Extracting the Key Electrical Properties of Semiconductors using Optical Pump Terahertz Probe Spectroscopy

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***Abstract*— We have used optical-pump-terahertz-probe spectroscopy (OPTPS) to study a range of novel of semiconductors including III-V nanowires and metal halide perovskites. We show that OPTPs allows key figures of merit to be extracted in a non-contact manner, including charge mobility, surface recombination velocity, and doping density. Furthermore, the technique allows charge recombination dynamics to be followed on a picosecond time-scale. This knowledge is useful in the design of new optoelectronic devices from lasers to solar cells as well as for the development and optimisation of new semiconductors.**

I. Introduction

Semiconducting materials are the basis of the modern electronics industry and thus play an increasingly important role in many areas of everyday living. While the vast majority of electronics is based on silicon there is much research into other semiconducting materials and nanostructured materials which offer great promise, in particular for optoelectronic applications. Understanding electron dynamics in these materials is key to be better understanding of the materials and thus developing new ways to engineer materials for device applications.

Optical-pump-terahertz-probe spectroscopy (OPTPS) measurements provide an ideal way to study electron dynamics in semiconductors. This technique allows the AC conductivity spectrum of a material to be measured as a function of time after photo-excitation. As the technique does not require any electrical contacts to be formed on the material it provides a fast, non-destructive method of characterizing semiconductor materials. Terahertz photoconductivity measurements have proved particularly important for studying materials that are difficult to contact electrically, or are perturbed by the fabrication of metal contacts. We have developed methods the extract key properties of planar and nanostructured semiconductors using terahertz spectroscopy. The semiconductor properties that may be extracted include photoconductivity lifetime, charge mobility, surface recombination velocity and doping concentrations.

II. Semiconductor Nanowires

Nanowires (NWs) of single-crystal group III-V semiconductors have the potential to be elements of future nanoelectronic devices. [1] Such nanowires typically have diameters in the range 20nm - 300nm and lengths ~10 micons. This high surface area to volume ratio is useful for sensing applications but also means that care must be taken when designing nanowires so that interfaces do not degrade the electrical performance of the NWs. In addition many

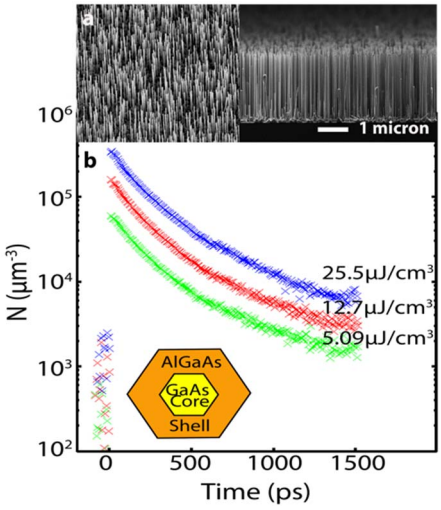

Fig. 1. (a) Scanning electron micrograph of core shell GaAs/AlGaAs nanowires after growth. (b) THz photoconductivity as a function of time after photoexcitation for an ensemble of these nanowires deposited on a quartz substrate. The nanowires were excited with 35fs 1.55eV photons at the fluences indicated on the graph.

electronic devices require accurate doping of nanowires. However controlled doping of naowires has been challenge owing to segregation and changes in growth morphology when dopants are introduced. Furthermore while characterising the electrical properties of nanowires using conventional techniques such as Hall measurements is possible [2] it has proved onerous owing to the small diameter of nanowires. Thus OPTPS is an ideal tool to extract the key electrical paremeters of nanowires in a non-contact fashion.

III. Extracting Electrical Properties of Nanowires using Optical Pump Terahertz Probe Spectroscopy

Owing the the high suface-area-to-volume ratio of semiconductor nanowires, it is important to be able to quantify trapping of charge carriers at NW surfaces We have devloped methods to extract the value of the surface recombination vecocity of NWs, [3] and found the values to be strongly depended on III-V composition [4]. However by overcoating a NW with another semiconductor with larger bandgap it is possible to reduce strongly surface recombination and at the same time increase electron mobility.[5]

Establishing the effectiveness of electrical doping of NWs is important for the development of NWs for electronic device applications. We have developed methods to determine the extrinsic electron (n) and hole (p) densities of ensembles of NWs. [6] We find that conventional “bulk” doping of NWs leads to poor charge mobilities, however by exploiting modulation doping in a NW heterostructure it is possible to

achieve controlled doping while maintaing very high electron mobilities.[7]

IV. Vapour Deposited Perovskite Semiconductors

Inorganic-organic metal halide materials have recently emerged as promising candidates for optoelectronic applications, particularly photovoltaics, owing to their good charge mobility and extremely high absorption coefficient at visible wavelengths [8-9]. This class of materials crystallize into a perovskite structure ABX_3 where A is typically an organic cation such as methyl ammonium $CH_3NH_3^+$ or formadmidinium $HC(NH_2)_2^+$, B is a metal cation such as Pb^{2+} or Sn^{2+} and X is a halide anion such as I^-, Br^- or Cl^- (see inset of Fig 1 for a diagram of the unit cell). In just a few years since their invention the power conversion efficiencies (PCE) of thin-film perovskite solar cells have already exceeded 20%[10], which is remarkable for such a new technology. Terahertz photoconductivity spectroscopy is an ideal tool for elucidating charge dynamics in these materials, which in turn is key to the the further development and optimization of perovskite solar cells.

V. Perovskite Film Growth

Thin films of perovskite semiconductors may be grown by a range of methods. The main two methods are solution processing and vapour deposition. Solution processing requires is very cost effective with very low capital costs, and the vast majority of published works on perovskite solar cells use this technique. Vapour deposition on the other hand requires significantly higher capital costs but offers better control over film thickness and uniformity (Fig 1a). We used vapour deposition to create the first high efficiency planar heterojunction perovskite solar cell based in the $CH_3NH_3PbI_{3-x}Cl_x$ system.[11] We have also produced $CH_3NH_3PbI_3$ films using co-evaporation of PbI_2 and CH_3NH_3I as well as sequential deposition of these two materials.[12]

VI. Terahertz Conductivity Dynamics of Perovskites

Optical pump terahertz probe spectroscopy allows the AC conductivity of a material to be determined in a non-contact fashion. Furthermore, the changes in the AC conductivity after photo-excitation can be monitored with picosecond time resolution. We have previously applied this technique to nanoscale systems such as semiconductor nanowires, where making physical contacts to the materials is difficult [13]. The technique has proved particularly useful for determining the electrical properties of thin films of metal halide perovskites such as charge mobility.

The decay of photoconductivity of an evaporated thin film of the perovskite $CH_3NH_3PbI_{3-x}Cl_x$ is shown in Figure 2b. When photoexcited with a high fluence (188uJ/cm^2) pulse of 3.1eV (λ=400nm) photons, the photoconductivity, which is displayed as red squares in the figure, can be seen to decay rapidly. [13] However at the lowest fluence (6uJ/cm^2, purple triangles) there is no observable change in photoconductivity over the 2.5ns measurement window. By globally fitting these data it is possible to extract the rate constants associated with charge-carrier recombination, namely the monomolecular rate associated with defect related recombination, the radiative bimolecular constant, and the (third order) non-radiative Auger constant. Analysis of measured rate constants and THz mobility allows device specific parameters to be quantified. [13,14] In particular the charge diffusion length is important for the design of planar heterojunction solar cells and the Auger constant is critical for the design of lasers.

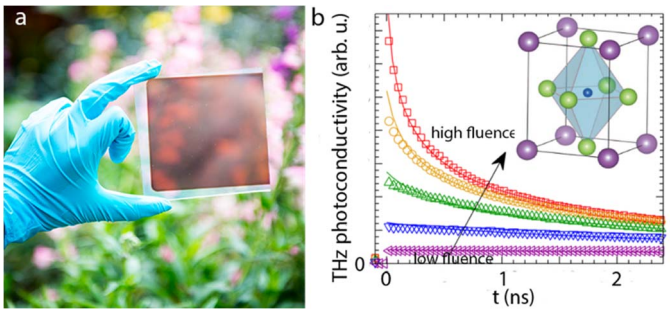

Fig. 2. (a) 330nm thick $CH_3NH_3PbI_{3-x}Cl_x$ film deposited using co-evaporation. (b) THz photoconductivity as a function of time after photoexcitation.

References

[1] HJ Joyce, et al "III-V semiconductor nanowires for optoelectronic device applications" *Prog. Quantum Electron.,* 35:23-75 (2011)

[2] K Storm, et al "Spatially resolved Hall effect measurement in a single semiconductor nanowire" *Nature Nanotechnology* **7**, 718 (1012)

[3] HJ Joyce, et al "Ultra-low Surface Recombination Velocity in InP Nanowires Probed by Terahertz Spectroscopy" *Nano Lett*., **12,** 5325-5330 (2012)

[4] HJ Joyce, et al "Electronic properties of GaAs, InAs and InP nanowires studied by terahertz spectroscopy" *Nanotechnology*, **24,** 214006 (2013)

[5] HJ Joyce et al "Electron Mobilities Approaching Bulk Limits in Surface-Free GaAs Nanowires" *Nano Lett.*, **14,** 5989-5994 (2014)

[6] JL Boland et al, "Increased Photoconductivity Lifetime in GaAs Nanowires by Controlled n-Type and p-Type Doping" *ACS Nano,***10,** 4219-4227 (2016)

[7] JL Boland et al "Modulation Doping of GaAs/AlGaAs Core--Shell Nanowires With Effective Defect Passivation and High Electron Mobility" *Nano Lett*., **15,** 1336-1342 (2015)

[8] L.M. Herz, "Charge carrier dynamics in organic-inorganic metal halide perovskites", *Annu. Rev. Phys. Chem*., **67**, 65 (2016)

[9] M.B. Johnston and L.M. Herz, Hybrid perovskites for photovoltaics: charge-carrier recombination, diffusion and radiative efficiencies, *Acc. Chem. Res.*, **49,** 146 (2016)

[10] http://www.nrel.gov/ncpv/images/efficiency_chart.jpg

[11]M. Liu, M.B. Johnston, and H.J. Snaith. Efficient planar heterojunction perovskite solar cells by vapour deposition, *Nature* **501**, 395 (2013).

[12] J.B. Patel, R.L. Milot, A.D. Wright, L.M. Herz, M.B. Johnston, Formation Dynamics of $CH_3NH_3PbI_3$ Perovskite Following Two-Step Layer Deposition *J. Phys. Chem. Lett.*, **7,** 96 (2016)

[13] JL Boland, et al. Modulation Doping of GaAs/AlGaAs Core--Shell Nanowires With Effective Defect Passivation and High Electron Mobility *Nano Lett.,* **15**, 1336 (2015)

[14] C. Wehrenfennig, M. Liu, H.J. Snaith, M.B. Johnston, L.M. Herz, Charge-carrier dynamics in vapour-deposited films of the organolead halide perovskite $CH_3NH_3PbI_{3-x}Cl_x$, *Energy Environ. Sci.*, **7**, 2269 (2014)

[15] R. L. Milot, G. E. Eperon, H. J. Snaith, M. B. Johnston, L. M. Herz *Temperature-Dependent Charge-Carrier Dynamics in $CH_3NH_3PbI_3$ Perovskite Thin Films* Adv. Funct. Mater., **25**, 6218 (2015)

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