power density. Renormalisation leads to a redshift of the peak with increasing incident power (Figure 4.2a),^[18,19] and intensity increases with laser power due to an increased generation of excitons, though this begins to saturate at higher laser powers (Figure 4.2b). For this reason we ensured a constant laser power of 1.1 mW or ~ 4 kW/cm² by controlling the temperature and current supplied to the laser diode, and ensuring consistent focus of the microscope. This was sufficient to provide an adequate signal-to-noise ratio, without inducing significant thermal effects.^[20,21]

The PL spectrum of WS₂ comprises two component emissions arising from the recombination of excitons (A) and trions (A⁻), the latter being quasiparticles composed of an exciton bound to either a hole or, in this case, an electron due to the intrinsic n-type doping of CVD-grown WS₂.^[17,22,23] Trion emission leads to broadening of the

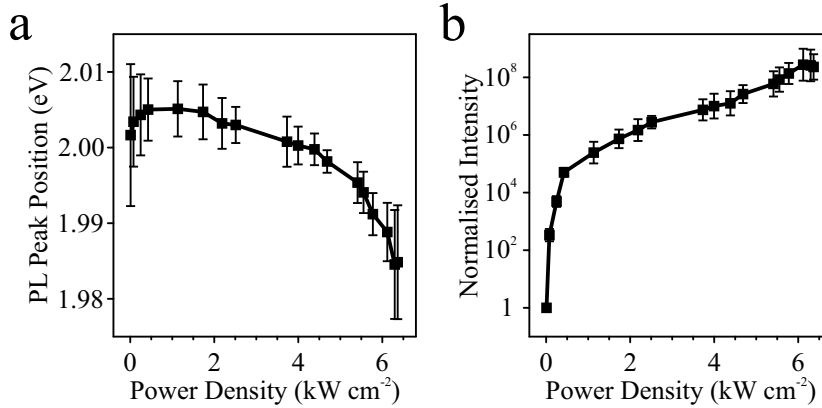


Figure 4.2: Effect of laser power on PL peak, demonstrating the need to carefully control the power density to prevent erroneous changes in position and intensity. (a) Peak position and (b) normalised PL intensity as a function of laser power density.

PL spectrum on the low energy side. Properties that can typically be drawn from these include the bandgap of the material, the level of doping and the trion binding energy.^[17,22,23] However, other mechanisms can change the peak shape and hamper the interpretation of these properties, so we have focussed on the mechanical interfacial interactions between the WS₂ and underlying materials and the substrate. Figure 4.3a shows the broadening of the peak that occurs after transfer from the growth substrate, likely caused by the higher substrate roughness causing uneven strain distributions; the further broadening and redshift occurs due to straining. Figure 4.3b–4.3d shows the general response of the fitted A and A⁻ emissions to strain cycling.

During the first strain cycle, an unexpected broadening and distortion of the peak shape occurs in all (>100) domains measured, leading to incorrect fitting of both the exciton and trion peaks. These changes, observable as a pronounced discontinuity in the fitted peak shapes, are shown in Figure 4.4. An example of the valid fitting is shown in Figure 4.4a, and the two variants of failed fitting for the strained PL

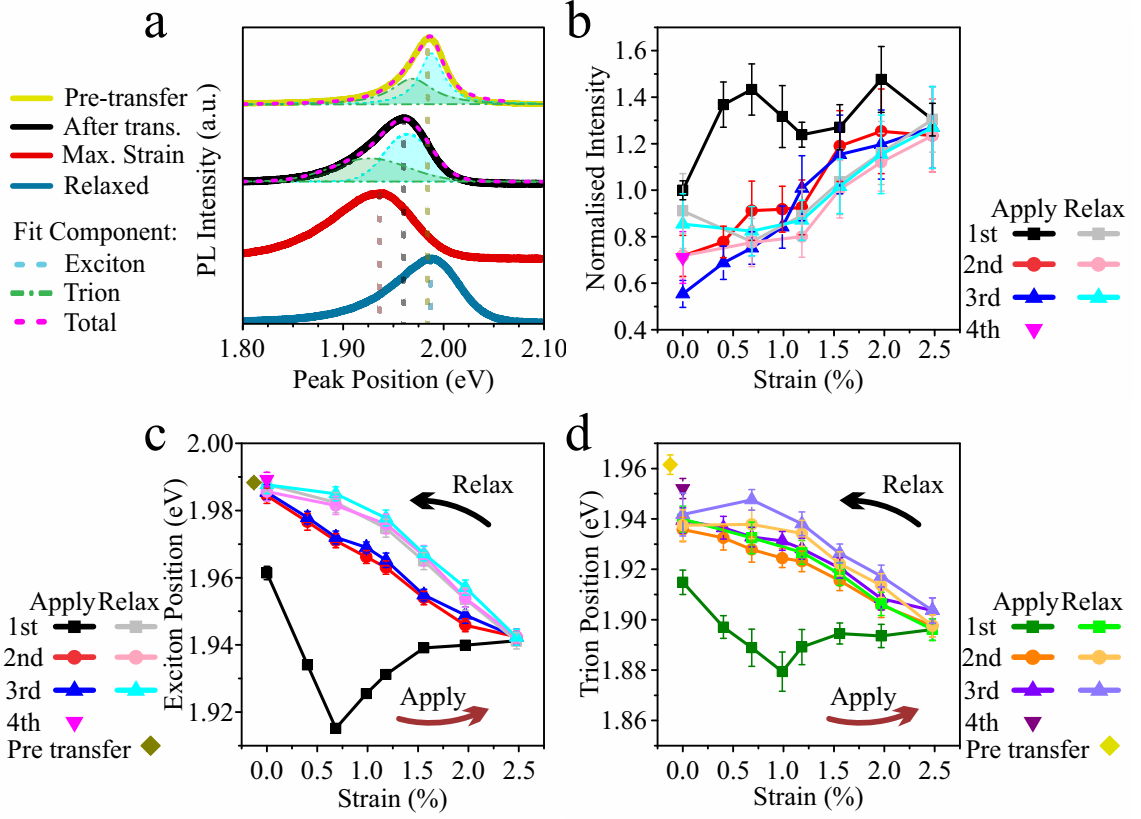


Figure 4.3: Example spectra and analysis of one of the studied heterostructures. (a) PL spectra of WS₂ taken before and after transfer, at maximum strain, and after strain was relaxed for the WS₂/graphene/PEN aq. heterostructure. Note that Lorentzian fits were used to extract information about the exciton and trion peaks on the pre-transfer spectrum, while due to broadening Gaussian fits were used post-transfer. (b) Changes in total emission intensity across three strain cycles in the WS₂/graphene/PEN non-aq. heterostructure as strain is applied and relaxed, and a fourth measurement at 0 % strain. Changes in (c) exciton (A) and (d) trion (A⁻) positions for same. Pre-transfer values and standard errors are also indicated. Note stabilisation to a hysteresis loop after the first application of strain for both A and A⁻ peaks.

spectrum are shown in Figure 4.4b & 4.4c. This accounts for the increase in the standard error of the peak intensity and trion position shown in Figure 4.3b–4.3d.

Our reasoning for the evolution of the peak shape is as follows. After transfer the peak is redshifted by two factors. First, a tensile strain is induced in the layers, arising from thermal mismatch and conformation of the sheet to the rough PEN surface. Second, the lower relative permittivity of the PEN substrate, compared to

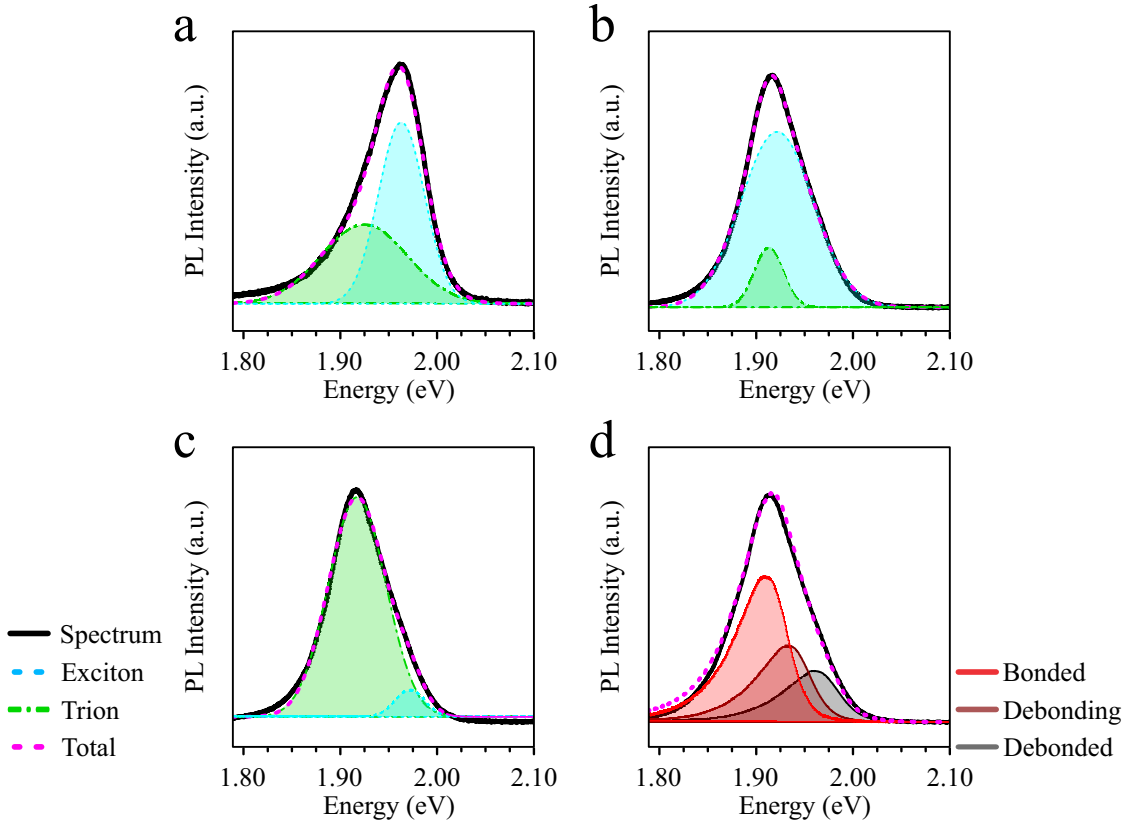


Figure 4.4: Fitting of exciton and trion peaks to the PL spectra. (a) Valid fitting of the unstrained PL signal. (b,c) Two variants of failed fitting of the strained spectrum, with discontinuities in peak position and intensity. (d) An approximation of the peak shape produced by summing multiple spectra over a distribution of energies.

the SiO_2 that the WS_2 was grown on, increases the binding energy of the excitons, thus lowering the energy released during recombination.^[9,24] When strain is applied, there is initially complete uptake of the applied strain by the WS_2 . Once a threshold of $\sim 0.7\%$ strain is passed, there is partial debonding and loss of coherency between the 2D materials and underlying substrate that leads to broadening of the PL peak. Once the strain is relaxed, as shown in Figure 4.3a there is a lingering blueshift relative to the initial position that is only partially recovered, caused by the debonding of the layers releasing the built in tensile strain described above. With this strain released,

when the substrate is relaxed the tensile strain in the WS₂ is less than before strain was applied, leading to the observed shift to the peak position. The peak shape during debonding can be more accurately approximated by summing multiple unstrained spectra across a distribution of energies, as shown in Figure 4.4d, the mechanism for which is outlined below.

The typical form of the changes in the spectrum is shown in Figure 4.5a for the application and relaxation of substrate strain. Intensity changes are omitted for clarity, but follow the same trends shown in Figure 4.7c—a pronounced increase with increasing strain. The strain in the WS₂ initially increases monotonically with the substrate, leading to a well-documented redshift common to TMDs due to a reduction of the bandgap. This reduction occurs due to the increase in interatomic spacing reducing the interaction strength between atoms, thereby reducing the binding energy of valence electrons.^[4,25–27] At strains of 0.4–1 %, there is a transition where sliding and debonding between the 2D materials and underlying substrate starts to occur. We recently also observed this transition in a Kelvin probe force microscopy (KPM) study of the WS₂/graphene/PEN heterostructure.^[28]

This general behaviour was common to the five heterostructure configurations tested, regardless of transfer method: a pronounced change in the peak shape resulting from partial debonding of the 2D materials perpendicular to the strain axis, beginning in the roughness ‘valleys’ of the substrate, leading to an inhomogeneous distribution of strain and so emission from a distribution of bandgaps (Figure 4.4d). This process is shown schematically in Figure 4.5b, and is similar to predictions in the ideal case by Kumar *et al.*,^[29] as well as the observations by Susarla *et al.*^[30] in synthesised

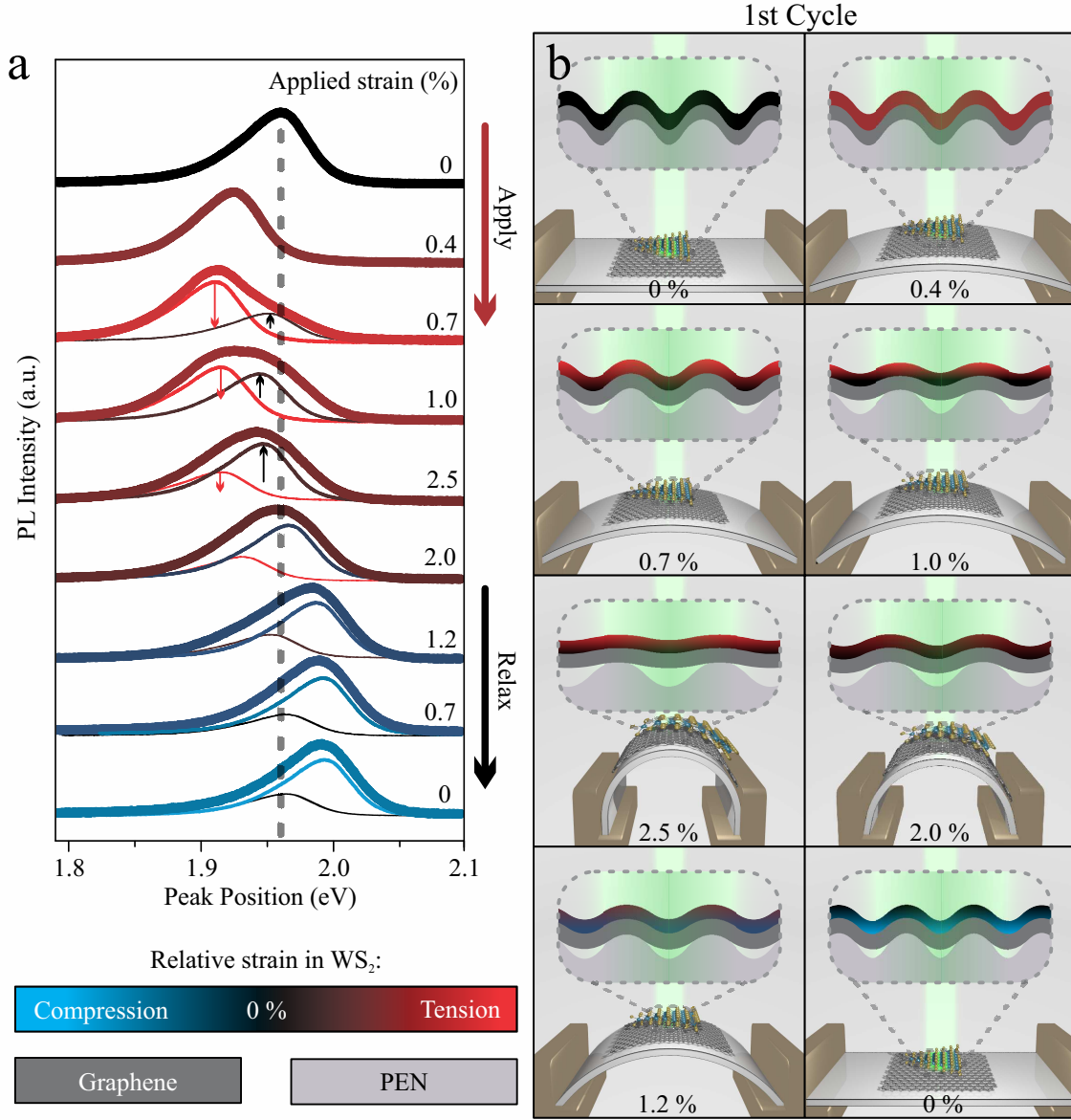


Figure 4.5: Details of the debonding process that takes place during the first strain cycle. (a) Example peak shapes (taken from the first strain cycle of the WS_2 /graphene/PEN aq. heterostructure) are shown normalised by intensity as strain is applied and relaxed, with approximate contributions from bonded (more tensile) and debonded (less tensile) regions indicated. (b) Schematics showing the debonding and loss of coherency between the WS_2 and underlying substrate in the first strain cycle, with exaggerated height profile indicating surface roughness inset. Colour indicates approximate strain, with 0 % set at the initial peak position. This shows the evolution of the peak shape, starting with a redshift while there is full coherency with the substrate, followed by a partial loss of coherency at higher strains and so an apparent broadening and blueshift. At the maximum strain, the original peak shape is practically recovered, indicating that the strain is mostly homogeneous. Intensity changes are consistent with changes shown in Figure 4.7c.

WS₂/MoS₂ heterostructures. Our transition occurs at lower strains than the latter due to weaker interlayer coupling, resulting from more interfacial contamination in our manually stacked structures.

As further strain is applied, the relative area that is debonded rapidly increases, owing to the unique ease of out-of-plane distortion in 2D materials. This leads to a decreased contribution from the redshifted component and so an overall blueshift to the peak position. With the roughness features occurring over length scales that are smaller than the laser spot size of $\sim 6\text{ }\mu\text{m}$, we effectively sampled the distribution of strain over many bonded and debonded regions. See Figure 4.6 for AFM profiles of the surface of the WS₂/graphene/PEN aq. heterostructure before and after the application of strain. We hoped to use AFM to image the debonding as a reduction in surface roughness, but were unable to resolve any difference. This again is likely due to the ease of out-of-plane distortions,^[7] and the limited resolution because of the high surface roughness of the substrate.

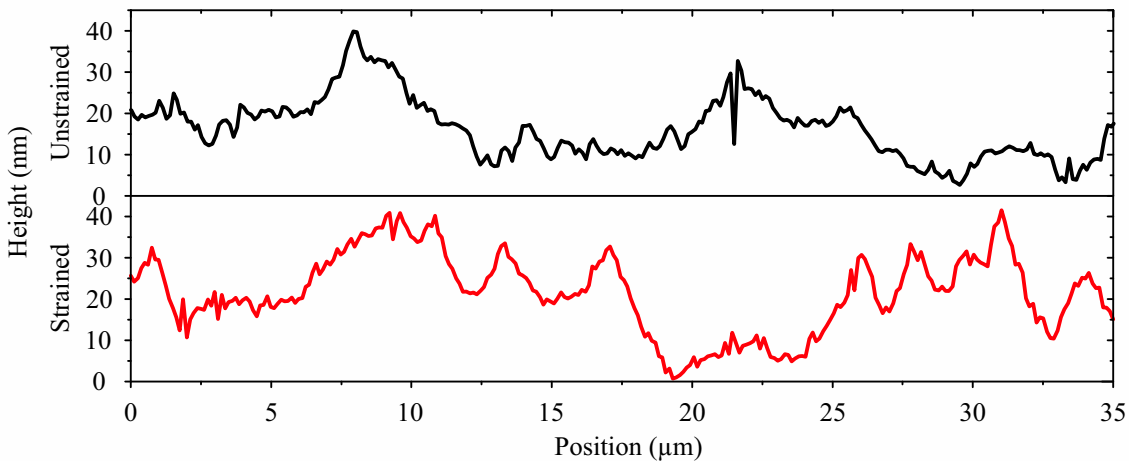


Figure 4.6: Typical line profiles from the WS₂/graphene/PEN aq. surface, taken by AFM (a) before and (b) after the application of strain, from different but comparable areas.

By 2.5 % strain, the emission is dominated by the debonded regions and the

initial peak shape is mostly recovered, with a smaller redshift due to the partial strain transfer. The transition can be best observed with reference to the changes in the global peak position (Figure 4.7a) and full-width half-maximum (FWHM) (Figure 4.7b), where there is a marked change above 0.4 % strain, with a partial reversal of the initially strong redshift and a broadening of the PL peak width. The cause of the increase in standard error at the onset of coherency loss is the inherent random nature of the debonding, which leads to different domains losing coherency at different rates. In Figure 4.7a we also plot the value of $-0.19 \text{ eV}/\%$ strain predicted by Su *et al.*^[31] for bandgap changes in WS_2 under tensile strain, indicating that even before coherency loss the WS_2 experiences less than half of the strain applied to the substrate. This is a result of the measurement geometry and the mismatch of Young's moduli between the film and the substrate. See Section 3.6 and Figure 3.5a for more information.^[32]

On the basis that the WS_2 experiences 50 % of the applied strain at the point debonding begins to occur (a value of 0.35 % strain in the WS_2), it is possible to estimate the shear stress necessary for debonding to take place. Using Equation 3.8 (as derived in Section 3.6) with the average distance from the edge $x = 20 \text{ }\mu\text{m}$ and the Young's modulus $E_f = 270 \text{ GPa}$,^[33] the interfacial shear stress is estimated to be $\tau_f = 28 \text{ kPa}$. While this is valid as a first approximation, the assumption of a planar interface likely causes underestimation of the true value due to stress concentrations in the valleys of the substrate surface seen in practice (Figure 4.6).^[34] This analysis also implies that the onset of debonding progresses rapidly across the domain, moving at a rate of $\sim 50 \text{ }\mu\text{m}/\%$ strain.

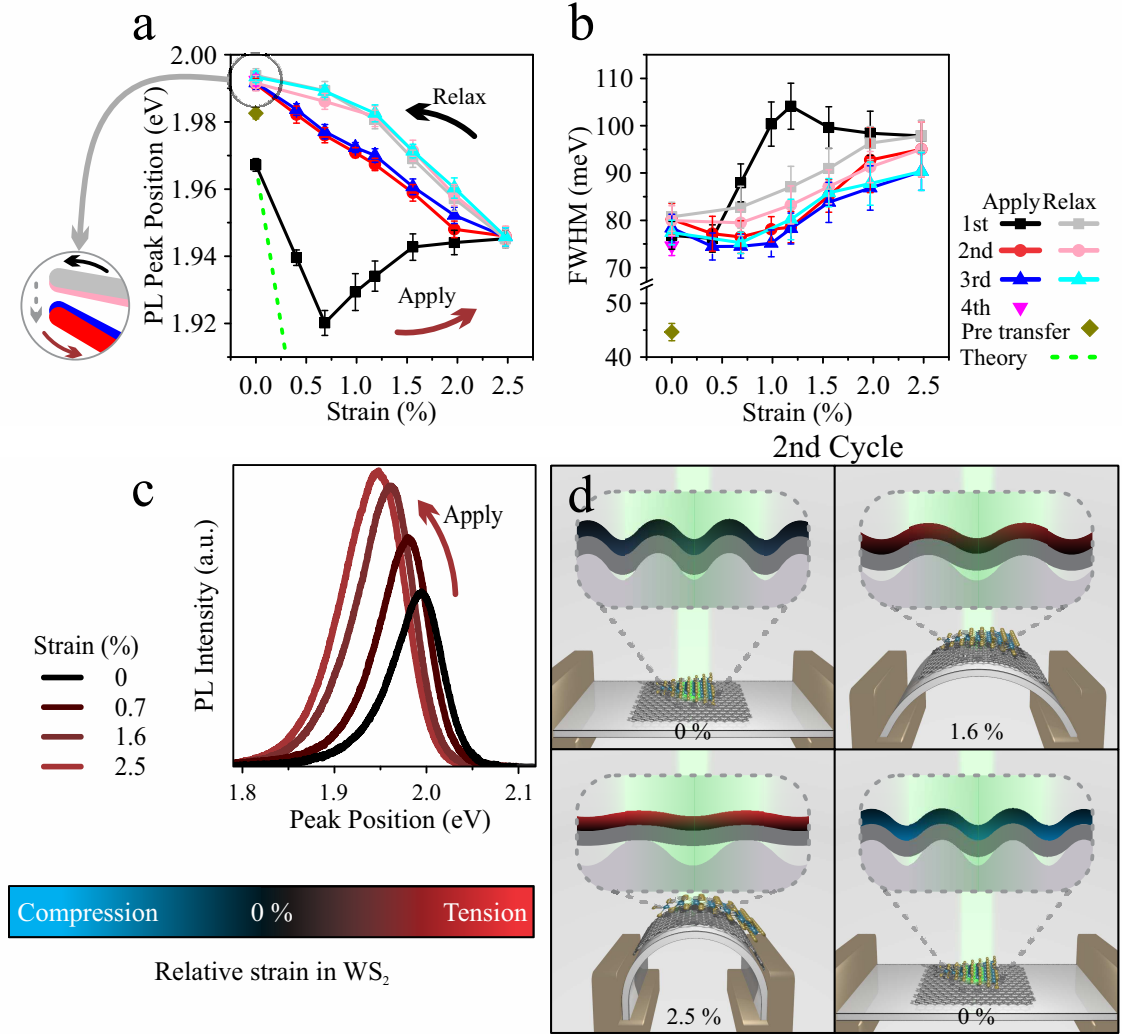


Figure 4.7: Changes in the peak position and shape, and details of the stabilised strain behaviour in subsequent strain cycles after debonding. (a) Overall peak position and (b) FWHM for the WS₂/graphene/PEN non-aq. heterostructure over 3 strain cycles, and before transfer. Pre-transfer values, the shift predicted by theory, and standard errors are also indicated. The inset in (a) shows the small relaxation/blueshift that occurs between strain cycles. (c) Changes in the peak position and intensity as strain is applied. Note no major changes in peak shape over full range of strain, indicating that a stable state has been reached. (d) Schematics showing the effect of strain on the WS₂ in the second strain cycle as a result of the debonding in the first cycle, with exaggerated height profile inset. Colour indicates approximate strain, with 0 % set at the initial peak position.

Figure 4.7c shows the changes to the emission during the second strain cycle. As the WS₂ has largely debonded from the underlying substrate, the degree of strain transfer and so the magnitude of the redshift is smaller, and the strain distribution is

largely homogeneous, as reflected in the more modest broadening. Two mechanisms contribute to the associated increase in luminescence intensity. Firstly, an increase in the absorbance cross-section as the bandgap narrows leads to more incident light being absorbed. Secondly, due to the increasingly large offset between the K (direct, radiative) and Σ (indirect, non-radiative) conduction band minima as strain increases, there is a reduction in the quenching caused by the drain of carriers from K to Σ ; this draining occurs since the Σ minimum is lowered in energy due to bandgap renormalisation caused by the high density of optically generated excitons.^[18] We believe that the expected quenching at higher strains is not observed due to the incomplete strain transfer, though if some parts of the WS₂ are above the expected threshold where the intensity begins to decrease again while others are below, this would explain the relatively modest PL intensity enhancement we observe compared to that predicted by Steinhoff *et al.* for MoS₂.^[18]

With reference to our recent KPM study on the WS₂/graphene/PEN non-aq. heterostructure, we propose that the debonding is primarily between the substrate and the first layer of 2D materials, but cannot comprehensively rule out debonding between layers of 2D materials. This study indicated a debonding transition at similar strains in the PL peak position (Figure 4.8a) and work function (Figure 4.8b), with only slight discrepancies in the changes to the work function of graphene and WS₂, implying that the effect happens nearly simultaneously in both materials.^[28]

Further strain cycling reveals stabilisation to a hysteresis loop, in which the debonding and interfacial sliding lead to incomplete strain transfer (Figure 4.7a). This is in contrast to the findings of Liu *et al.*,^[6] who observed no hysteresis in their meas-

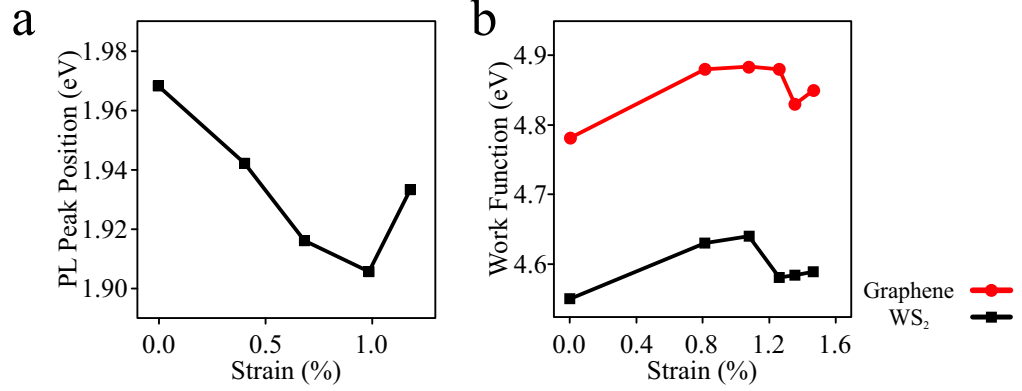


Figure 4.8: Comparison of debonding observed in PL and KPM measurements of WS₂/graphene/PEN non-aq. heterostructure. (a) PL peak position from WS₂ and (b) work function from graphene and WS₂. Note transition at similar applied strain ($\sim 1\%$) in both cases, implying that debonding takes place predominantly at the interface with PEN. This figure is adapted from Sarwat *et al.*^[28]

measurements of strained MoS₂ on PDMS, though they observed a similar incomplete strain transfer. This hysteresis originates from the compressive strain in the WS₂ once the substrate strain is relaxed, a result of the partial relaxation of tensile strain in the WS₂ following the debonding as strain was applied. Over time, this compressive strain relaxes and the heterostructure partially reconfirms with the substrate, leading to the small redshift highlighted in the inset of Figure 4.7a. When the substrate is subsequently strained again, the initial uptake of the strain is lower than in the first strain cycle and decreases further at higher strains. The reverse is true as the strain is relaxed, initially blueshifting the spectrum more rapidly before levelling off as substrate strain approaches zero.

To validate the debonding mechanism, we conducted local mapping of the peak positions during the same strain cycling described above on the WS₂/graphene/PEN non-aq. heterostructure, and compared this to the mapping of the same hetero-

4.2. RESULTS AND DISCUSSION

structure with a 50 ± 5 nm poly(methyl methacrylate) (PMMA) coating applied to the PEN surface to modify the surface roughness. The roughness of the PEN and PMMA/PEN substrates was characterised by AFM (Figure 4.9a–4.9c), and found to be $R_q = 6.89 \pm 1$ nm for PEN and $R_q = 9.49 \pm 1$ nm for PMMA/PEN. The PMMA film thickness was measured by cross-sectional SEM, an example of which is shown in Figure 4.9d.

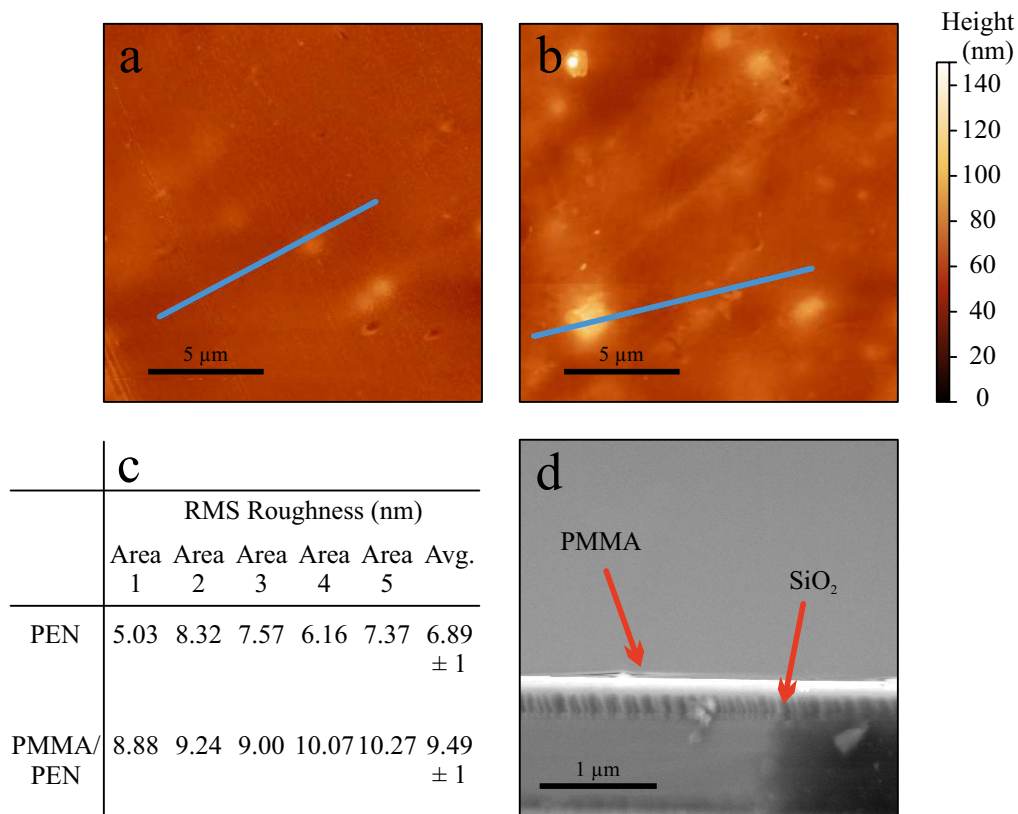


Figure 4.9: Characterisation of the surface topography and roughness for the PEN substrate with and without PMMA coating. Example AFM images taken on PEN (a) without and (b) with a layer of A1 495K PMMA spin coated onto the surface (scale bar 5 μm), and (c) a table summarising the RMS roughness values of multiple line profiles take from both. (d) Example of a cross-sectional SEM image used in determining the film thickness of the 50 ± 5 nm PMMA layer deposited onto a silicon wafer with 300 nm oxide layer by the same parameters. Scale bar is 1 μm.

To transfer onto the PMMA/PEN substrate, some modifications to the standard

procedure were required, since the PMMA layer precluded the use of acetone. By first transferring the WS_2 onto the graphene by aqueous methods, the entire heterostructure could then be transferred in a single step using a scaffold composed of the IPA soluble photoresist ma-N 1420 (Micro Resist). While this film was found to be more fragile than the usual PMMA scaffold, sufficient regions withstood the transfer to be measured.

In the first strain cycle, we observed small variations over the area we examined for the structure without PMMA (Figure 4.10a) and larger variations in the structure with PMMA (Figure 4.11a), in accordance with the increase in roughness. The later and broader onset of debonding in the PMMA structure is caused by the lower degree of strain transfer from the substrate through the softer PMMA layer (cf. Figure 4.10c & 4.11c). This is also the reason for the observed smaller total peak shift in this structure. After debonding has taken place, the effect of the differing roughness values is reduced (cf. Figure 4.10d & 4.11d), though the degree of hysteresis during strain cycling is larger with PMMA. The debonding is accompanied by a reduction in the spread of the peak positions in both cases (cf. Figure 4.10e & 4.10f, and 4.11e & 4.11f). In Figure 4.11g we also illustrate line profiles taken before and after the application of strain in the first cycle, revealing a quasiperiodic distribution that is globally redshifted but is otherwise largely unaffected by strain. This likely indicates a dependence on the larger scale variations of the substrate surface which remains significant even at the maximum applied strain of 2.5 %.

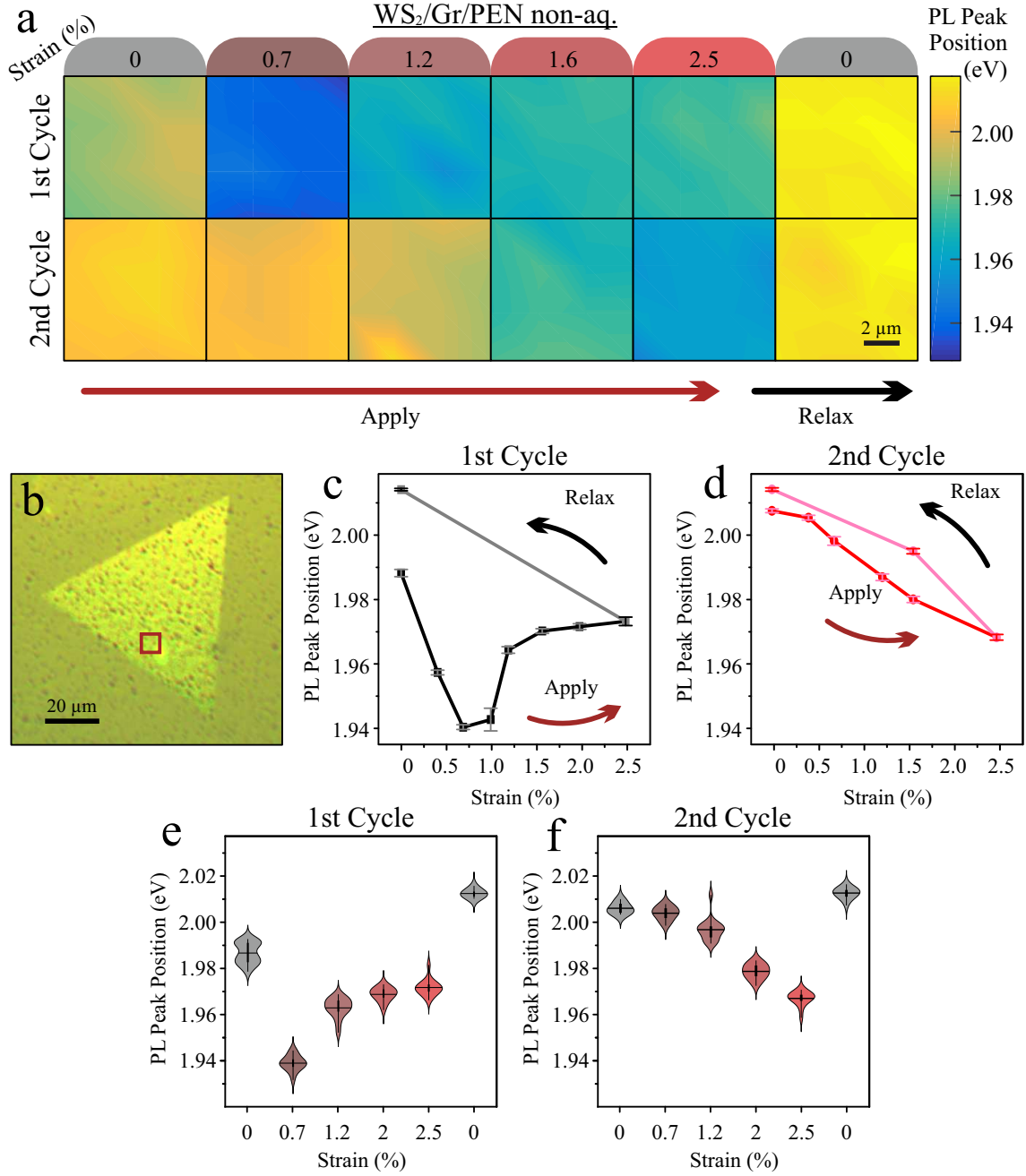


Figure 4.10: Local mapping of the peak shifts during strain cycling of the $\text{WS}_2/\text{graphene}/\text{PEN}$ non-aq. heterostructure. (a) Maps of PL peak positions during the first and second cycle, as strain is applied and relaxed. Scale indicated in the last frame is 2 μm . (b) False colour micrograph with the mapping area indicated and a 20 μm scale bar. (c,d) Average peak positions at each strain position for the (c) first and (d) second cycles, and (e,f) violin plots showing the distribution of peak positions within the mapped area for same. Note the large scale shift and release during the first strain cycle and comparatively small shifts during the second cycle, accompanied by a reduction in the spread of the data in the second cycle. Each map was acquired in approximately 15 minutes.

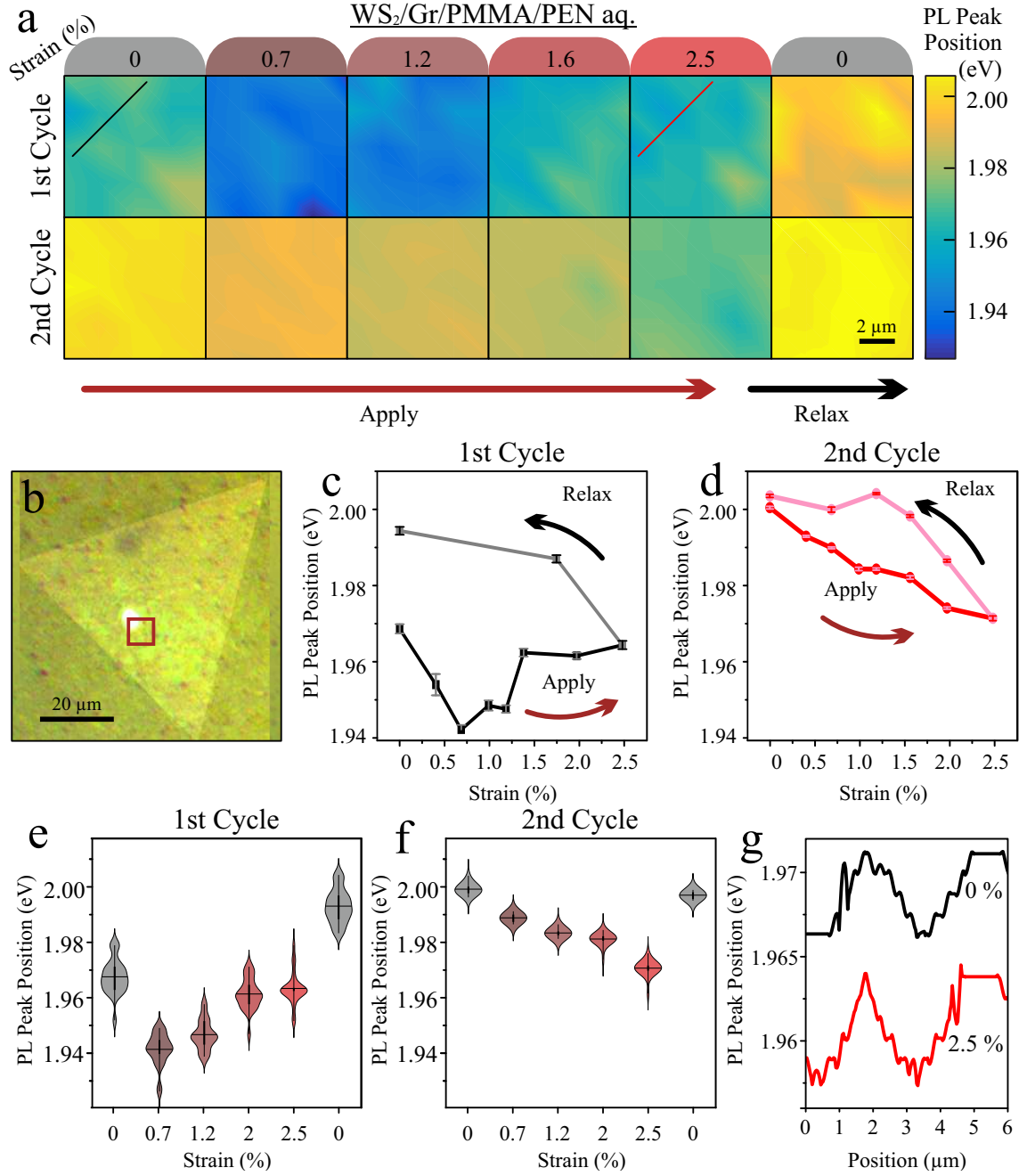


Figure 4.11: Local mapping of the peak shifts during strain cycling of the $\text{WS}_2/\text{graphene}/\text{PMMA}/\text{PEN aq.}$ heterostructure. (a) Maps of PL peak positions during the first and second cycle, as strain is applied and relaxed. Scale indicated in the last frame is 2 μm . (b) False colour micrograph with the mapping area indicated and a 20 μm scale bar. (c,d) Average peak positions at each strain position for the (c) first and (d) second cycles, and (e,f) violin plots showing the distribution of peak positions within the mapped area for same. Note similar trends to $\text{WS}_2/\text{graphene}/\text{PEN}$ case shown on the previous page, but featuring a broader region of debonding and larger hysteresis loop as a result of the lower modulus of PMMA. Each map was again acquired in approximately 15 minutes. (g) Line profiles taken before and after the application of strain, as indicated in (a).

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Little difference was observed in the response of the different heterostructures, and in all cases the same debonding and coherency loss occurs. The key changes are summarised in a bar chart in Figure 4.12. Small variations up to ~ 10 meV were found between the peak positions pre-transfer, attributed to compositional changes and differing amounts of post growth strain. Random variations in the surface contact also led to different magnitudes of observed shift post-transfer, after the release of the built-in strain, and over each strain cycle. On the basis of the value calculated by Su *et al.* for bandgap shifts due to strain (-0.19 eV/%),^[31] the magnitude of strain transferred never exceeds ~ 0.45 %, which is less than a fifth of the applied substrate strain. This again contrasts with the findings of Liu *et al.*,^[6] who found that for MoS₂ the strain transfer was low for low modulus substrates, but increased dramatically for higher modulus substrates such as PEN.

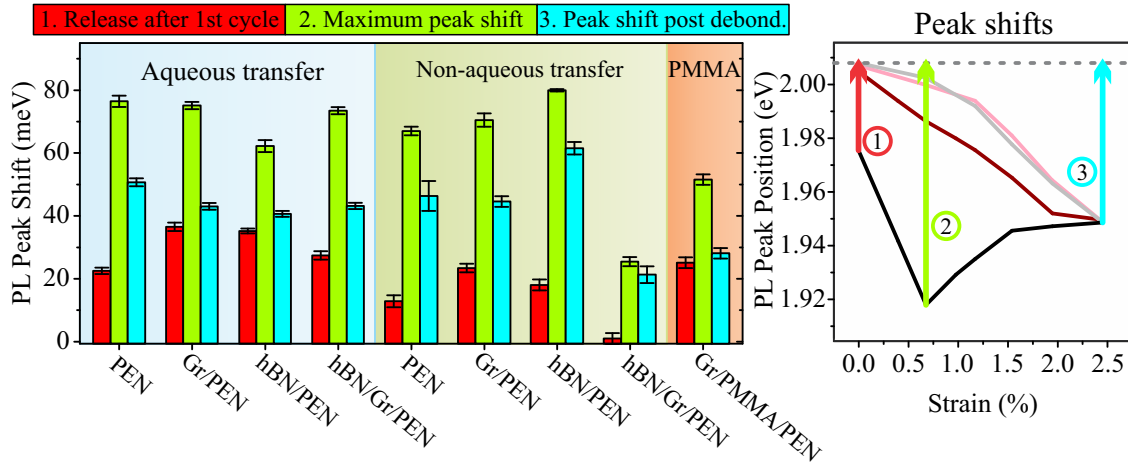


Figure 4.12: Summary of the key changes in the peak position during straining, for all heterostructures transferred by both aqueous and non-aqueous methods, as well as the WS₂/graphene/PMMA/PEN aq. heterostructure. This illustrates the similarities in the responses of all heterostructures, in terms of the: amount of strain released after the first strain cycle, maximum change between the unstrained position and at the point of coherency loss, and total changes between 0 and 2.5 % strain for the second strain cycle (i.e. after debonding). These peak shifts are detailed in a simplified plot of peak position as a function of strain.

To study the time-dependent redshift that occurs between measurements, we chose the WS₂/hBN/PEN aq. heterostructure as an example in an attempt to control other possible influences on the properties from electronic effects, since hBN has been shown to behave as an excellent screening layer when used as a substrate for other 2D materials.^[35,36] PL measurements were performed over the course of several hours at regular intervals, after holding the substrate at 2.5 % strain and then returning to zero. This confirmed that a residual blueshift remained after the substrate strain was relaxed. As described above, the blueshift following the first strain cycle can only be partially recovered following the removal of the substrate strain, due to the release of the built-in tensile strain arising from the transfer process (Figure 4.13a). After the second strain cycle, the magnitude of blueshift is significantly smaller (Figure 4.13b).

By annealing the structure at the glass transition temperature of the substrate (PEN $T_g = 120$ °C), we found that the emission was blue shifted, and the peak slightly sharpened (Figure 4.13c & 4.13d). This can be explained by an increase in the coherency between the substrate and WS₂ leading to a slight compressive strain as the debonded regions flatten out. The sharpening of the peak is caused by an increase in the homogeneity of the strain, and was stable over the time measured.

To demonstrate the resilience of these structures, after annealing we repeated the strain cycling up to 200 times, measuring the PL response at several intervals. This shows the stability of the response, in terms of the peak position—barring strain relaxation effects—as well as the FWHM and PL intensity (Figure 4.13e–4.13g). To ensure consistency between measurements, all spectra were taken one hour after the strain cycling was performed, limiting the influence of the previously described re-

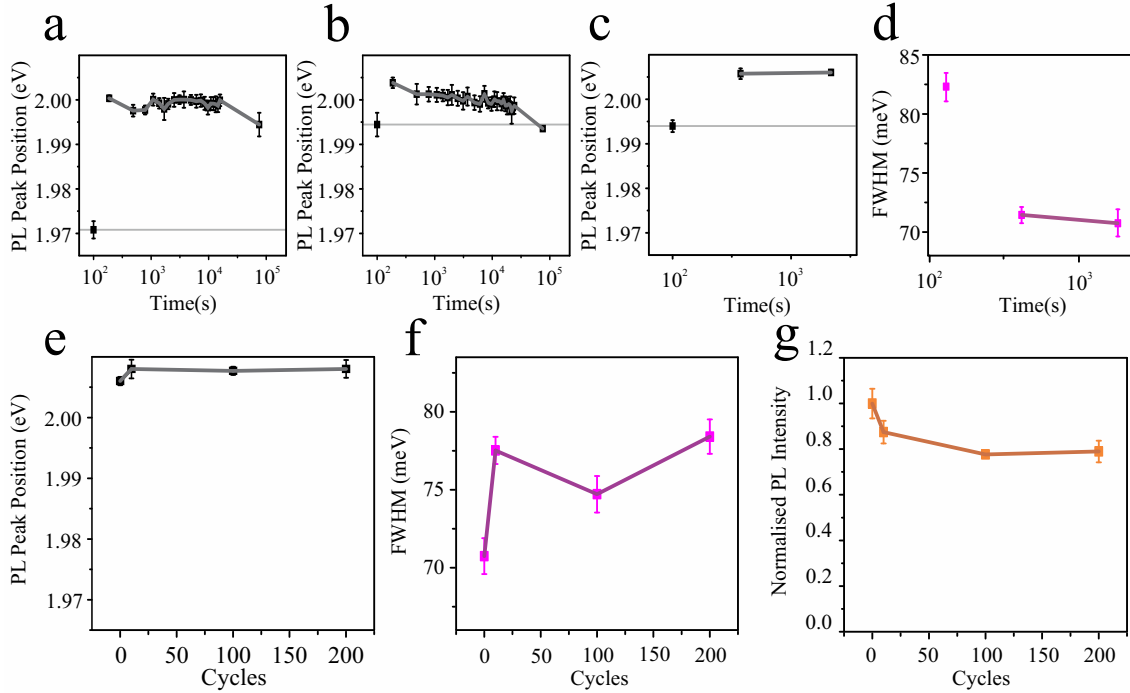


Figure 4.13: Changes in the PL peak over time before and after annealing, and as a result of repeated strain cycles. Positions following strain cycling for the (a) first and (b) second time, and (c) after annealing and straining for the first time. (d) The reduction in FWHM after annealing. The isolated points show the position immediately before the application of strain, with horizontal lines plotted as a guide to the eye. (e) Peak position taken 1 hour after cycling strain up to 200 times, and the corresponding (f) FWHM and (g) normalised intensity. All peak position plots are displayed over the same energy range for ease of comparison.

laxation mechanism. This provides additional evidence for the fact that the strain transfer reaches a stable state following the initial strain cycle, where the strain is no longer high enough to produce any more slippage so the peak position at 0 % strain does not change further. The reason for the observed broadening of the peak is the increased inhomogeneity of the strain following cycling compared to immediately after annealing.

4.3 Conclusions

In summary, we have demonstrated a mechanism by which the expected incomplete strain transfer to 2D materials on flexible PEN substrates takes place, broadly independently of the different heterostructure configurations and fabrication techniques used. These findings serve to illustrate that for 2D heterostructures to be used in flexible electronics, careful control of the processing will be required in order to avoid the unstable behaviour we have observed to varying degrees across all of the different structures studied. Since the debonding transition occurs within what we consider to be the useful operating strain range, this suggests the need for extra processing steps to release the built-in tensile strain arising from the fabrication process to produce stable and consistent behaviour across multiple devices. However, the demonstration of stable behaviour following the initial debonding is encouraging, as this indicates that after an initial ‘preconditioning’ strain cycle the properties of the heterostructures are consistent, and as such would be suitable for service.

4.4 Acknowledgements

AFM mapping of the PEN and PMMA/PEN surface was carried out by Miss Nicola Flanagan, and AFM and KPM of the strained heterostructures was performed by Mr Syed Ghazi Sarwat. The majority of the 2D materials used here were grown by the author, but occasionally materials were provided by: Dr Yuewen Sheng (WS₂, graphene), Miss Linlin Hou (WS₂), and Miss Wenshuo Xu (hBN).

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Chapter 5

All-2D Transparent Photodetector Arrays on Flexible Substrates

5.1 Introduction

In Chapter 4, we described the formation of heterostructures on flexible poly(ethylene naphthalate) (PEN) substrates, and discussed a mechanism by which tensile strain is accommodated in 2D materials during substrate bending. We concluded by discussing the possible ramifications of this debonding mechanism for the fabrication of flexible devices. The initial instability of the behaviour suggested that further processing would likely be necessary; the stabilisation apparent from the second strain cycle, as well as the universality of the mechanism across all heterostructures, encouraged us that this would not be especially challenging.

This chapter details the fabrication of transparent graphene-WS₂-graphene lateral heterostructured photodetectors on PEN substrates, devices that contain two

5.1. INTRODUCTION

of the systems studied in the previous chapter, using conventional photolithographic fabrication techniques adapted for compatibility with soft matter substrates. These devices consist of a $50\text{ }\mu\text{m}$ wide graphene electrode with a $5\text{ }\mu\text{m}$ gap, across which is placed a single crystal of 2D tungsten disulphide (WS_2), leading to the formation of the back-to-back Schottky barriers typical of a metal-semiconductor-metal (MSM) photodetector. Photons incident on the WS_2 generate excitons that are subsequently separated by an electric field applied across the device, leading to current flow and thus photodetection. There have been many demonstrations of this and similar types of device in recent years,^[1,2] commonly using metal electrodes such as gold^[3,4] and also exploring techniques like chemical doping,^[5] plasmonic nanostructures and others^[1] to improve the sensitivity. This work represents an extension of our previous work on graphene- WS_2 -graphene^[6] and graphene- WS_2/MoS_2 -graphene^[7] devices on silicon (SiO_2/Si) substrates, showing scalable on-chip fabrication of remotely addressable all-2D photodetector arrays on flexible and transparent polymer substrates. A schematic and an image of the completed device are shown in Figure 5.1.

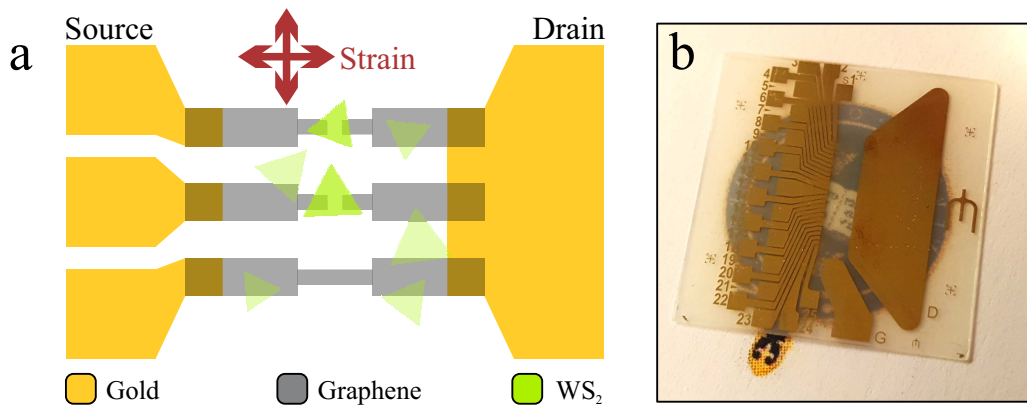


Figure 5.1: All 2D flexible photodetector arrays. (a) Simplified schematic of the device design, featuring two gapped electrodes with WS_2 domains, and one ungapped control electrode. (b) Image of the completed device, demonstrating the transparency. Hazing is a result of the high substrate thickness used.

Initial successes in fabrication using similar methods to those demonstrated previously were met with problems of device failure under strain. An analysis of the failure mechanism led to the development and subsequent characterisation of a modified lift-off process for graphene patterning, to replace the traditional plasma etching used initially. Though capable of slightly lower resolution, this technique produced graphene of equivalent electrical quality to the first devices, while eliminating the need for plasma etching entirely. This technique has the further advantage of potentially facilitating patterning on top of existing structures with differing geometry, impossible with plasma etching due to the requirement that each subsequent pattern must contain the previous one if etching of the preceding layers is to be avoided. Characterisation of these devices revealed that they too fail during the application of strain, though in this case the exact nature of the failure mechanism remains unclear.

5.2 Results and Discussion

As even graphene is too delicate to be contacted directly, the first step in making devices from 2D materials is the deposition of gold contacts to enable the connection of source and drain electrodes. On silicon and other rigid substrates, a thin layer of chromium or titanium is commonly deposited as an adhesion layer before the deposition of the gold, due to the higher reactivity of these metals. This is important as pure gold has very low peel resistance and, should the pattern even survive the lift-off process, the electrodes will quickly be damaged by the application of probes.^[8] This layer is very effective at promoting adhesion on SiO₂ and should also be for PEN, due to the formation of strong bonds with oxygen, in the latter case bonding to the

ketone group in the ester bridge.^[9] However, due to the propensity of adhesion layers to cause fracture of the deposited film during straining, we chose to pursue alternate means of promoting adhesion.^[10]

Films of positive photoresist were deposited on PEN substrates and patterned as described in Section 3.3.2. We tested several different techniques for promoting the adhesion of 100 nm gold films: a 5 nm Cr adhesion layer, transferring a layer of graphene prior to resist deposition, a post-lithography oxygen plasma pretreatment of 90 W for 2 minutes, and the plasma pretreatment plus a post-deposition hardbake at 120 °C for 20 minutes, as well as a control where pure gold was deposited directly onto the PEN. Lift-off was performed as described in Section 3.3.3.2. The key outcomes are demonstrated in Figure 5.2.

The control samples (Figure 5.2a) and graphene samples showed very poor adhesion, with large regions of the pattern removed entirely. As expected, chromium was effective as an adhesion promoter (Figure 5.2b), but was still avoided due to the aforementioned embrittlement this can cause. The plasma treatment also created very good adhesion, but lift-off was challenging and required significant ultrasonication, degrading the edge quality. This was solved by the hardbake, which helped to loosen the gold prior to lift-off and enabled the sharpest patterning (Figure 5.2c). Later, AFM analysis revealed significant etching of the PEN surface following plasma treatment, leading to the formation of a ~ 100 nm trench, accompanied by an increase in surface roughness. This helps to explain the improved adhesion and lift-off, and by depositing a 100 nm thick layer of gold we are able to fill this trench, producing well defined contacts without significant step height. The remaining photoresist was

removed using acetone, and complete lift-off was accomplished by up to 1 minute of ultrasonication, followed by rinsing in isopropyl alcohol (IPA). This process is outlined schematically in Figure 5.2d, and the full procedure is detailed in Section 3.3.3.

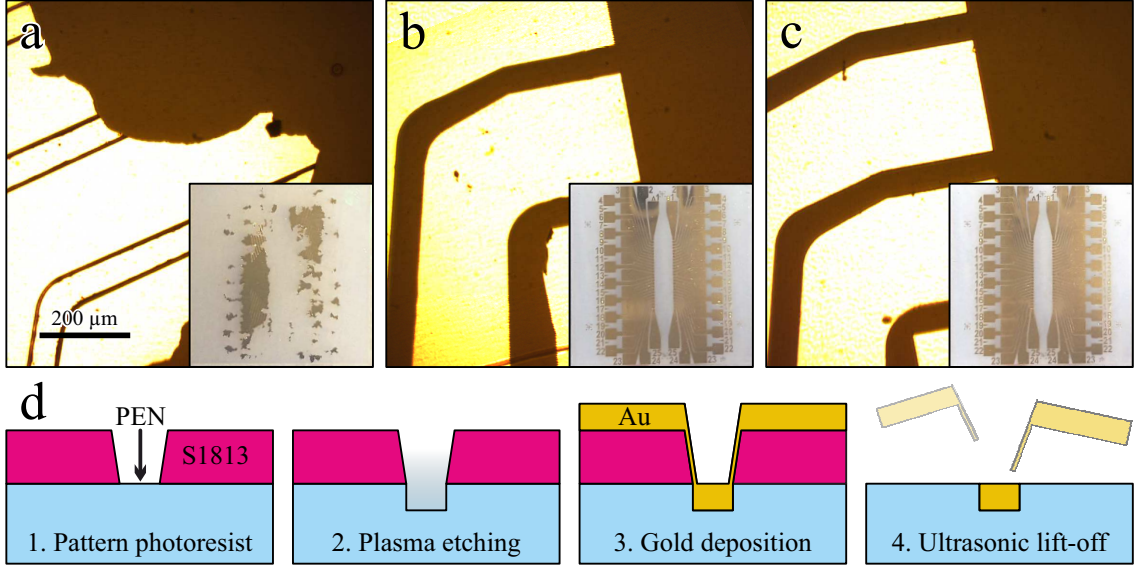


Figure 5.2: Details of the fabrication process for gold contacts. (a–c) Post lift-off optical images with pictures inset of (a) 100 nm Au with no adhesion layer or surface treatment, (b) 95 nm Au with 5 nm Cr adhesion layer, (c) plasma treated substrate with hardbake. Scale bar in (a) is 200 μm. (d) Schematics of the final process for the formation of gold contacts on PEN.

Films of graphene and domains of WS_2 were grown by CVD. Due to the undesirably high level of nucleation and consequent uneven surface morphology, we initially turned our attention to improving the graphene growth process. As-rolled copper foil has significant surface striations that, along with grain boundaries, serve as nucleation sites for graphene growth, leading to a reproduction of this texture in the graphene film even after the growth substrate is removed.^[11] To increase the homogeneity of nucleation while decreasing its density, we trialled two forms of abrasive polishing: a *manual polish* with Brasso[®] metal polish, and a two stage *mechanical polish* using

stitched polishing mops with progressively finer polishing compounds.

Polishing and growth were performed as described in Section 3.2.1. SEM images of the graphene in each case are shown in Figure 5.3. Note the strongly striated surface of the copper observed at low magnification in Figure 5.3a, visible as changes in the contrast and direction of graphene ripples due to the texture of the copper. The manual polish produced significant improvement in the surface finish, but some scratches remain. We also found that despite significant cleaning of the foil before CVD was performed, some residual silica particles from the polish could be observed on the surface (Figure 5.3b). Further improvement was possible with the mechanical polish, which provided additional reduction in the appearance of scratches on the surface of the foil (Figure 5.3c). Another advantage was that the foils were easier to clean, likely due to the ready etching of residual ferric oxide particles from the jeweller’s rouge used in the polishing by the HCl used to clean the foil before CVD was performed,^[12] in contrast to the silica particles found in Brasso[®].^[13]

We transferred the films onto silicon wafers and examined them using Raman spectroscopy. While we were still able to observe areas of thicker/multilayer graphene, we found films composed predominantly of a mixture of mono- and bi-layer graphene, identifiable by the differing ratios of G to 2D peak intensity (Figure 5.3d). Raman spectroscopy of graphene on PEN was not possible due to the intense signals produced by the PEN in the same region as those of graphene, including additional G-band signals from the sp^2 bonded polycyclic aromatic naphthalene group,^[14,15] severely exceeding the limits of the detector before sufficient signal from the weaker emission of graphene could be collected (Figure 5.3e). As such, we relied on microscopy and

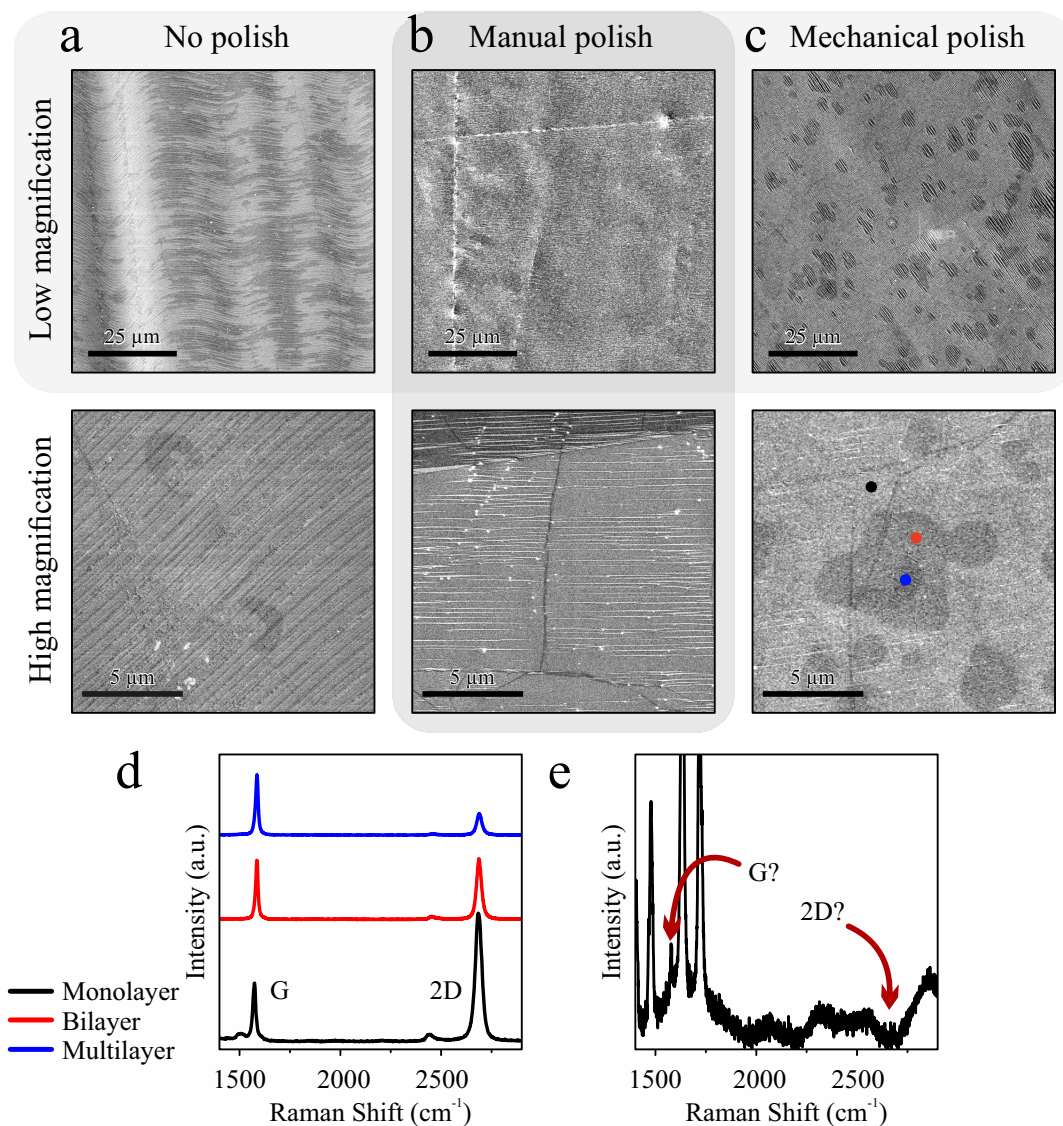


Figure 5.3: Characterisation of graphene films grown on unpolished and polished copper. (a–c) SEM images at low and high magnification of (a) unpolished copper; (b) manually polished copper, with silica particle contamination clearly visible on the surface and decorating remaining scratches in the low magnification image; and (c) mechanically polished copper, showing good homogeneity of nucleation with limited second layer formation (identifiable by darker contrast). Scale bars are 25 μm and 5 μm for low and high magnification respectively. (d) Raman spectra taken from the mechanically polished case after transfer to silicon wafer, with G/2D ratio indicating monolayer coverage, with small bilayer and multilayer regions. Typical locations from which these spectra can be measured are indicated in (c). (e) Raman spectrum taken from graphene on PEN illustrating the obfuscation of the G and 2D peaks by the intense signals from PEN.

electrical measurements to confirm the transfer of continuous, unbroken films to PEN.

Initially, graphene patterning was performed by first transferring a graphene film onto the patterned gold electrodes and using photoresist to protect the desired areas. The exposed graphene was then etched in oxygen plasma; parameters are detailed in Section 3.3.4. The remaining photoresist was removed by dissolution in acetone at 45 °C for 3 hours. These process is typically used for patterning on silicon substrates and produce a clean, sharp interface. However, as detailed below, this technique proved problematic due—perhaps unsurprisingly—to the step formation at the edge of the graphene ribbon where the PEN was etched away by the plasma. The plasma etching process is outlined schematically in Figure 5.4.

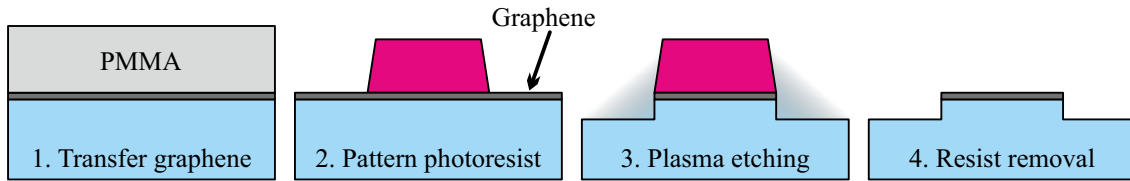


Figure 5.4: Schematics of the graphene etching process. Note the formation of a step in the PEN substrate in step 3.

Optical images of the typical appearance of the patterned graphene are shown at low and high magnification in Figures 5.5a and 5.5b respectively. Measurements of the gap reveal a degree of overexposure, with the measured width being approximately 3 μm larger than the target width at $\sim 8 \mu\text{m}$. This is a consequence of the use of positive photoresist with an ‘open-window’ photomask—necessary due to observations within the group of the greater potential for graphene contamination with negative resists. These residues are detrimental to device performance as they cause doping changes and increased contact resistance.^[16]

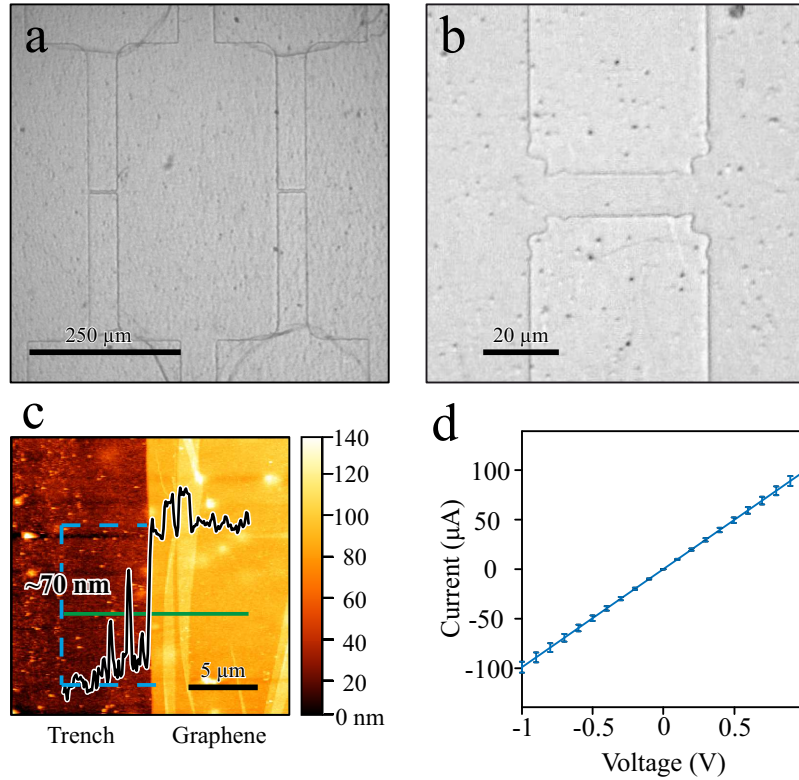


Figure 5.5: Characterisation of graphene electrodes patterned by oxygen plasma. (a) Low and (b) high magnification images detailing the junction of the gapped electrodes. Scale bars are $250\ \mu\text{m}$ and $20\ \mu\text{m}$ respectively. (c) AFM image of the step formed at the edge of the graphene electrodes during the plasma etching process (scale bar $5\ \mu\text{m}$). (d) Typical electrical measurement of the ungapped graphene electrodes, with standard error indicated.

The excellent contrast of the ribbon edges was the first indication of the deleterious effect of the plasma on the PEN substrate; as we will observe later, due to its high transparency, optical images of graphene typically require significant contrast enhancement. To measure the magnitude of this step, we examined the edge of the graphene at the device channel using AFM (Figure 5.5c). This image clearly reveals the large step height of $\sim 70\ \text{nm}$. The etching also led to a near-doubling of the surface roughness from $R_q = 6.9 \pm 1\ \text{nm}$ (as measured in Figure 4.9) to $R_q = 12.1 \pm 1\ \text{nm}$. Nevertheless, we proceeded with the device fabrication using this method, to deter-

ine: whether photodetection was still possible, and what effect the step would have on device performance. We measured the ungapped control electrodes and found them to be highly conductive, comparable to electrodes fabricated on silicon substrates (see Figure 5.11c). A typical I-V curve is shown in Figure 5.5d, showing linear behaviour over the full range of applied bias. Electrical measurements were performed by contacting the source and drain electrodes and measuring the current flow as a bias was applied across the device. The full procedure is described in Section 3.7.1.1.

Having successfully fabricated highly conductive electrodes, we went on to measure the changes to the I-V behaviour during the application of strain. As in Chapter 4, strain was applied *in situ* using a custom-built holder mounted to the sample stage. This enabled fine control of the radius of curvature of the substrate, and thus the strain in the substrate surface. An image of the setup, showing a device in position during testing, is shown in Figure 5.6a. As strain was applied, we observed a pronounced reduction in the conductivity of the graphene ribbons, likely indicating damage as this exceeds previous observations of increased resistance in strained CVD graphene (Figure 5.6b).^[17–19] This reduction occurs similarly and proportionally for all electrodes measured, in spite of small variations in the initial conductivity. As strain was relaxed, there was a very small increase in the conductivity, and a further small increase after some time had elapsed. This gives further evidence that the graphene is permanently damaged by the application of strain, likely through fracture at the graphene–Au interface, although this could not be resolved in SEM images.

In spite of the substantial reduction in conductivity as a result of strain cycling, given the apparent stabilisation once strain was relaxed we proceeded to transfer

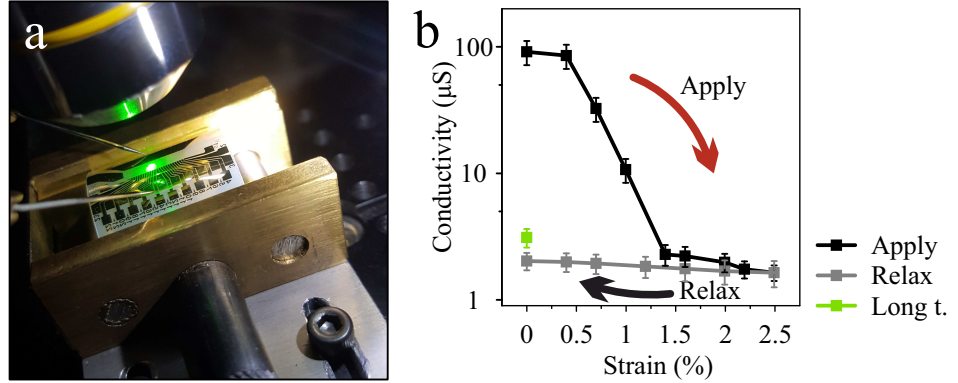


Figure 5.6: Measurement of strained devices. (a) Image of the strain holder and device *in situ*, with laser spot and probes to left hand side. (b) The effect of strain on the conductivity of the ungapped control electrodes, detailing the large reduction as strain is applied. Note the apparent stabilisation at strains above 1.4 %, and the slight increase as strain is relaxed, as well as a further increase to a stable value once the sample was relaxed for >24 hours.

WS_2 to the gapped electrodes using the non-aqueous transfer technique described in Section 3.3.1. This completes the photodetector, as shown in Figure 5.1. The presence of WS_2 across the channel was verified by inspection with optical microscopy, and the fact that it was monolayer was verified by the strong photoluminescence (PL) signal, as described in Chapter 4.

We pumped the device with a 532 nm laser and measured the photoconductivity over a range of illumination powers. In the absence of strain the devices show fairly weak photoconductivity (Figure 5.7a), significantly less than those demonstrated on silicon for the same gap width (cf. the μA order currents observed by Tan *et al.*,^[6] ~ 2 orders of magnitude larger than those observed here), with responsivity (ratio of incident power to measured photocurrent)^[20] of up to $\sim 5 \mu\text{A}/\text{W}$ at a bias of 6 V and an illumination power of 0.83 kW cm^{-2} . We believe this is likely due to a reduction in the exciton lifetime as a result of the higher substrate roughness, the larger channel

length and the effect of the step in the substrate at the graphene edge. We later fabricated control devices on silicon substrates and found more comparable photocurrents (Figure 5.12b).

Time dependent measurements reveal that the photocurrent is reasonably stable, with modest rise and fall times (the time taken to reach 90 % of the current in the on or off state, respectively) of ~ 2 seconds. (Figure 5.7b). At higher laser powers we did observe some reduction of photoconductivity, presumably due to laser induced damage, but with control of the laser power stable behaviour could be reached. However, during the application of strain the devices rapidly failed, with all photoconductivity lost by around 1 % strain (Figure 5.7c & 5.7d). This far outstrips the reduction in conductivity observed in the graphene control electrodes, with $\gg 99$ % of the applied voltage dropped over the WS_2 junction even at the lowest conductivity for the graphene, indicating an additional mechanism that is leading to device failure.

To elucidate the cause of device failure, we compared SEM images of the devices before and after the strained photoconductivity measurements had been performed. Prior to the measurements, the channel could be imaged free of charging due to the conductive WS_2 and graphene dissipating the build up of charge. Once the device had been strained, we observed fracture/removal of the WS_2 at the interface with the graphene electrode that resulted in exposure of the PEN substrate, as indicated by the obvious charging visible in this region at higher magnification (Figure 5.8). Though this damage was always seen at the edge of the graphene electrode, in Figure 5.8a it can be seen that the failure is in a monolayer region (again confirmed by PL measurement), while in Figure 5.8b failure occurs at the tip of a multilayer region

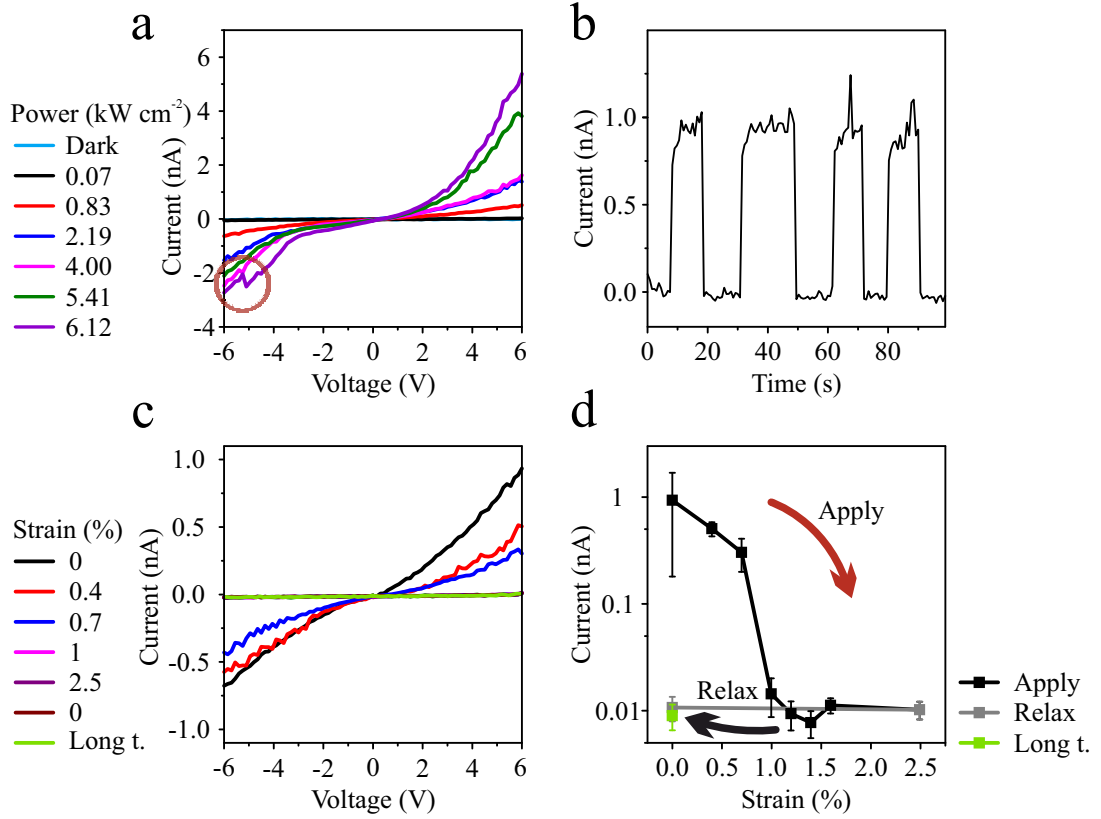


Figure 5.7: Electrical measurements of the plasma patterned photodetectors. (a) Power dependence of a typical device, showing the small photocurrent generated and its increase with irradiation intensity. An example of the reduction in current due to damage at higher laser power is circled in the lower left. (b) Typical time dependent measurements of a plasma patterned device, showing the stability and modest rise and fall times of ~ 2 seconds. (c,d) Strain dependence of the measured photocurrent. A constant laser power of 0.83 kW cm^{-2} and bias of 6 V was used unless otherwise stated.

that we commonly find at the centre of CVD-grown WS_2 . The latter case is likely due to a concentration of current flow into the monolayer region from the top point of the more highly conductive multilayer triangle. Due to the observed damage from the plasma etching process at the graphene electrode edges, it was necessary to determine whether the resultant step and increased roughness were responsible for breaking the WS_2 , likely through stress concentration at the sharp interface.

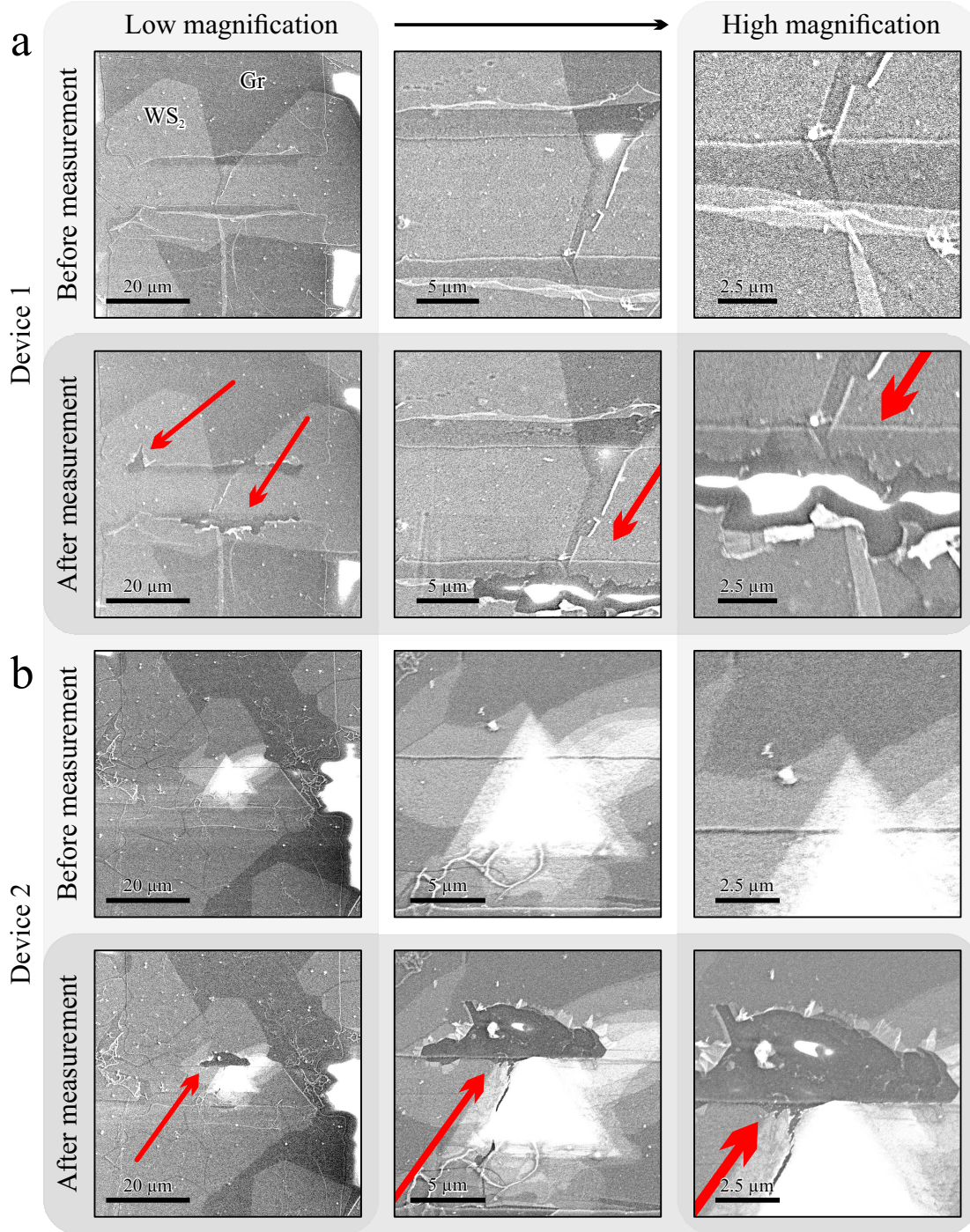


Figure 5.8: SEM images showing two devices before and after the photoconductivity measurement under an applied strain of 1.6 %. As indicated (red arrows), both devices show clear evidence of failure after the measurement, with device 1 (a) showing fracture across monolayer regions, and device 2 (b) showing fracture concentrated around a multilayer island, identifiable by its triangular shape and strong contrast. Note bright charged regions at damage sites in after images at higher magnification. From left to right, scale bars are: 20 μm , 5 μm , and 2.5 μm .

A different patterning approach was required for producing graphene electrodes without damaging the PEN substrate. Recently, Trung *et al.*^[21] demonstrated a process analogous to the gold lift-off process used here (described in Section 3.3.3). Here the photoresist is used not to protect selected areas of the graphene from removal, but to mask off areas such that a transferred layer of graphene may only contact the substrate in the desired pattern. A substantially thinner PMMA scaffold was used to facilitate improved conformation of the transferred graphene film with the patterned photoresist. We tested a 50 nm film (as was used to modify the surface of the PEN substrate in Chapter 4), but found that this was too fragile to transfer and resulted in fragmentation of the film; a 100 nm film was found to give acceptable results. The samples were dried overnight, hardbaked to ensure proper contact of the graphene with the PEN surface, and the photoresist and transfer scaffold removed in acetone. The excess graphene not in contact with the substrate was scissored using a brief ultrasonic treatment and washed away, leaving the desired pattern on the substrate. A schematic detailing the process is shown in Figure 5.9, and the specifics are described in Section 3.3.4.2.

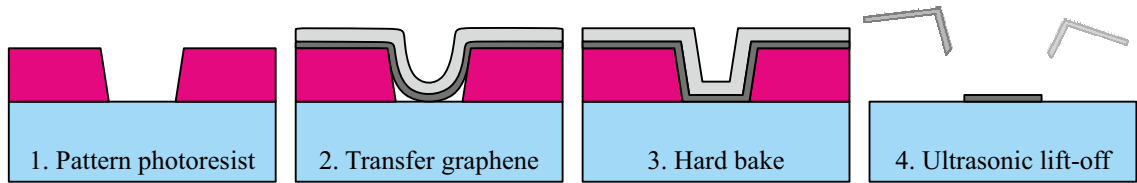


Figure 5.9: Schematic detailing the graphene lift-off process. A layer of graphene with 100 nm PMMA scaffold is transferred onto the patterned resist (1 μm S1813), left to dry, and baked to ensure conformation to the pattern. The excess graphene is removed by ultrasonication and washing with IPA.

Next, we focussed on optimising the photolithography process to achieve stable

and consistent patterning with the minimum possible gap width. The 45 mJ cm^{-2} dose used for the gold patterning was found to be too high to reproduce the $5 \text{ }\mu\text{m}$ gap on the mask, resulting in removal of this region due to overexposure. By reducing the dose to 25 mJ cm^{-2} , we were able to preserve this feature while still producing clean surfaces after development. As the resist profile can be strongly affected during development, we also tested the development time by parametrising the patterned ribbon quality in terms of gap width before and after graphene patterning, and the yield of successful patterning. These results are summarised in Figure 5.10a. Shorter times led to underdevelopment, resulting in an apparent gap width several microns larger than the desired gap before patterning due to residual resist at the pattern edges, and a final ribbon width at least $1 \text{ }\mu\text{m}$ larger. Increasing the development time up to 70 seconds gave a reduction down to $5\text{--}6 \text{ }\mu\text{m}$, which was considered acceptable for our purposes. For all development times, the yield remained above $>90 \%$.

Example images of the patterned ribbons are shown at low and high magnification in Figures 5.10b and 5.10c respectively. Note the reasonably sharp ribbon edges and lack of visible damage, representing a fourfold improvement in patterning resolution when compared to the work of Trung *et al.*^[21] Ultrasonication time also plays an important role in the final ribbon quality, with 30 seconds found to be adequate. Shorter times result in residual graphene at the ribbon edges, a typical example of which is shown in Figure 5.10d, imaged identically to the well defined ribbon shown in Figure 5.10c. We also demonstrated this patterning on silicon wafers, with comparable results obtained using the same parameters, though a much shorter ultrasonication time of 5 seconds was sufficient to scission the excess graphene, and in fact still

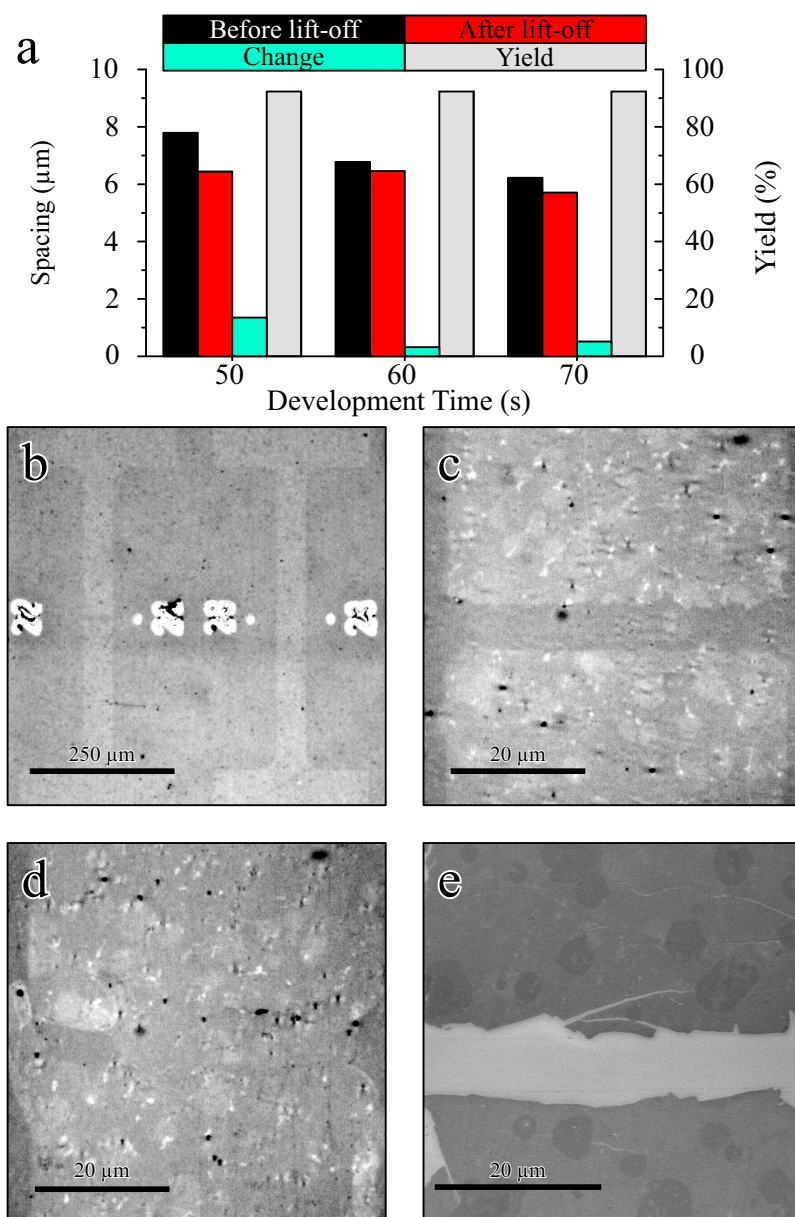


Figure 5.10: Characterisation of the graphene electrodes patterned by lift-off. (a) Changes to the measured gap width before and after lift-off with increasing development time, and the yield of successfully patterned junctions. (b) Low magnification (scale bar 250 μm) optical image of successfully patterned ribbons on PEN. (c-e) High magnification (scale bar 20 μm) optical images of: (c) successfully patterned gap and (d) unsuccessfully patterned gap, due to insufficient sonication; and (e) SEM image of a gap patterned by lift-off on silicon wafer. Note wider gap and presence of cracking visible in (e) due to more efficient transmission of vibration through silicon than PEN.

resulted in cracking to the graphene edges and a noticeably larger gap width of $\sim 8\text{ }\mu\text{m}$ (Figure 5.10e).

The graphene control electrodes were once again characterised by I-V measurement. Before the application of strain, they show near identical conductivity to the plasma-patterned electrodes demonstrated above, indicating that patterning by lift-off produces ribbons of equivalent quality to plasma patterning, without the associated damage to the PEN substrate. When strain was applied, we once again found that the graphene ribbons experience a significant reduction in conductivity, confirming that this effect is independent of the graphene patterning technique used (Figure 5.11a). We tested the effect of a mild vacuum annealing process ($120\text{ }^{\circ}\text{C}$ at $6\text{ }\mu\text{bar}$ for 8 hours) to see if this could be used to improve the conductivity of the ribbons, but this was found to instead be slightly detrimental (Figure 5.11b). We also tested if this technique might be used to restore the conductivity after straining but observed no significant change.

With the quality of the graphene electrodes confirmed, we again proceeded to fabricate photodetectors by transferring domains of WS_2 to the gapped electrodes, and performed measurements as before. Unstrained behaviour was similar, with weak but measurable photoconductivity that increased with laser power (Figure 5.12a). As mentioned above, control devices fabricated on silicon using the same technique showed photocurrent 1–2 orders of magnitude greater than the PEN devices (Figure 5.12b). Time dependent measurements reveal an improvement to the rise and fall times, typically found to be less than the measurement interval of 80 ms (Figure 5.12c). We then performed the strain dependent measurements. Once again, the

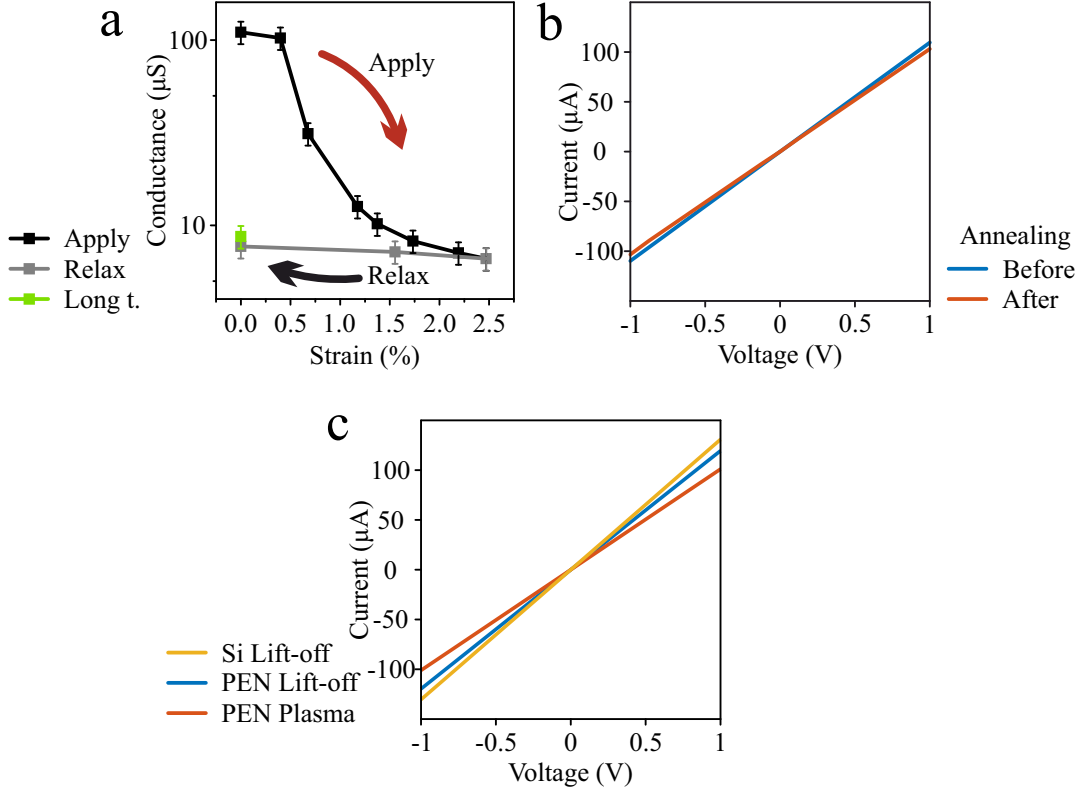


Figure 5.11: Changes to the conductivity of ungapped lift-off patterned graphene electrodes. (a) Large reduction as a result of strain cycling and (b) small reduction as a result of vacuum annealing. (c) Comparison of lift-off patterning on silicon wafer and PEN substrate, with plasma-patterned graphene replotted for reference.

devices failed (Figure 5.12d & 5.12e). However, in this case we measured a transient increase of up to one order of magnitude as shown in Figure 5.12d, the mechanism for which we propose below.

To ascertain if the devices were failing by the same mechanism as the graphene electrodes, where the conductivity reduced to a stable value for a given applied strain, we performed a small strain cycle several times to the devices and repeated the measurements again. In contrast to the ungapped electrodes, the behaviour was not stable with successive cycles, with complete loss of photoconductivity in all devices

following the second cycle (Figure 5.12f). This suggests that failure occurs by strain- and-laser-mediated electrical damage.

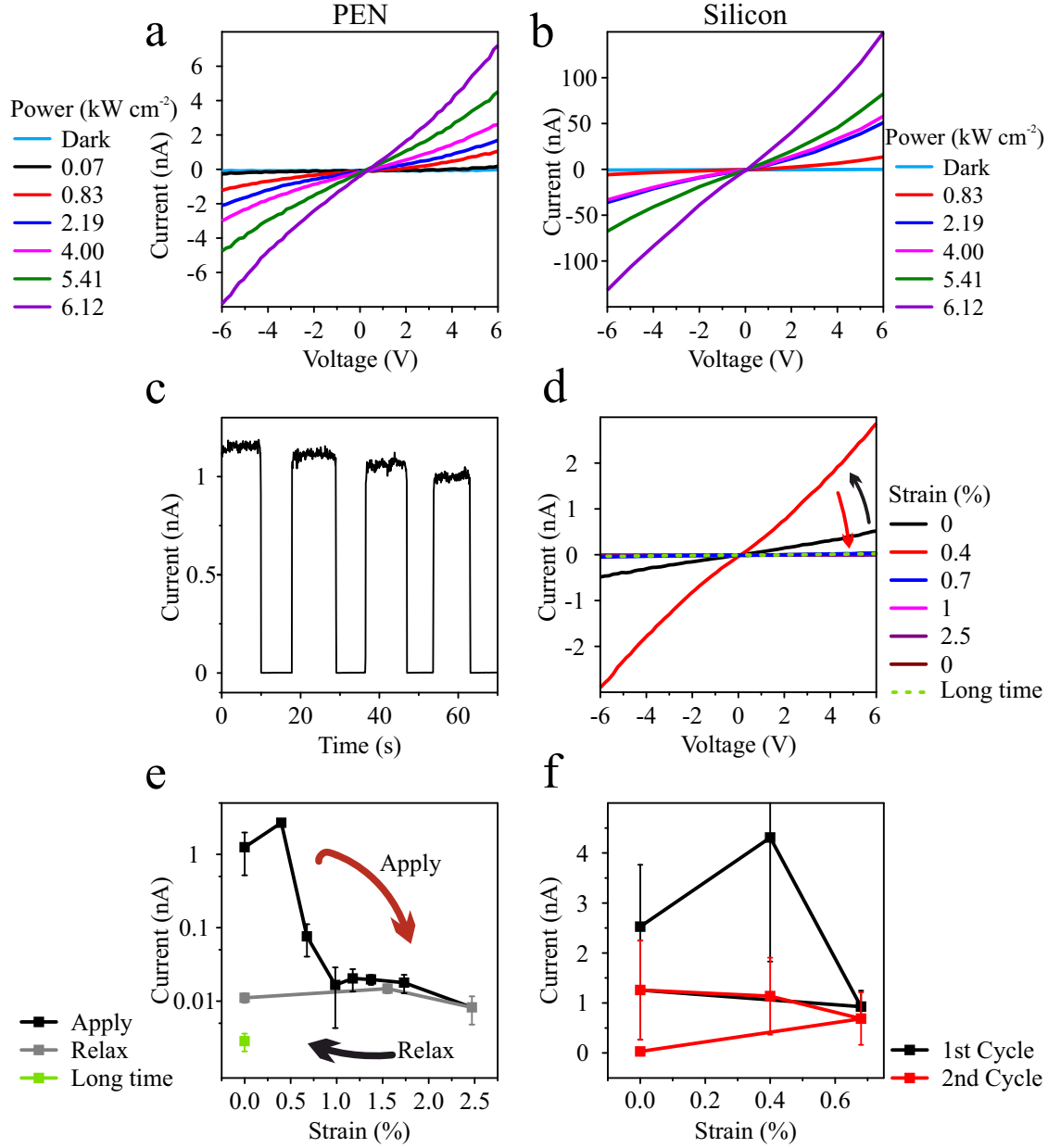


Figure 5.12: Photodetection of the lift-off patterned devices. Laser power dependence of the measured photocurrent for devices on (a) PEN and (b) silicon substrates, showing 1–2 orders of magnitude enhancement for silicon over PEN. (c) Typical time dependence for device on PEN, showing rapid switching. (d) Example I-V curves showing the largest transient increase of photocurrent observed, and (e) average response of the devices to strain cycling. (f) Small strain cycling of devices showing that the mechanism contributing to failure is cumulative. A constant laser power of 0.83 kW cm⁻² and bias of 6 V was used unless otherwise stated.

Band structures for the photodetector are shown in Figure 5.13. In the unbiased case (Figure 5.13a), no current is observed as there is no field to separate the strongly bound excitons nor overcome the potential barriers at either interface. In contrast, a single Schottky barrier produces current at zero bias due to separation of excitons in the depletion region. Applying a small bias without strain (Figure 5.13b) leads to limited current flow, however the majority of electrons remain ‘trapped’ in the potential well between the two Schottky barriers. Applying a larger bias reduces the height of the forward biased barrier, eventually leading to the *flat-band* condition as shown in Figure 5.13c and enhanced photocurrent due to ready separation of excitons.^[22]

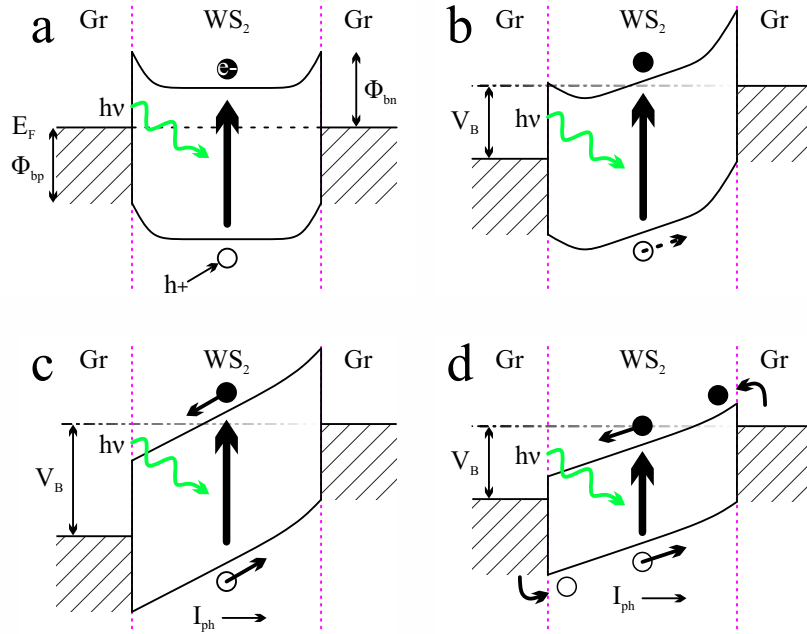


Figure 5.13: Idealised band structures for the photodetectors, showing the back to back Schottky barriers typical for MSM photodetectors. (a) Equilibrium diagram showing a photogenerated exciton trapped in a potential well, with no photocurrent (I_{ph}) generated. (b–d) Non equilibrium diagrams at (b) small bias with potential well still present and (c) large bias in the flat-band condition. (d) The application of strain lowers the magnitude of the bias necessary for the flat-band condition.

We propose that at small strains and prior to device failure, the transient enhancement of photocurrent occurs by a reduction in the bias required to achieve the flat-band condition (Figure 5.13d) due to the reduced bandgap and the piezotronic effect (where the Schottky barrier height is reduced by polarisation charges in strained TMDs).^[23] Here we also illustrate a further possible mechanism for photocurrent generation: photoexcitation of carriers over the barrier from graphene to WS₂, similarly enhanced by the reduction of the bandgap.^[24] Further increases may be ascribed to similar reasons as the strain-induced increase in PL intensity described in Chapter 4—an increase in the absorbance cross-section and reduction in the drain of carriers from the K to the Σ conduction band minima limiting recombination.

In an effort to isolate the cause of failure, we separately measured devices that had been: strained (Figure 5.14a); strained and biased (Figure 5.14b); strained and irradiated (Figure 5.14c); and strained, biased, and irradiated (Figure 5.14d). Prior SEM measurements demonstrate that the WS₂ was intact across at least part of the junction in all cases. We then measured the devices and verified stable photoconductance prior to the application of strain. Despite the absence of obvious damage, with no observable difference between the before and after images in Figure 5.14, in all cases the devices were confirmed as having failed after the application of 1.2 % strain, regardless of bias or irradiation.

Given the resolution limitations of SEM images as a result of the insulating PEN substrate, one explanation for failure could be the formation of cracks of a size below these limits. AFM was not attempted due to the high substrate roughness preventing imaging of 2D materials (as described in Chapter 4). In the plasma etched case, the

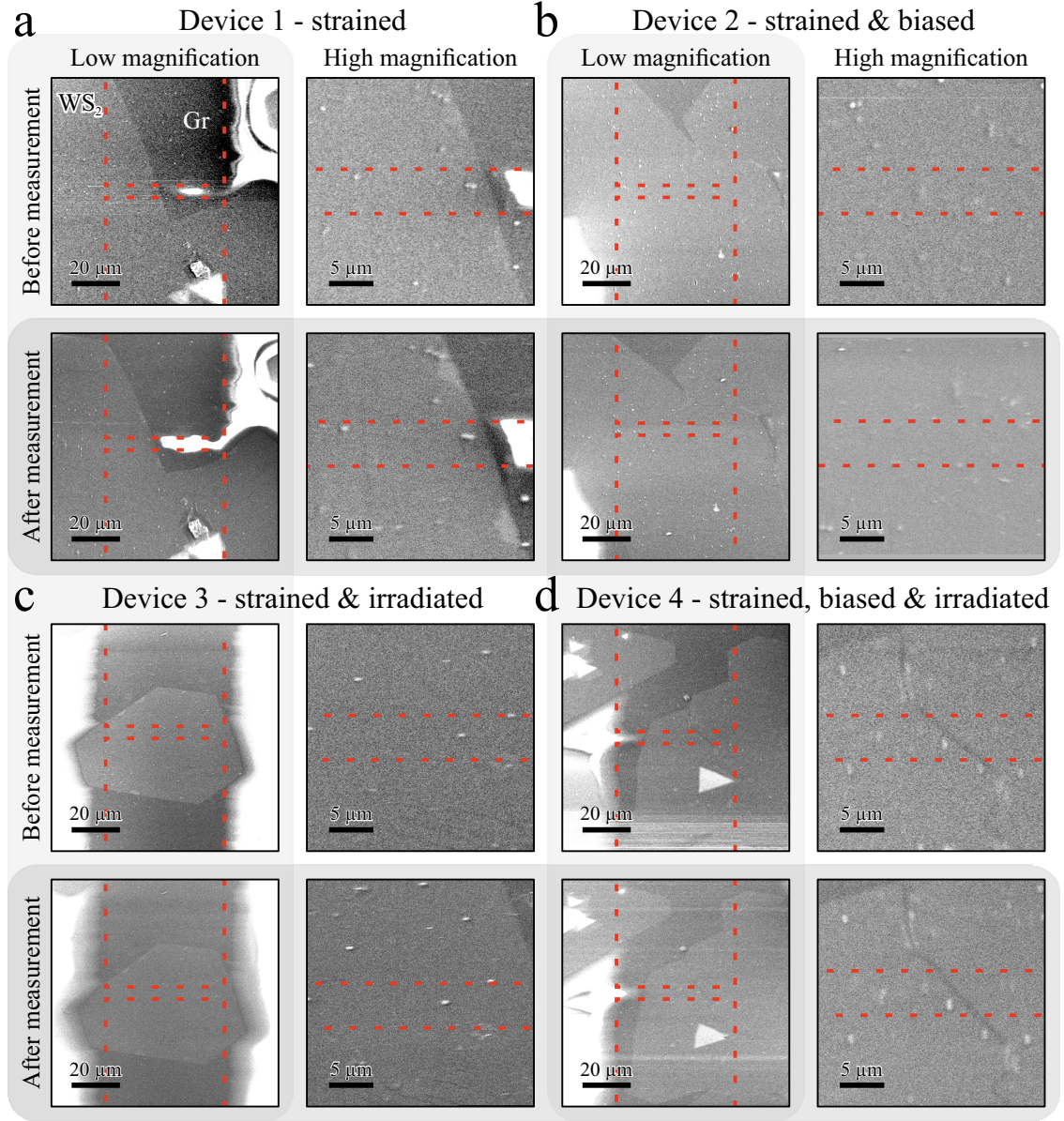


Figure 5.14: SEM images of the lift-off patterned devices, immediately after WS_2 had been transferred and following the measurement. We applied (a) strain; (b) strain and bias; (c) strain and laser irradiation; and (d) strain, bias, and laser irradiation. The dashed lines indicate the approximate position of the graphene electrodes. Scale bars are $20\ \mu\text{m}$ and $5\ \mu\text{m}$ for low and high magnification respectively.

step at the electrode edge will introduce tension to the WS_2 , likely expanding these cracks to dimensions that are more easily imaged. Further experimentation is required to verify this, either using substrates that permit higher resolution in one or both of

these techniques, or using more advanced imaging techniques such as KPM that may permit higher resolution. It is also possible that the debonding effect described in Chapter 4 results in the loss of sufficient contact between the WS_2 and graphene for measurable current to flow.

5.3 Conclusions

In this chapter, we explored conventional and new fabrication techniques for the production of all-2D lateral photodetectors on flexible substrates. During the course of studying what impact the use of soft matter substrates had on their efficacy, several issues with the conventional techniques were identified. We first modified the gold contact patterning process to remove the need for an adhesion layer, then used the typical oxygen plasma etching process to pattern graphene and produce working devices that showed measurable photoconductivity, but found that the devices failed rapidly upon the application of small tensile strains.

Analysis of the devices before and after the application of strain and consequent failure revealed a stable reduction of the conductivity of the graphene electrodes, presumably due to damage at the graphene–gold interface sustained during straining, but this was not sufficient to explain the complete loss of photoconductivity. More importantly, significant damage to the WS₂ was observed at the edge of the graphene electrodes following the strained photoconductance measurements—suspected to be a consequence of damage to the substrate surface sustained during the plasma etching of graphene. In response to this, we developed a modified lift-off process that enabled high quality patterning of graphene without damaging the PEN substrate surface and refined this process to produce features down to <10 μm resolution, an improvement over previous demonstrations of this technique. We proceeded to fabricate photodetector devices using this method. Despite minor improvements and an initial transient enhancement of the measured photocurrent by up to one order of

magnitude, we found that the devices still failed in response to small tensile strains.

Due to resolution limits imposed on both SEM and AFM by the polymer substrates, we were unable to directly determine the cause of failure of the lift-off patterned devices. In contrast to the damage to the devices that were patterned with plasma, which could be imaged by SEM due to built in tension opening the fracture interface sufficiently for it to be imaged, we propose that failure occurs by damage at the interface between the graphene and WS₂ of a scale below these resolution limits.

5.4 Acknowledgements

AFM mapping of the graphene electrodes was performed by Mr Xiaochen Wang. As in Chapter 4, the majority of the 2D materials used here were grown by the author, but some materials were provided by: Dr Yuewen Sheng (WS₂ and unpolished graphene that was used in early device tests), and Miss Linlin Hou (WS₂). Photomasks were generously provided by Dr Chit Siong Lau. Dr Jason Brown was of great help during the photolithographic fabrication process, and Dr Haijie Tan contributed to the device design and fabrication processes.

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Chapter 6

Piezoelectric Sensors with Graphene Electrodes for Pre-Clinical Cardio-Respiratory Monitoring

6.1 Introduction

As outlined in Section 2.3.3.8, there are a number of drawbacks with the existing cardiac and respiratory monitoring technology used in small animal MRI and CT imaging. These devices are used to monitor the key sources of body motion during imaging, enabling correction and stabilisation of the image in a process known as *gating*. This leads to improved image resolution, and is necessary to avoid artefacts that can lead to misdiagnosis.^[1,2] Current respiratory monitoring technology (pneumatic capsules known as *respiratory balloons*, Figure 6.1a & 6.1d) is not favoured due to complicated setup, sensitivity to changes in air pressure, and the need to recalibrate

if the animal is moved between different pieces of equipment. Silver-contacted piezoelectric sensors (Figure 6.1b & 6.1e) have been demonstrated to be effective at solving these issues but are almost universally avoided due to the use of metal components, which lead to significant artefacts in both imaging techniques.^[3–7]

In this chapter, we demonstrate that large area, CVD grown monolayer graphene films are the ideal electrode material for replacing metallic conductors in piezoelectric respiratory monitors. Graphene inks were also trialled, but significant reductions in the measured respiratory signal from early prototypes during MRI scanning precluded further study. We explore the necessary modifications to the existing fabrication processes, and characterise the graphene films to demonstrate the high quality of graphene before and after transfer. The fabricated devices (Figure 6.1c) are studied in a range of different mounting configurations to determine the optimal mounting conditions, and assessed for their fatigue resistance. We further go on to demonstrate their use for respiratory gating *in vivo* as part of an all carbon based monitoring and life support cradle, showing that high quality images can be obtained without metal induced artefacts, and with facile device mounting and setup.

In marked contrast to the complicated setup and observation of significant artefacts when using respiratory balloons or metal contacted piezoelectric devices, respectively, our device was easily and rapidly implemented in both imaging techniques, was highly radiolucent, and was found to cause little distortion to the magnetic field of the MRI scanner. We further demonstrate that due to the high sensitivity of the sensor it is possible to measure the animal’s cardiac cycle, offering the possibility of combining both cardiac and respiratory gating facilities into a single unit.

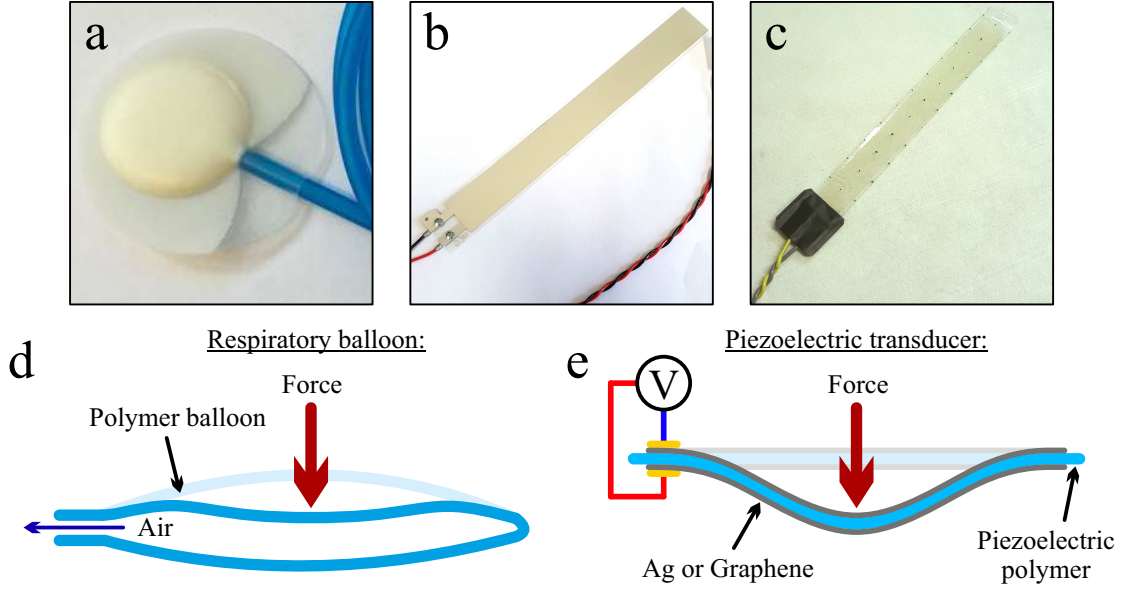


Figure 6.1: Images and schematics of the existing technology and our sensor. (a–c) Images of the (a) respiratory balloon,^[8] (b) silver-contacted sensor, and (c) graphene-contacted sensor. (d,e) Diagrams of the (d) respiratory balloon and (e) piezoelectric transducer. The design in (e) is shared by the existing silver-contacted sensor and our graphene-contacted sensor.

6.2 Results and Discussion

We again grew films of graphene by our previously reported methods (detailed in Section 3.2.1). SEM images of the as grown graphene films are shown in Figure 6.2a & 6.2b. Large area films up to 70×120 mm were spin coated with PMMA, and etched and washed as before. In this case we etched the copper foil in large trays, and exchanged the etchant using large volume syringes to minimise disturbance to the film. The etchant also had to be refreshed once during etching to ensure complete removal of the copper. We used $110 \mu\text{m}$ thick, uniaxially oriented films of the piezoelectric polymer poly(vinylidene fluoride) (PVDF; Precision Acoustics) as a substrate, chosen for its large piezoelectric coefficient ($d_{33} = -30 \text{ pC/N}$).^[9] This relatively thick film was chosen for its balance of durability and strength, flexibility, and magnitude of

generated voltage. The voltage generated may be increased by using a thicker film, at the cost of increased stiffness and decreased internal capacitance—leading to more rapid signal decay and, as we will see later, an increase in the cut-off frequency below which signals are attenuated.^[10]

Transfer was complicated by the requirement that graphene be transferred onto both sides of the film. This issue was compounded by the low working temperature of PVDF (75 °C), which precluded the baking steps usually used before transfer to remove any solvent residues, and after transfer to promote adhesion, as higher temperatures will degrade device performance by causing misorientation of the polymer chains.^[9,10]

In lieu of baking, we opted instead to drive off solvent residues by placing the cleaned PVDF in a vacuum desiccator for 30 minutes. Adhesion was promoted after transfer by simply extending the drying time, and the redeposition of a thin layer of PMMA to aid conformation of the graphene to the substrate surface. Previous work has demonstrated that this is effective at improving the quality and reducing the resistance of transferred graphene films.^[11,12] SEM images of graphene films transferred by aqueous methods are shown in Figure 6.2c & 6.2d. Note the similar appearance at low magnification and general continuity of the films, though we were able to image small cracks and damage over the surface—observed as brighter regions in the images due to substrate charging, as well as a reproduction of the surface texture of the PVDF. We again turned to Raman spectroscopy to verify the presence of graphene post transfer. Raman spectra of the graphene transferred to silicon are reprinted for comparison from the previous chapter in Figure 6.2e, and spectra from PVDF samples

are shown in Figure 6.2f. Note the retention of both peaks after transfer. Film sheet resistances were found to be modest at around $3 \text{ k}\Omega/\square$. This value is around $4\text{--}5\times$ larger than that observed for transfer to PET substrates,^[13,14] a difference that may be due to the greater surface roughness of the PVDF ($R_q = 11.8 \text{ nm}$).^[15] This could potentially be improved by using thicker graphene films, but did not appear to impact the effectiveness of the finished devices and as such was not investigated further.

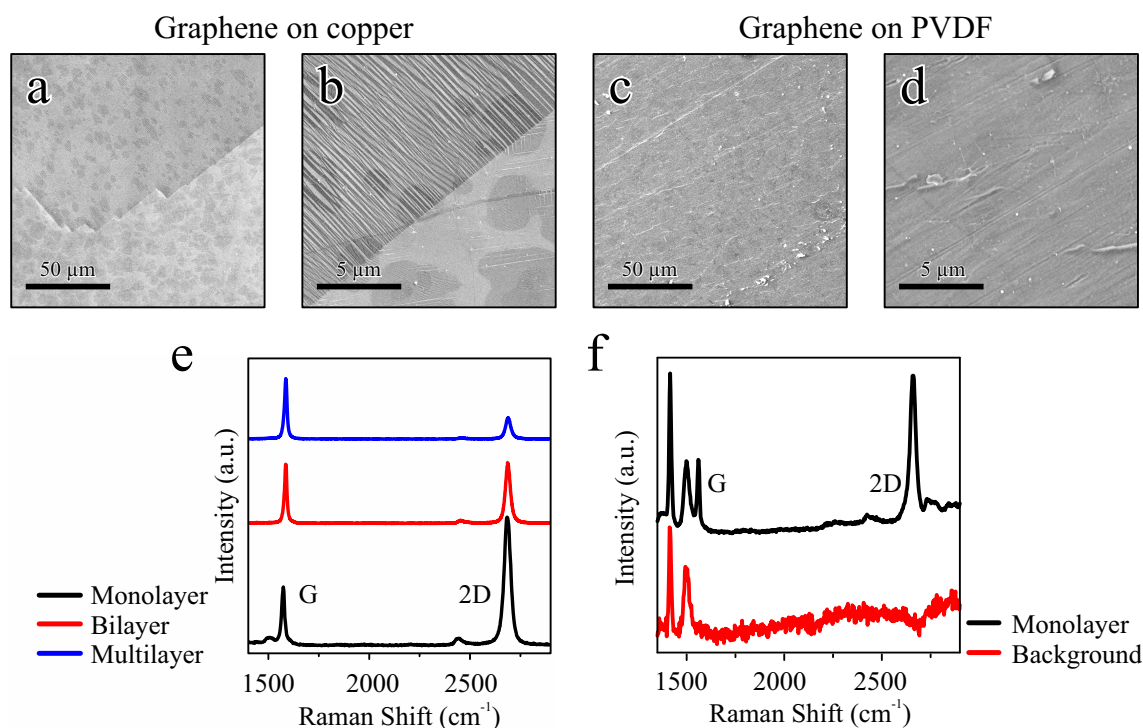


Figure 6.2: Characterisation of the graphene film before and after transfer to PVDF. (a–d) SEM images of the graphene film as grown on copper at (a) low and (b) high magnification; and images of the same after transfer to PVDF at (c) low and (d) high magnification. Scale bars are $50 \mu\text{m}$ and $5 \mu\text{m}$ respectively. (e,f) Raman spectra of graphene transferred to (e) a silicon wafer with 300 nm oxide layer, indicating predominantly monolayer with bi- and multilayer islands (reprinted from Chapter 5), and (f) the PVDF film, clearly showing the characteristic peaks after transfer, with the PVDF background also indicated.

A second layer of graphene was then transferred onto the back side of the PVDF, and processed in the same way as the first. As well as improving the quality of

the transferred film, the redeposition of PMMA has the additional benefit of sealing the edges, thereby preventing delamination of the first layer during transfer of the second. The protected film was subsequently diced into strips of appropriate dimensions, discarding the edges due to poor graphene adhesion visible here. The PMMA was removed in acetone as before, but performed at room temperature for 48 hours to again minimise the possibility of degrading the piezoelectricity of the PVDF. We initially trialled thermal evaporation of gold as a method of forming the electrodes before transfer, but found that even at deposition rates $<0.1 \text{ nm s}^{-1}$, there was sufficient flux of heat into the PVDF to cause significant warping. We instead formed electrodes using silver paint (RS Components) encapsulated in epoxy (Araldite®). The device was completed by laminating the entire assembly in polypropylene (PP) tape bonded with pressure sensitive adhesive, protecting the exposed graphene from damage. This process is outlined schematically in Figure 6.3.

We first fabricated small scale prototype devices ($10 \times 50 \text{ mm}$) using the above methods, to test the efficacy of graphene in this application. Facile mounting of the device—by simply placing it in contact with the body when it was loaded into the cradle—led to very effective monitoring of the respiratory cycle and, to our surprise, we were additionally able to measure clear signals from the cardiac cycle. Data from this early prototype device, as well as from a respiratory balloon monitoring the same subject, are plotted in Figure 6.4a. Note the faster rise and fall times produced by our sensor, as well as the presence of cardiac signals that are absent in the respiratory balloon trace. We also plot an example of the trigger produced from the peak of the respiratory signal that is subsequently converted into a gating signal—

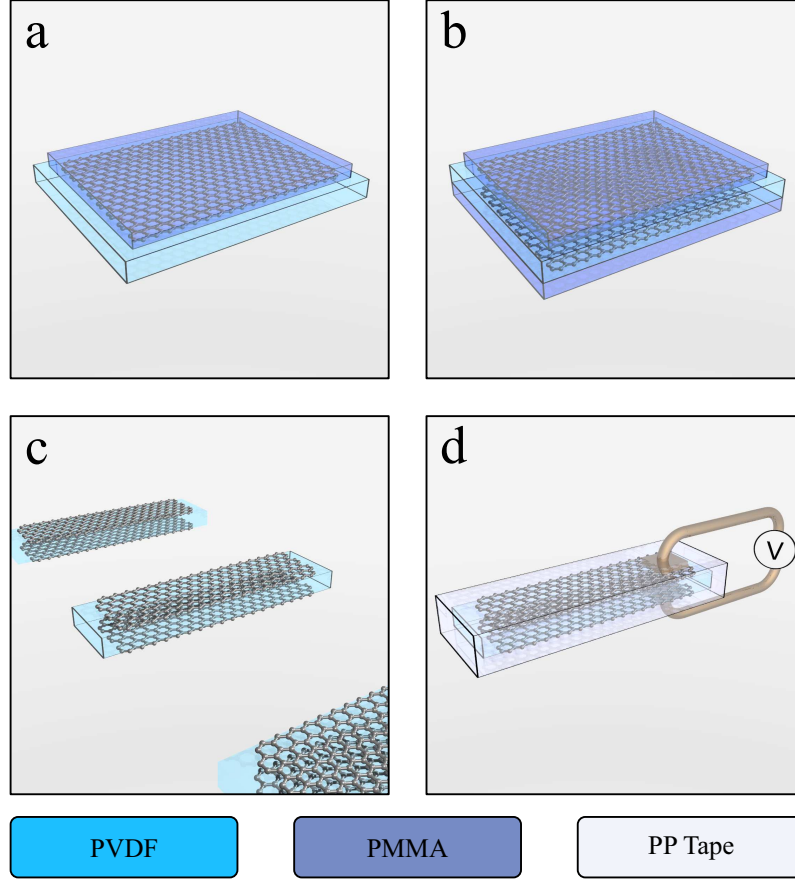


Figure 6.3: Schematics detailing the fabrication of the graphene contacted respiratory monitor. (a) A layer of graphene is transferred to one side of the PVDF. (b) After drying, a second layer of PMMA is deposited on the transferred film to prevent detachment during transfer of a second graphene layer to the other side. (c) The film is cut into strips of the requisite dimensions, and the PMMA removed. (d) Contacts are fabricated and the device is encapsulated in polypropylene (PP) tape.

where acquisition is turned on during the peaks and off during the troughs, when the body is in motion. We went on to perform basic scans to prove the functionality of the device. In the ungated image (Figure 6.4b), respiration causes distortion of the image, most prominently causing the liver to periodically move out of frame. With gating, the image is stable (Figure 6.4c). Figure 6.4d shows a CT image of the mouse with the region where the most disturbance occurs around the liver and lungs highlighted. Having verified the working principle and MRI compatibility, we

proceeded to design a sensor that could be integrated into a custom 3D printed cradle with built in carbon-fibre based heating and ECG measurement technology.

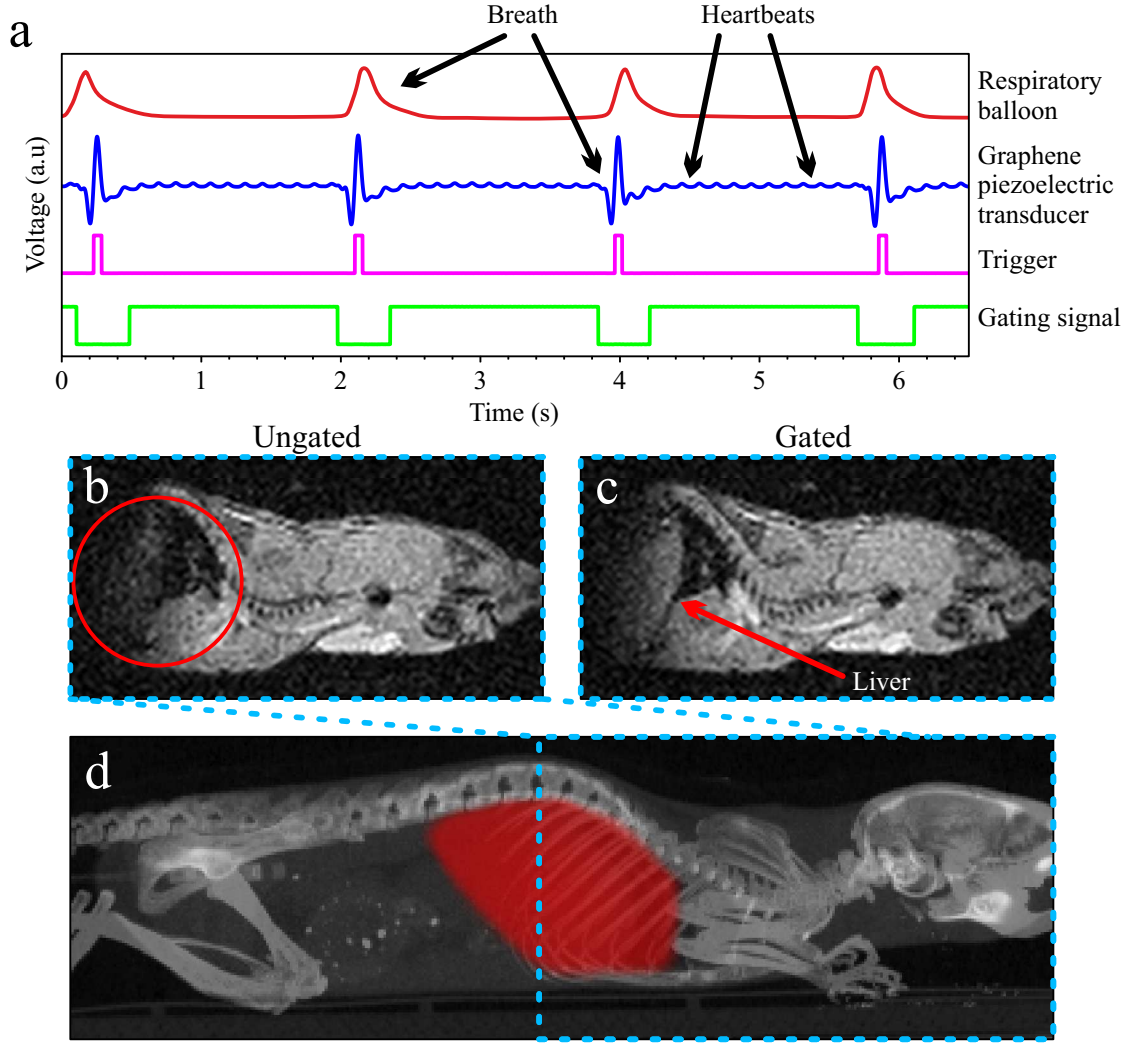


Figure 6.4: Data from the first prototype device in use *in vivo*. (a) Comparison of the typical trace of the pulsed breathing of a sedated mouse measured using a respiratory balloon and our sensor. Note shorter signal decay time and visible heartbeat from the graphene transducer. We also plot the trigger and gating signals generated from the respiratory signal. (b,c) Stills from a dynamic MRI scan, showing a cross-section of the upper body: (b) without gating, and (c) respiratory gated with the prototype graphene transducer. (d) 3D CT image of a mouse with the region around the liver and lungs highlighted—this is the primary region where motion artefacts are visible in ungated scans. The region where the MRI images in (b) & (c) were taken is also indicated.

To remove the metallic electrodes from the vicinity of the body, we fabricated

larger sensors (12×120 mm). In an effort to quantify their behaviour and determine the optimal mounting geometry, we simulated the respiratory signal by using a custom built actuator, equipped with a small cantilever arm mounted to a DC motor and controlled by a timing circuit (RS Components), to apply force to the sensor. The resultant signals were measured using a Biopac MP150 unit with DA100C amplifier, as detailed in Section 3.7.2, but first required conditioning as they were found to exceed the limits of the detector. We reduced the signal magnitude by means of a resistive voltage divider of appropriate transfer function (the ratio of output to input voltage, H_{div} ; Equation 6.1), in which the input signal is applied across a pair of resistors (R_1 and R_2) and the output taken across the second.

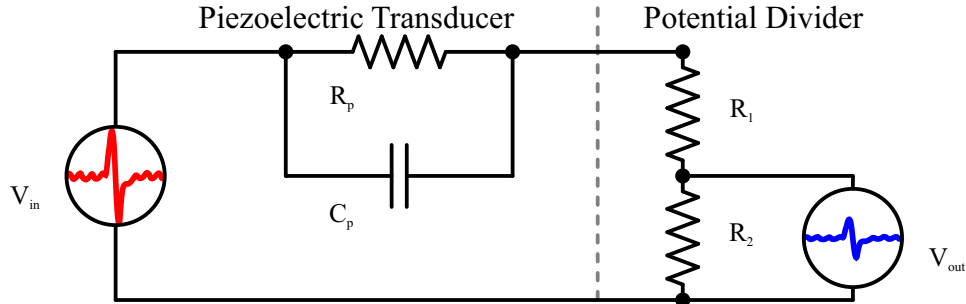


Figure 6.5: Equivalent circuit diagram for piezoelectric sensor connected to voltage divider. Adapted from Karki.^[16]

$$H_{div} = \frac{R_2}{R_1 + R_2} \quad (6.1)$$

Calibration of the potential divider was necessary due to the low frequency transient signal generated by the sensor causing deviation from Equation 6.1. This can be understood with reference to the equivalent circuit shown in Figure 6.5: the transducer itself contains a series resistance and capacitance which forms another poten-

tial divider in the form of a passive high pass filter, the effect of which varies with frequency.^[10,16] Since a more detailed analysis of the electronic properties was beyond the scope of this study, rather than attempt to measure these and calculate H directly we chose instead to estimate it by applying a very small mechanical signal, and comparing the amplitude of divided and undivided (i.e. $R_1 = 0$ and $R_2 = \infty$) signals. We achieved sufficient signal reduction with $R_1 = 39 \text{ k}\Omega$ and $R_2 = 12 \text{ k}\Omega$, leading to $H_{\text{div}} = 0.147 \pm 0.003$ (cf. $H_{\text{div}} = 0.235$ given by Equation 6.1).

The high level of amplification resulted in significant detection of 50 Hz mains hum, so the entire divider assembly was shielded using BNC cables and an aluminium enclosure, and a twisted pair lead used to connect the sensor to the divider. We further retrospectively subtracted a fitted 50 Hz sine function from the measured potential. This was found to better preserve the signal amplitude, in contrast to low pass or Butterworth notch filtering, both of which led to significant signal attenuation.

The sensor was mounted in a range of configurations and force applied along its length, to both the negative and positive sides of the PVDF (as defined by the manufacturer). The maximum applied force as given by the stall torque of the motor at 6 V was 193 mN, and the maximum deflection of the cantilever arm in the absence of physical resistance was 5 mm. An image of the measurement setup is shown in Figure 6.6a: a mechanical signal (1) stimulates the sensor (2), which is fixed to two linear translation stages (3), producing a signal that is reduced by the potential divider (4) before being amplified (5) and measured (6), a read out of which is recorded and displayed on a connected PC (7). The measured potentials and illustrations of the various mounting geometries are displayed in Figure 6.6b–6.6f.

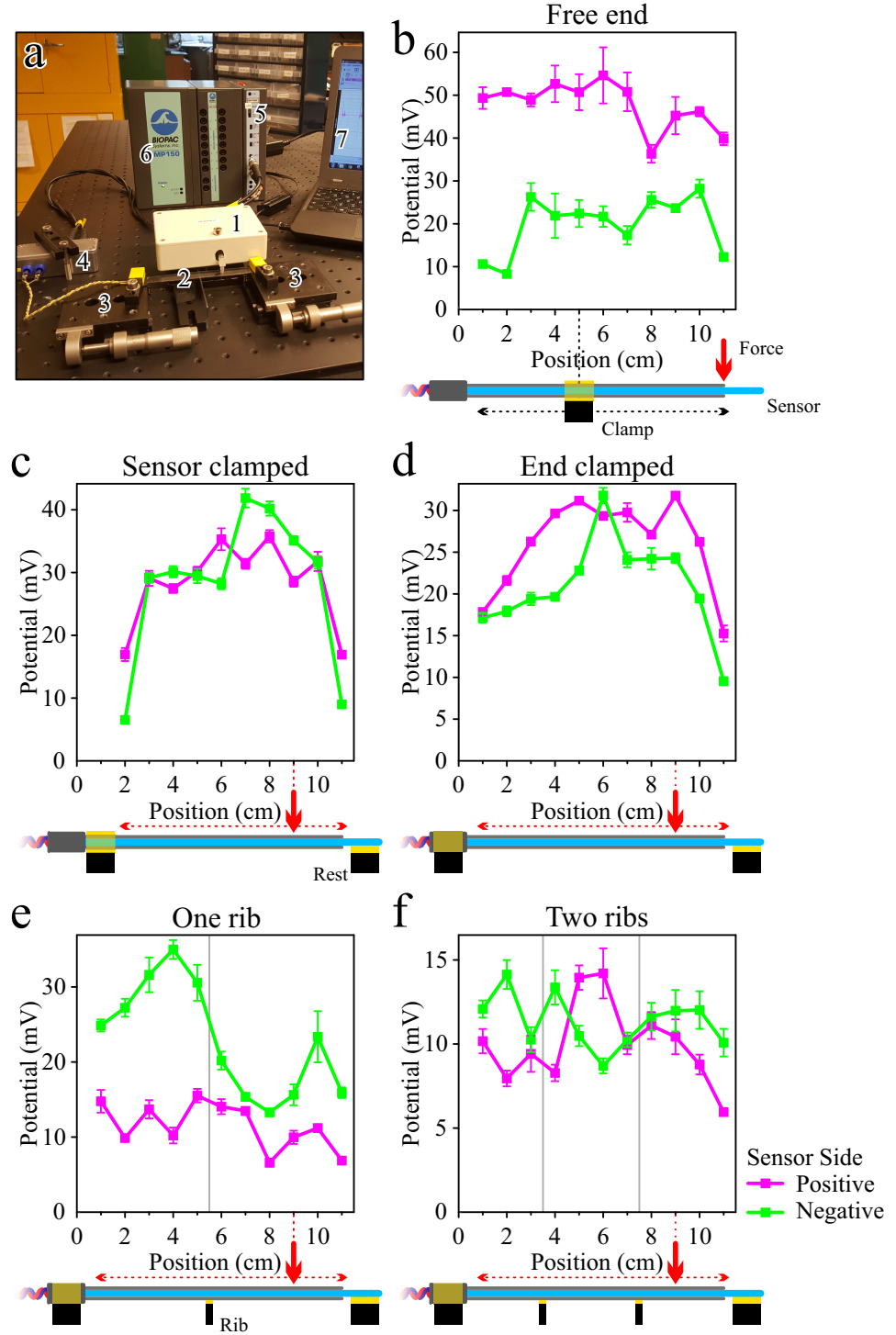


Figure 6.6: Effect of mounting geometry on the measured potential. (a) Image of the measurement setup. (b–f) Plots of measured potential: (b) clamped at each point along the length and driven at point 11, (c) clamped on the sensor at position = 1 with end of sensor resting, (d) clamped over the electrodes with the end resting, (e) clamped over the electrodes resting at 5.5 cm and the end, and (f) clamped over the electrodes and resting at 3.5 and 7.5 cm and the end.

In general, the signal intensity was found to be similar on both sides of the sensor, with notable exceptions in the *free end* (Figure 6.6b) and *one rib* geometries (Figure 6.6e). These differences can be explained by the convex curvature along the length of the positive side (and therefore concave curvature of negative side, analogous to a retractable tape measure). In both cases, the curvature of the film enables easy deflection on the positive side, while resisting deformation on the negative side. In the *free end* geometry (Figure 6.6b), the cantilever type deflection is easier on the positive side, and in the *one rib* geometry (Figure 6.6e), the 3-point bending is easier on the negative side. In the *two ribs* geometry (Figure 6.6f), the magnitude of deflection of the sensor is more strongly inhibited by the supporting ribs, leading to similar responses on both sides, and reduced overall magnitude.

The maximum signal amplitude was achieved by *free end* mounting (Figure 6.6b), up to 55 ± 6 mV. However, since the body of the animal needs to be supported, this would be difficult to practically achieve in the final cradle. We settled instead on the inclusion of ribs, similar to the geometry depicted in Figure 6.6f. While this produced the lowest signal amplitude—a fourfold reduction from the maximum measured value—this geometry has the advantages of ease of mounting and animal placement, and the stability of the signal along the length of the sensor ensuring a high degree of consistency in spite of inevitable variations in body position.

We also tested the response of a silver-contacted sensor, mounted in the *sensor clamped* geometry (Figure 6.7a). The behaviour was similar to that of our graphene contacted device, with the larger signal intensity a result of the greater width of the strip (18 vs. 12 mm) and lower resistance of the comparatively thick silver film.

The maximum signal magnitude and position for all geometries and both sides are summarised in Figure 6.7b. We also plot the potential measured from the silver contacted sensor for comparison.

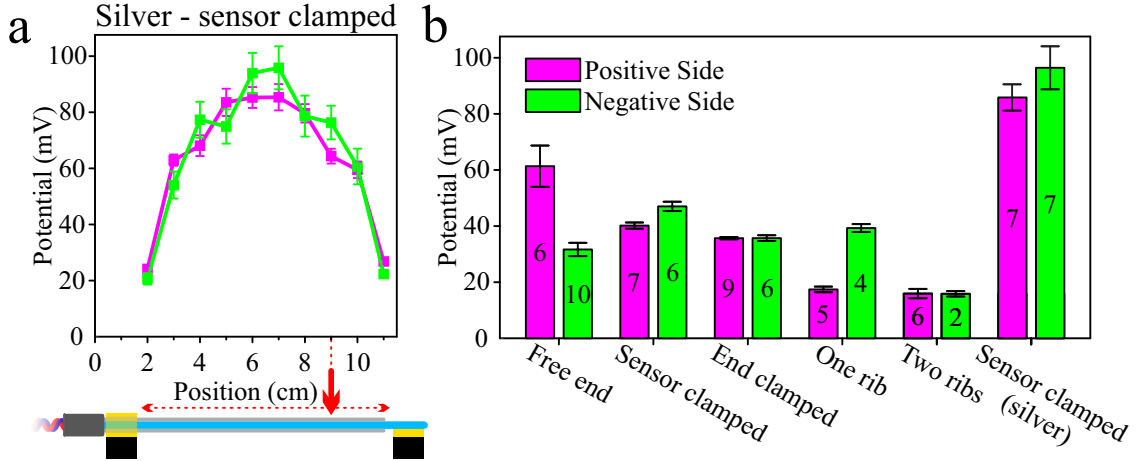


Figure 6.7: Test of existing silver contacted sensor and summary of maximum potentials in different geometries. (a) Potential produced by silver contacted sensor in *sensor clamped* geometry. (b) Bar chart summarising the maximum signal generated in each of the mounting positions shown in Figure 6.6, with position of measurement indicated: clamped at each point along the length and driven at point 11, clamped at position one with end of sensor resting, clamped over the electrodes with the end resting, clamped over the electrodes resting at 5.5 cm and the end, and clamped over the electrodes and resting at 3.5 and 7.5 cm and the end.

We continued our study on the effects of mounting geometry by examining the effect of tensile stress on the generated voltage. The sensor was clamped as in Figure 6.6c, and a second clamp placed at the sensor end. A tensile stress (up to $\sigma \approx 2$ MPa) was applied by means of the spring loaded linear translation stage. In this mounting geometry, the signal from the negative side was typically found to be ~ 50 % larger than the positive side, though this difference appears to decrease with increasing stress, until the positive side exceeds the negative side. These changes are summarised in Figure 6.8. Throughout all of the above tests, which involved several

thousand separate measurements, we observed no reduction in the signal amplitude for any of the mounting geometries used. This establishes that the sensor is robust and reliable, in spite of the mechanical clamping forces used to fix it in place, and the repeated cycling of applied tensile stress.

To determine if we could reduce the active sensor area and thereby lower potential production costs, we tested the effect of reducing the sensor width on the measured signal amplitude. The width of the PVDF was reduced, and the encapsulating tape was retained as shown in Figure 6.9a. We observed a sharp decline in the measured potential in all three of the geometries measured (*end clamped*, *one rib*, and *two ribs* geometry), deviating from linearity likely due to presence of defects and cracks in the graphene film (Figure 6.9b–6.9d). As these defects decrease the number of conduction pathways and therefore the measured potential, the effect becomes more significant when the width of the strip is reduced. The non-zero potential at zero strip width is a result of a small amount of charge generated by the remaining stub of PVDF in contact with the electrodes as a result of deflection of the encapsulating tape, despite the absence of PVDF in the sensor area. Due to the large decrease in signal magnitude and the instability in the signal along the strip as the width decreased, we proceeded with the initial strip width of 12 mm.

The final sensors were then integrated into the cradle. By compressing the sensor and securely clamping the ends and thus introducing a small positive curvature, we were able to ensure consistent contact with the animal while limiting the pickup of vibrations during scanning, with deflection of the sensor enabled by several ribs along the length of the cradle. A schematic of the final cradle is shown in Figure 6.10a, and

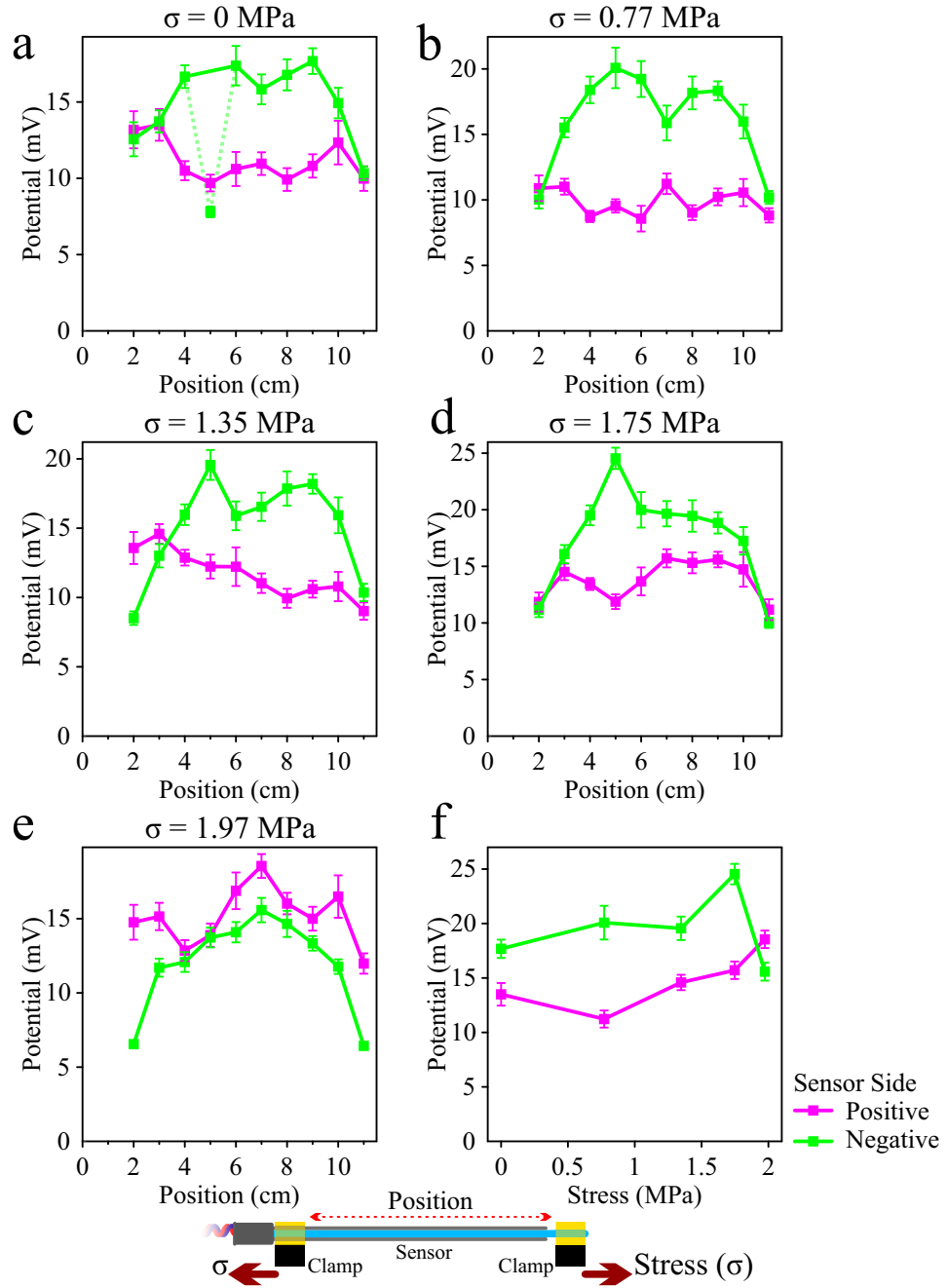


Figure 6.8: Effect of tension on the measured signal. As can be seen, there is little variation in the magnitude of the signal, though the difference between the two sensors decreases with increasing stress. (a–e) Plots showing the variation of signal intensity along the sensor length as tension is increased up to ~ 2 MPa. (f) Summary of the maximum intensities, plotted against applied stress.

an image of the cradle with animal in place prior to insertion into a CT scanner is shown in Figure 6.10b. This cradle permits fully integrated MRI and CT compatible

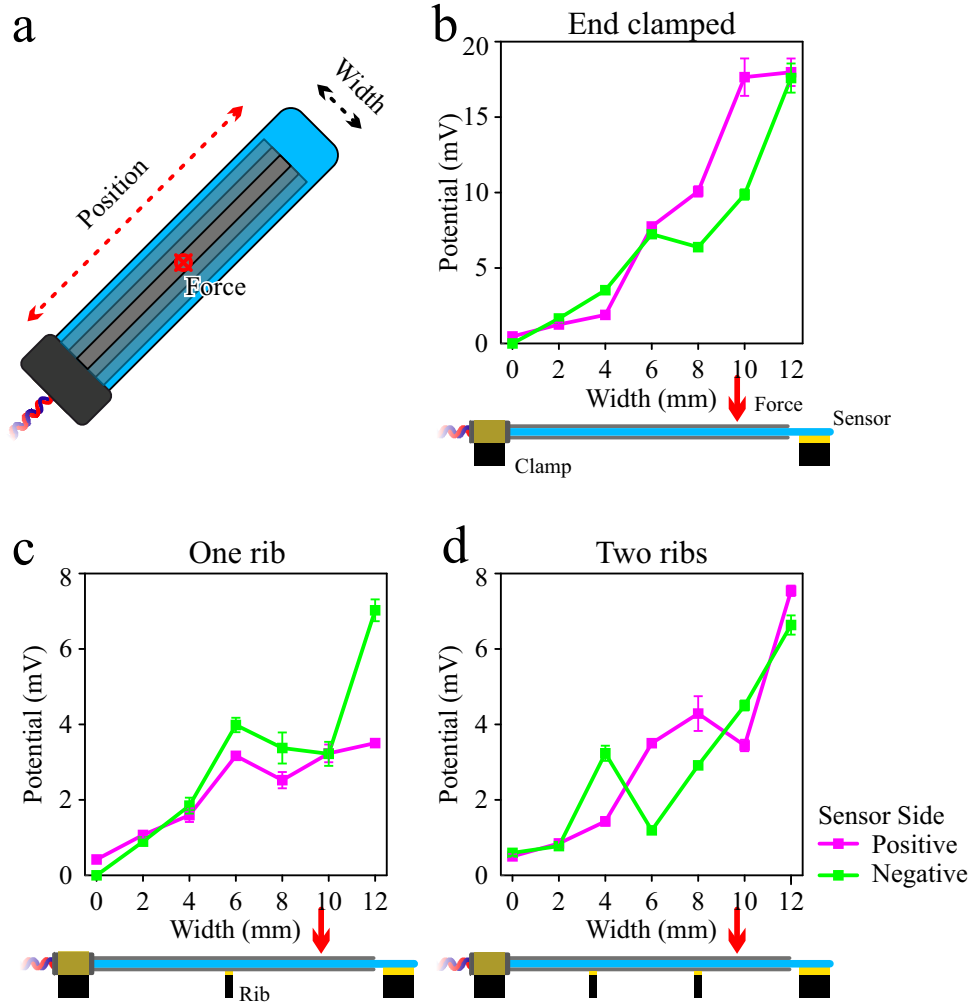


Figure 6.9: Effect of reducing the area of Graphene/PVDF/Graphene in the sensor. (a) Schematic showing the reduction in width. (b–d) Plots of measured potential with strip width in the (b) end clamped, (c) one rib, and (d) two ribs geometry respectively, showing rapid decline with decreasing width.

homeothermic maintenance and measurement of ECG and respiratory signals, the latter facilitated by our sensor, in a single user-friendly unit.

To verify the function of the final sensor *in vivo*, we performed MRI and CT imaging of live subjects using the measurement apparatus detailed in Figure 6.10. MRI imaging was performed using a 7 T magnet, as outlined in Section 3.4.4. We performed a dynamic scan without gating (Figure 6.11a), and compared this to a scan

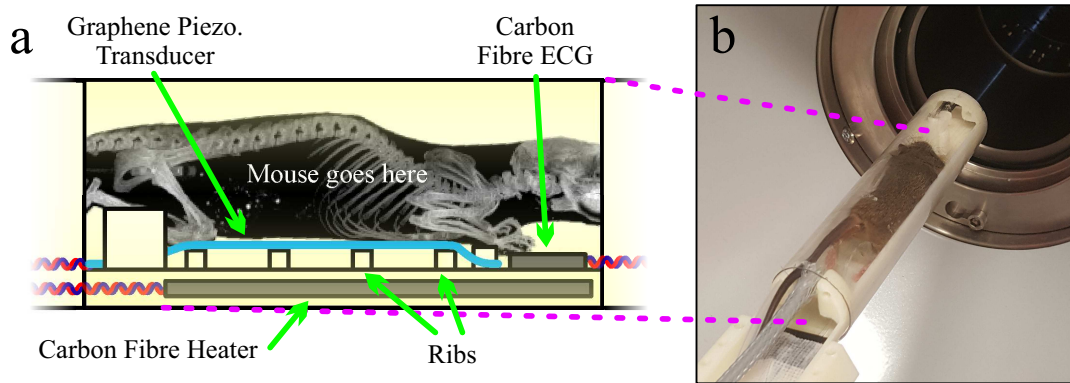


Figure 6.10: Details of the cradle used to hold the animal. (a) Schematic of the cradle detailing key components. (b) Image of the cradle with animal in place, ready for insertion into the CT scanner.

using our device for respiratory gating of the image acquisition (Figure 6.11b). Despite again being able to also measure cardiac signals with our device, due to complications with signal processing we elected only to demonstrate respiratory gating at this stage. The two signals could simply be used in tandem, or owing to their different rates could be separated by means of band pass filters. With reference to the average gated scan the effect of respiration on the ungated image is clear, with significant time dependent movement visible across the sequential frames shown, in contrast to the good stability of the gated images.

To show this graphically, we measured the mean pixel values across a cross-section in the area of the liver, and plot this against time for both the ungated and gated scans in Figure 6.11c, showing the marked increase in stability afforded by our device. This represents a near sevenfold reduction in the standard deviation of the mean pixel values in this area of greatest distortion, and a twofold reduction in the standard deviation of the overall image.

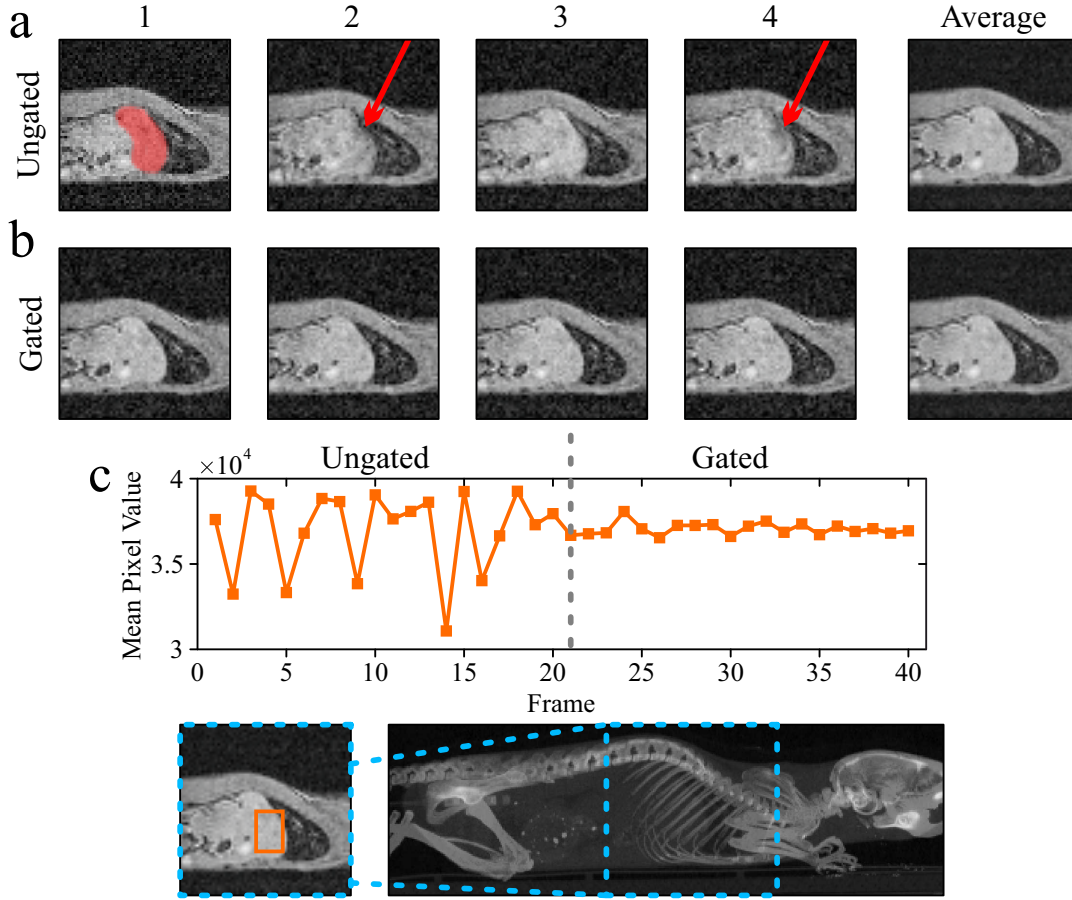


Figure 6.11: Effect of gating on a dynamic MRI scan. Four consecutive frames taken from (a) an ungated scan and (b) a scan gated using the graphene transducer, compared to an average image of the four gated frames. Note blurring of ungated images, especially in the area of the liver as highlighted in (a). (c) Mean pixel values over 20 frames for ungated and gated scans in the area of the liver showing increase in stability with gating, with the averaged region highlighted in inset MRI image, and location in body indicated in a 3D CT image.

We subsequently performed high resolution image acquisition with and without gating. These images serve to further highlight the impact of respiration on image quality: without gating, blurring around the lungs, liver, and surrounding tissues occurs, and significant artefacts can be observed around the the body at higher contrast (Figure 6.12a); with gating, the image is largely free of artefacts and streaking (Figure 6.12b). The response of the graphene sensor was largely stable throughout

MRI scanning, and we observed very little shift to the signals produced. We emphasise that while respiratory gating has been possible using a variety of techniques for several decades,^[1,2,17–19] our device enables this with, to the best of our knowledge, an unprecedented level of simplicity, signal stability, and flexibility to different systems, with clear benefits over existing technology to small animal imaging in terms of both throughput and user error minimisation.

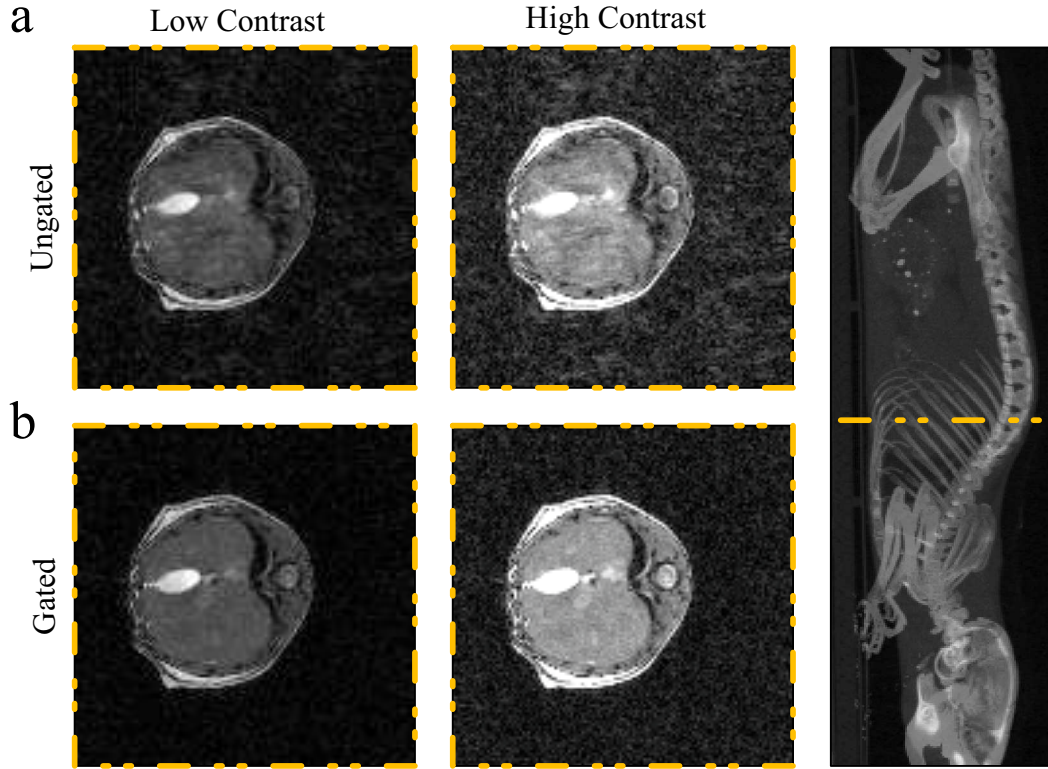


Figure 6.12: Cross-sections taken from a high resolution scan with and without gating. (a) Ungated images show significant distortion and blurring, and at higher contrast significant artefacts outside the body of the animal are visible. (b) Gated images at equivalent contrast show a marked reduction in artefacts, both inside and outside of the body. The position of all scans is indicated on a 3D CT image.

We further demonstrated the utility of the device to applications requiring co-registration by transferring the sedated animal and cradle to a CT scanner. By removing the need to repressurise and calibrate the respiratory balloon, the cradle can rapidly be reconnected to the new scanner’s monitoring systems, with minimum disturbance to anaesthesia and thermoregulatory systems. Body and sensor movement are minimised without the need to securely clamp the animal—reducing the risk of injury in contrast to respiratory balloons—by the secure mounting of the respiratory monitor over the entirety of the bottom surface of the cradle. As a consequence, we observed very little change in the measured respiratory signal as a result of the transfer.

In keeping with the MRI measurements, we performed an ungated scan (Figure 6.13a), and compared this to a scan gated with the graphene contacted sensor (Figure 6.13b). Note the blurring around the liver and the area of the thoracic cavity highlighted in the ungated images. The graphene transducer is visible as the grey line immediately beneath the animal.

Since its impact is much more noticeable and therefore more readily visualised than the detuning of the magnet and smaller artefacts in MRI, here we also demonstrate the effect of a silver contacted transducer on the reconstructed scan, with the bright streaked artefacts in Figure 6.13c resulting from the strong X-ray scattering of the sensor. The silver contacted sensor was placed on top of the animal to avoid disturbing its posture between scans. While the effect of respiration on the image quality is limited, we reiterate that our device simplifies cradle transfer without disturbing the animal’s position, with the result that the resolution of the co-registered

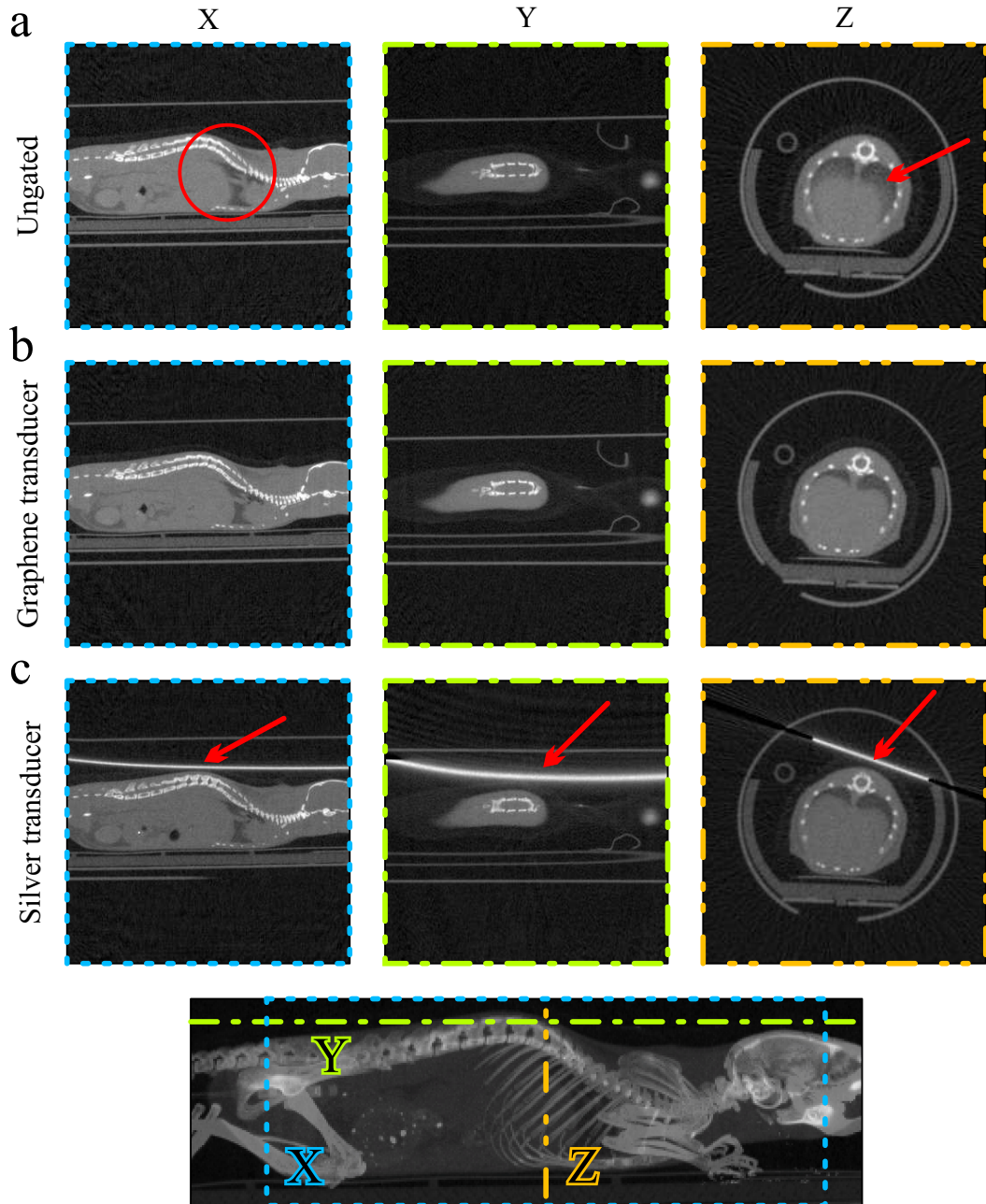


Figure 6.13: Cross-sectional CT images showing the artefacts from the silver contacted sensor. (a–b) Images containing only the graphene sensor beneath the body: (a) ungated, artefacts highlighted; and (b) gated. (c) Images containing both the graphene and silver sensors, with significant artefacts visible resulting from X-ray scattering from the silver contacted sensor. The position of each dimension is indicated on a 3D CT image.

image is enhanced. This versatility can be further extended to techniques requiring co-registration where the stability afforded by gating is more important, for example

imaging techniques such as positron emission tomography,^[20,21] or treatment methods like radiotherapy.^[17] As in the simulated respiration measurements outlined in Figures 6.6–6.8, we observed no reduction in the sensitivity of the device in the >20 hours of *in vivo* testing.

6.3 Conclusions

In conclusion, in this chapter we have demonstrated the novel application of graphene as an ideal planar electrode material in piezoelectric respiratory monitors. This device has clear advantages over existing technology, overcoming as it does the difficulties with user error and the recalibration requirements of respiratory balloons, and the MRI and CT incompatibility of silver contacted piezoelectric devices. It also has important implications for the *3Rs* of animal research (*Replacement*, *Reduction*, and *Refinement*): minimising the duration of anaesthesia by reducing transfer time in co-registration applications, and reducing trauma and the risk of injury by removing the need to securely clamp the animal to the sensor as is required when using respiratory balloons.^[22]

We characterised the response of the device to mechanical stimuli, and optimised its geometry to facilitate its integration into an all carbon based monitoring and life support cradle. We went on to test the finished device *in vivo*, proving its utility in both MRI and CT imaging, with further potential for improving other diagnostic and also treatment techniques. Though a demonstration of this was beyond the scope of this study, in addition to improved acquisition of the respiratory signal we also showed that, using the same device, we could simultaneously measure cardiac signals of sufficient magnitude to be used for gating. Several finished devices are now in service in the Oxford Institute for Radiation Oncology.

6.4 Acknowledgements

Dr Sean Smart and Mr Stuart Gilchrist were responsible for identifying deficiencies with the current technology that led to the inception of this device research, contributed to the device design, and developed the cradle depicted in Figure 6.10. Dr Veerle Kersemans performed all of the *in vivo* MRI and CT imaging used in this study. Mr Stuart Gilchrist provided the signal generator for respiratory simulation, and Mr Reuben Harding provided a number of insights and assistance in the signal conditioning used in the non-*in vivo* device measurements (Figures 6.6–6.9). All graphene used here was grown by the author.

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Chapter 7

Conclusions

The research presented in this thesis runs the gamut of research into 2D devices: material synthesis, transfer techniques, device design and fabrication, and characterisation. Improvements and modifications to the processes used to synthesise the materials and to the fabrication techniques are outlined in Chapter 3, and when relevant and requiring further explanation are presented in greater detail in Chapters 4–6. Each of these chapters otherwise details an interrelated but largely self contained study into 2D flexible electronics.

The successful implementation of 2D materials in flexible electronics depends on a robust understanding of the influence of strain on the properties of the component materials and their heterostructures. It is well known that weak van der Waals bonding at an interface can lead to incomplete strain transfer between materials. In Chapter 4, we set out to study in detail the effect of strain on a range of heterostructures representing device contacts, channels, and gated channels composed from boron nitride, tungsten disulphide (WS_2) and graphene on flexible poly(ethylene naphthal-

7. CONCLUSIONS

ate) (PEN) substrates.

In this study, we hoped initially to observe changes to the band structure using photoluminescence (PL) spectroscopy, but instead revealed a strain release mechanism that occurred independently of the heterolayer configuration. While this led to convolution and broadening of the PL spectra that obstructed our initial goals, we studied this effect in detail and propose here a mechanism by which the strain is released inhomogeneously during the first strain cycle, with the debonded film experiencing $<20\%$ of the applied strain in subsequent strain cycles. We verified this effect in all of the heterostructure permutations, and also demonstrated it after modifying the PEN surface with a thin layer of poly(methyl methacrylate) (PMMA) to increase the surface roughness and lower its modulus—revealing a similar effect, albeit with a smaller total magnitude of strain transfer and broader period of debonding during the application of strain. A complimentary study into one of the heterostructures ($\text{WS}_2/\text{graphene}/\text{PEN}$) using Kelvin probe force microscopy helped to further verify the mechanism, and showed corresponding shifts to the work function of both graphene and WS_2 during straining.

We went on to demonstrate a strain relaxation mechanism responsible for the observed hysteresis between strain cycles. This hysteresis was attributed to reformation of the film with the substrate and the relaxation of a slight residual compressive strain following strain cycling, leading to a gradual blueshift over time that was characterised over a period of ~ 24 hours. Finally, we studied the effect of cycling the strain up to 200 times, confirming the stabilisation of the properties after the first strain cycle. We concluded that this debonding effect suggests the need to

precondition flexible devices by strain cycling before stable behaviour can be achieved.

Encouraged by the conclusions drawn in Chapter 4, we proceeded with the fabrication of all-2D flexible photodetector devices. Chapter 5 details the fabrication of lateral metal-semiconductor-metal (MSM) photodetectors on PEN substrates, consisting of a single crystal of WS₂ contacted by graphene electrodes.

Several modifications were made to the fabrication techniques normally used for rigid substrates—namely modifications to both the gold and graphene patterning processes. The latter was made in response to the significant damage to the substrate observed at the edges of the graphene electrodes as a result of the plasma etching. This damage was suspected as the cause of device failure at moderately low strains, by producing stress concentrations at the sharp edges where the substrate was etched away. A lift-off approach for patterning graphene was developed and characterised, producing similar results to the plasma etching process without damaging the substrate. Control devices fabricated on silicon substrates showed comparable behaviour to previous demonstrations of this device architecture that were produced using plasma etching. This alternative approach was then used to fabricate functional devices on PEN, which showed improved properties in the form of a twofold increase in photoresponsivity during the application of strain. Unfortunately, further application of strain led again to device failure.

Finally, in Chapter 6 the novel application of graphene in a device for cardio-respiratory monitoring in multi-modal small animal imaging was demonstrated. The behaviour of this device was studied in detail and its function in MRI and CT imaging verified *in vivo*. This device outperforms existing technology by simplifying the user

experience, utilising the unique electronic and mechanical properties of graphene to monitor the key sources of body motion and facilitate image gating, without inducing artefacts. Image gating is made possible without complicated setup or recalibration upon transfer of animals between different pieces of equipment. This work was part of a collaboration with the Oxford Institute for Radiation Oncology, where several of the finished prototypes are now in use. A patent has also been filed, in hopes of expanding production of these sensors for supply to the pre-clinical market.

Future Outlook

While the debonding mechanism presented in Chapter 4 was universal to all of the heterostructures and substrates in this study, this still represents a small subset of the probable permutations and materials that we may find in future flexible devices. To gain a more complete understanding of the interfacial dynamics of 2D materials, further studies would include the effect of other substrate materials, surface treatments, and heterostructure configurations. The use of a broader range of measurement techniques such as Raman, SEM or ultrasonic force microscopy to directly image the debonded regions of the strained heterostructures would help to verify this mechanism. Finally, a greater focus on strain distribution with a more extensive use of mapping (beyond the scope of this study due to equipment limitations) would be valuable. Though there is still much to discover, this work contributes to the growing body of knowledge on friction in 2D materials, with important ramifications for their implementation in flexible devices.

Although the flexible photodetectors demonstrated in Chapter 5 ultimately failed

in response to strain, there are a number of important details revealed by this work that have implications for the field of 2D microelectronics. The lift-off patterning approach detailed in this chapter is a fairly new approach that could find application in producing both rigid and flexible devices since it removes the requirement that underlying layer(s) must be protected during patterning, be it a 2D material, polymer, or another plasma sensitive material. This patterning approach could be extended to produce vertically heterostructured flexible devices that may have more favourable performance than those demonstrated here.

The transient increase in photocurrent observed in the lift-off patterned devices during straining indicates that, as is the case with conventional semiconductors, strain engineering is an approach that can lead to significantly enhanced device properties—if it can be controllably applied. Finally, this study reveals that additional design considerations must be made to protect 2D devices from the deleterious effect of strain, perhaps by device encapsulation or the introduction of a compressive strain during fabrication, approaches that were not explored here but may be essential for 2D materials to be viable in this application. To ascertain the exact nature of device failure in the lift-off patterned devices, conductive AFM or *in situ* SEM would both be viable techniques to reveal the location and mechanism of failure.

Implementation of the cardio-respiratory monitor technology demonstrated in Chapter 6 is already underway, but as with all 2D devices a major difficulty lies in scaling production up from the laboratory. As such, future work will involve determining how to produce the devices on a larger scale, as well as studying possible improvements to the device design. Additionally, though we are confident of its utility

throughout the field of small animal imaging, a complete demonstration of the function of the device in other imaging and treatment techniques would be valuable—a comprehensive and conclusive demonstration of the superiority of a novel technology being a prerequisite for successful disruption of the existing one.