

Workshop on Charge Trapping Defects in Semiconductors and Insulators

York Medical Society, York, 20-21 March 2017

<http://www.ctdsi.sciencesconf.org/>

Welcome to this Workshop on Charge Trapping Defects in Semiconductors and Insulators organised by the University of York.

The trapping of electrons and holes at defects in semiconductors and insulators is an important issue that controls the performance of materials for applications in areas such as photovoltaics, electronics and catalysis. Point defects such as vacancies or impurities as well as extended defects such as surfaces, grain boundaries and dislocations are all known to trap charge. Both theoretical (e.g. density functional theory) and experimental approaches (e.g. spectroscopic and scanning probe techniques) have been employed to characterise the electronic properties of defects however many open questions and challenges remain. This workshop aims to bring together leading researchers working in this field to review the progress and challenges in understanding charge trapping at defects and highlight technological applications where it is critical for materials design and optimisation.

Workshop organisers:

Keith McKenna, Department of Physics, University of York

Richard Douthwaite, Department of Chemistry, University of York

Workshop sponsors:

EPSRC

University of York

General Information

- Talks will be held in the York Medical Society Lecture Theatre.
- Coffee/tea breaks and lunch (on Tuesday 21st) will be served in the oak paneled room.
- For those who confirmed they would like to attend the conference dinner it will take place on Monday 20 March at Rustique Restaurant and Bistro, 2A Lendal, York, YO1 8AA at 7pm.
- Streamline Taxis: 01904 656565; York Cars Taxis: 01904 765765

13.00 Arrival and coffee/tea

13.30 Workshop opening: Keith McKenna

Session 1 (chair: Keith McKenna)

13.40 David Scanlon (*University College London, United Kingdom*)

I1. Charge Trapping in Transparent Conducting Oxide SnO₂

14.20 Jack Strand (*University College London, United Kingdom*)

C1. The role of bipolarons in the formation of defects in amorphous hafnia

14.40 Razak Elmaslmane (*University of York, United Kingdom*)

C2. Electron Trapping in TiO₂ Rutile and Anatase

15.00 Coffee break

15.20 Alex Shluger (*University College London, United Kingdom*)

I2. Intrinsic electron and hole trapping in amorphous oxides

16.00 Aaron Deskins (*Worcester Polytechnic Institute, United States*)

I3. Disorder, Defects and Charge Trapping in Titania

16.40 Antton Curutchet (*ENS de Lyon, France*)

C3. DFT Study of trapped electrons in hackmanite-type minerals

17.00 Close of session

19.00 Workshop dinner

Session 2 (chair: Jon Major)

09.00 Filippo De Angelis (*Istituto di Scienze e Tecnologie Molecolari del CNR (CNR-ISTM), Italy*)

I4. Defect chemistry of organohalide perovskites: Implications for solar cell operation

09.40 Chris Moore (*Dyesol Ltd.*)

I5. The Necessity to Understand Charge Trapping in Order to Enhance the Commercialisation Potential for Perovskite Solar Cells

10.20 Coffee break

10.40 Alison Walker (*University of Bath, United Kingdom*)

I6. Charge transport in amorphous systems and systems with mobile defects

11.20 Michele Reticcioli (*Wien Universität Austria*)

C4. Polaron-mediated surface reconstruction in the reduced Rutile TiO₂ (110) surface

11.40 Lee Burton (*Université Catholique de Louvain, Belgium*)

C5. Electronic Structure and Defect Physics of Tin Sulfides: SnS, Sn₂S₃, and SnS₂

12.00 Migle Grauzinyte (*University of Basel, Switzerland*), C6. Defects in rutile SnO₂

12.20 Lunch and discussion time

Session 3 (chair: David Scanlon)

14.00 Jon Major (*University of Liverpool, United Kingdom*)

I7. Deep level links to device performance in CdTe solar cells

14.40 Oliver Dicks (*University College London, United Kingdom*)

C7. Intrinsic charge trapping in amorphous Al₂O₃

15.00 John Buckeridge (*University College London, United Kingdom*)

C8. Oxygen vacancies as electron traps in wide gap semiconducting oxides: a hybrid QM/MM study

15.20 Jonas Joos (*Ghent University, Belgium*)

C9. Mn impurities in CaZnOS: insight from luminescence spectroscopy and density functional theory

15.40 Coffee break

16.00 Kevin Sivula (*Ecole Polytechnique Fédérale de Lausanne, Switzerland*)

I8. Charge transport, recombination, and defects in solvent-exfoliated semiconducting transition metal dichalcogenides

16.40 Jana Tittmann-Otto (*Chemnitz University of Technology, Germany*)

C10. Charge traps in carbon nanotube-based field-effect transistors

17.00 Close of Workshop

Invited (I) and Contributed (C) Talks

11. Charge Trapping in Transparent Conducting Oxide SnO₂

David Scanlon^{1,2}

¹University College London - London's Global University (United Kingdom), ²Diamond Light Source Ltd (United Kingdom)

Abstract

The need for a high performance, earth abundant transparent conducting oxides (TCOs) is ever present in the expanding electronics and photovoltaics industry. TCOs possess large optical band gaps (> 3.1 eV) in order to avoid the absorption of visible light, resistivities as low as $\sim 10^{-5}$ Ωcm as well as large carrier concentrations (10^{20} cm^{-3}). All the industrially used TCOs (i.e. ITO, ZnO:Al, SnO₂:F) are n-type, which limits their applications to those of transparent electrodes. To extend the utility and applications of TCOs further, p-n junctions composed of all-oxide TCOs must be achieved, meaning that the discovery of a high performance, p-type TCO has become a much sought after goal for materials scientists. Decades of attempts to fabricate the elusive p-type TCO have been centred on doping of the natively n-type TCOs to make them p-type, with little success. Arguably the flagship TCO material is In₂O₃:Sn (Tin doped Indium Oxide, ITO) with resistivities as low as 10^{-5} Ωcm making this material ideal for consumer electronics. A main limitation of this material however, is the high cost of indium and the rarity of the element in the earth's crust which drives the search for a cheaper alternative. Stannia (SnO₂ or stannic oxide) is an n-type, wide band gap oxide semiconductor which crystallizes in the tetragonal rutile (Cassiterite) structure. It possesses a fundamental band gap of 3.6 eV at the Gamma point, can achieve conductivities of $\sim 10^4$ Scm^{-1} when donor doped, and displays a high thermal and chemical stability, making it excellent for transparent conducting oxide (TCO) and gas sensing applications. High conductivities can be achieved by doping with Antimony (Sb) or Fluorine (F) which are the most common choice for donor dopant in SnO₂ resulting in resistivities as low as 10^{-4} Ωcm , which falls short of the performance of ITO. One reason is that these these dopants appear to be inherently self-limiting. In this presentation I will present a survey of the defect chemistry of SnO₂, explaining why the material can never be made p-type, and identifying novel doping strategies which can surpass the self limitations of the currently utilised donor dopants.

C1. The role of bipolarons in the formation of defects in amorphous hafnia

Jack Strand¹, Moloud Kaviani², Alexander Shluger¹

¹*University College London - London's Global University (United Kingdom)*, ²*WPI-AIMR, Tohoku University (Japan)*

Abstract

Modelling the generation of oxygen vacancies in amorphous HfO_2 is important for improving its functionality in transistor and resistive random-access memory devices. Degradation in transistor gate stacks is believed to be rooted in the existence of defects such as oxygen vacancies in the gate oxide. Hybrid DFT calculations were used to investigate the generation of oxygen vacancies in a- HfO_2 via the creation of Frenkel pairs. We find that the existence of self-trapping sites plays a role in the generation of new defects. It is proposed that Frenkel defects can form via the conversion from deep electron and hole bipolaron sites. Defects were simulated under conditions of electron or hole injection and calculations of the stability of Frenkel pairs and the barrier heights to their formation were made. It is found that presence of the deep bipolarons leads to higher formation energies of Frenkel pairs in amorphous HfO_2 when compared to monoclinic HfO_2 .

C2. Electron Trapping in TiO₂ Rutile and Anatase

Razak Elmaslmane, Keith McKenna

Department of Physics, University of York, York (United Kingdom)

Abstract

The rutile and anatase phases of the ionic crystal TiO₂ are subject to the effects of charge trapping, potentially hindering their performance when used for industrial applications. Applications of these phases include uses in solar cells, water purification, self-cleaning windows and portable energy storage. Controlling this effect would allow for improved efficiency of devices where these materials are used. We use ab initio DFT to model the trapping properties of small localised polaron states in TiO₂. Approximate DFT carries with it the self-interaction error (SIE) which forces the localised polaron states in TiO₂ into delocalised states, contradicting some experimental results. It is therefore necessary to use a method which counters the SIE, such as DFT+U or hybrid DFT. These methods introduce free parameters which can give rise to inaccurate physics if set to inappropriate values. In our research, we use a non-empirical method of determining the additional parameters generated by using these methods [1]. For the hybrid DFT functional used, we found the predicted percentage of exact exchange to be 12.5 for both phases of TiO₂. For DFT+U, we found that the predicted Hubbard-U values to be 2.80 eV and 4.70 eV on titanium and oxygen in rutile. In anatase, we found the Hubbard-U corrections to be 2.30 eV and 3.85 eV on titanium and oxygen. We also assessed the predictive power of both DFT+U and hybrid DFT by fitting to a system with an oxygen vacancy. Our findings show that hybrid DFT yields results which are much more transferrable, allowing us to study defects in the material in greater detail.

References:

[1] Stephan Lany and Alex Zunger, Phys. Rev. B 80, 085202

12. Intrinsic electron and hole trapping in amorphous oxides

Alexander Shluger¹, Moloud Kaviani², Jack Strand¹, Oliver Dicks¹, David Gao¹

¹University College London - London's Global University (United Kingdom), ²WPI-AIMR, Tohoku University (Japan)

Abstract

I will present the results of our recent theoretical studies of intrinsic electron and hole trapping in amorphous SiO_2 , HfO_2 and Al_2O_3 films. These materials in a bulk crystalline phase exhibit only hole polarons with trapping energies of about 0.2 eV. Recent experimental evidence suggests that both negative and positive charging can occur in amorphous oxides in much deeper states. To investigate whether such charging can be caused by intrinsic electron and hole trapping, we modelled the behaviour of extra electrons and holes in stoichiometric amorphous SiO_2 , HfO_2 and Al_2O_3 structures using classical simulations and Density Functional Theory. The results demonstrate that single- and bi-polaron electron and hole states can form in a- SiO_2 and a- HfO_2 , where the effect of local disorder is amplified by polaronic relaxation of amorphous network. Only hole trapping is found in a- Al_2O_3 . Both electron and hole bi-polarons can convert into Frenkel pairs of oxygen vacancies and interstitial oxygen ions. These results broaden the concept of intrinsic polaron trapping to disordered oxides. I will discuss challenges in constructing amorphous structures, predicting polaron trapping and comparing the predicted properties with experiment.

13. Disorder, Defects and Charge Trapping in Titania

Aaron Deskins¹, Juan Garcia², Michael Nolan³

¹*Worcester Polytechnic Institute (United States)*, ²*Argonne National Laboratory (United States)*, ³*Tyndall National Institute (Ireland)*

Abstract

Disordered materials may have unique properties with regards to charge trapping and defect formation. In this work I highlight our density functional theory modeling of disordered titania (TiO₂) to further quantify the electronic, chemical, and physical properties of such materials. My first results focus on mixed phase titania photocatalysts, which involve particles with both rutile and anatase phases. Our structural models show a disorderd region at the interface between the two phases with several under-coordinated Ti sites. We analyze how electron localization and vacancy formation may occur at these interfaces, and repurcusions of these under-coordinated sites. I also present results on amorphous titania, which may be used as coatings or photocatalysts. Defects have been suggested as key to their properties (such as reaction sites or increasing charge conductivity), and we have modeled reduced amorphous titania through oxygen removal. Our results predict how the structure of amorphous titania may affect its electrochemical and photocatalytic properties, such as introducing gap states or how Ti coordination number is related to electron localization. Our work provides valuable insight on how disorder is related to electronic properties and trapping sites in titania.

C3. DFT Study of trapped electrons in hackmanite-type minerals

Antton Curutchet

Laboratoire de Chimie, ENS de Lyon (France)

Abstract

Photochromic materials are the basis of several high-tech devices targeting numerous applications including optical memories, rewritable papers, photochromic glasses... Among numerous different photochromic compounds, mostly organic, this talk will focus on hackmanite, which is a sodalite-type mineral of $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$ formula, doped with sulphur species. They go from colourless to dark blue upon UV irradiation and returns to colourless upon white light irradiation. For a long time, these properties have remained poorly investigated. Some studies proved that the colour was due to a photo-induced electron transfer from the sulphur dopant to a chlorine vacancy. The trapped electron in the vacancy, called F-center, has quantified levels and absorbs the light giving the colour to the material. But the influence of the composition, of the nature of the dopants and of the size of the vacancy on the properties of the trapped electron are still unclear. The lecture will present a computational study of photo-induced F-center and of the spectroscopic properties of the trapped electron, based on the experimental characterisation of sodalite compounds done by Williams et al. [1] The geometries of the two colourless ([S22-,VCl]) and colored ([S2-,VCl-]) forms were determined by DFT using periodic boundary conditions, with CRYSTAL14 code, while F-center absorption was studied by a cluster-type approach, using TD-DFT and SAC-CI methods (GAUSSIAN09 code). For the latter, the cluster was surrounded by point charges to simulate the long-range electrostatical interactions with its environment. The vibronic coupling between the F-center and the surrounding atoms was taken into account to improve the simulation of the F-center color.[2]

References:

- [1] E. R. Williams, A. Simmonds, J. a. Armstrong, M. T. Weller, *J. Mater. Chem.* 2010, 20, 10883-10887
- [2] A. Curutchet, T. Le Bahers, *Inorg. Chem.* 2017, 56, 414-423

I4. Defect chemistry of organohalide perovskites: Implications for solar cell operation

Filippo De Angelis

Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), CNR-ISTM, Perugia (Italy)

Abstract

Organohalide lead perovskites are revolutionizing the scenario of emerging photovoltaic technologies. Being solution processed from earth abundant materials, they deliver photovoltaic efficiency exceeding 22%, effectively competing with conventional inorganic semiconductors. Organohalide perovskites have shown a surprisingly low concentration of traps, ranging from $\sim 10^{11}$ to 10^{16} cm⁻³ in single crystals and polycrystalline thin films, respectively, despite the inherent soft nature of these materials. Defects must however be very abundant in these hybrid perovskites, implying an unusual defect chemistry in the prototypical MAPbI₃ perovskite whereby the typical cation (MA, Pb) and anion (I) vacancies or interstitials would only introduce shallow states in the material band gap. We illustrate the results of ab initio molecular dynamics simulations coupled to first principles electronic structure calculations on the effect of defects on the electronic and dynamical properties of organohalide lead perovskites. The role of the organic cation dynamics and of ion/defect migration is analyzed in relation to photoinduced structural transformations and solar cell operation. It is found that Frenkel defects, relatively abundant in MAPbI₃ and related perovskites, undergo a light-induced dynamical transformation which may account for the observed enhanced photoluminescence quantum yield following sample irradiation. We also show how most of perovskites unusual properties in terms of defects and trapping dynamics can be explained by the close similarity between the perovskite properties and the photochemistry of iodine, both for 3D and 2D materials. The unusual defect chemistry of organohalide perovskites largely contributes to their outstanding optoelectronic properties and is likely the key to their success in solar cells.

References:

- J.M. Azpiroz et al. *Energy Env. Sci.* 2015, 8, 2118.
- C. Quarti et al. *Energy Env. Sci.* 2016, 9, 155.
- E. Mosconi et al. *ACS Energy Lett.* 2016, 1, 182.
- E. Mosconi et al. *Energy Environ. Sci.* 2016, 9, 3180.
- D. Cortecchia et al. *J. Am. Chem. Soc.* 2017, 139, 39.
- K. Domansk et al. *Energy Environ. Sci.* 2017, DOI: 10.1039/C6EE03352K.
- J. Bisquert et al. *ACS Energy Lett.* 2017, 2, 520.

I5. The Necessity to Understand Charge Trapping in Order to Enhance the Commercialisation Potential for Perovskite Solar Cells

Chris Moore

Dyesol Ltd.

Abstract

Recent discovery of the photo-physical properties of organo-lead halide perovskite materials has stimulated a global effort to design and manufacture solar photovoltaic devices utilising this unique material. Although solar cells constructed using this family of materials have achieved conversion efficiencies approaching, and in some circumstances exceeding those of incumbent first and second generation devices, there remains significant potential for further optimisation in processing and architecture, which will be a key enabler to the successful commercial exploitation of such devices. Whilst the photo-generation of charges within the organo-lead halide perovskite material is becoming better understood, their effective extraction from the extensive range of architectures made possible by these materials is less clear. The trapping of both electrons and holes within the sometimes complex device architecture is known to constrain device efficiency, and a better understanding of trapping mechanisms will create strategies for optimisation, thereby enhancing commercial viability of devices based on these material. Dyesol, as a company engaged in the commercialisation of devices based on perovskite materials has a key interest in determining the causes and implementing associated mitigation of electron and hole trapping in the light harvesting and associated semiconducting materials within its device configurations. The evolution of materials and device architecture will be driven by a better understanding of such trapping mechanisms, and facilitate the widespread application of this disruptive PV technology.

I6. Charge transport in amorphous systems and systems with mobile defects

Alison B Walker

Department of Physics, University of Bath Bath BA2 7AY (United Kingdom)

Abstract

Charge transport in systems with disorder and defects has attracted interest in two recent contexts, organic semiconductor, OSC, electronics and perovskite photovoltaics, PV.

Regarding OSCs, I will present a coherent description of charge transport and the different roles of electronic coupling, structural ordering and conductive pathways in films of OSCs with varying levels of disorder. In OSCs, free charges hop between localized states that have a wide distribution of energies with disorder widths typically 0.1 eV. The hopping rates depend sensitively on the molecular packing arrangements, the morphology, and on the chemical structure of the molecules. We investigate a system of hexa-octylthio-triphenyl-ene (HOTT) molecules. These molecules are discotics, forming columnar phases when cooling down from the isotropic phase. They show a strongly anisotropic charge mobility in their columnar phase. We investigate the effects of structural ordering on charge mobilities, using simulated morphologies of HOTT molecules at 280K and 400K.

In conventional perovskite solar cells, the active layer is a hybrid organic-inorganic semiconductor of the perovskite structure that has high optical absorption and charge carrier mobilities, resulting in cells whose power efficiencies exceed 20%. However, these cell characteristics often show hysteresis. I will show how this hysteresis arises through point charge defects, iodide ion vacancies, that move while the J-V curves are being measured and change the local field seen by the free charge carriers.

C4. Polaron-mediated surface reconstruction in the reduced Rutile TiO₂ (110) surface

Michele Reticcioli¹, Martin Setvin², Xianfeng Hao³, Ulrike Diebold², Cesare Franchini¹

¹*Faculty of Physics and Center for Computational Materials Science, Wien Universität (Austria),*

²*Institute of Applied Physics, Technische Universität Wien (Austria),* ³*Key Laboratory of Applied Chemistry, Yanshan University (China)*

Abstract

The role of polarons is of key importance for the understanding of the fundamental properties and functionalities of TiO₂. We use density functional theory with an on-site Coulomb interaction and molecular dynamics (DFT+U MD) to study the formation and dynamics of small polarons in the reduced rutile (110) surface. We show that excess electrons donated by oxygen-vacancies (VO) form mobile small polarons that hop easily in subsurface and surface Ti-sites. The polaron formation becomes more favorable by increasing the VO concentration level (up to ~20%) due to the progressively lower energy cost needed to distort the lattice. However, at higher VO concentration the shortening of the averaged polaron-polaron distance leads to an increased Coulomb repulsion among the trapped charges at the Ti-sites, which weakens this trend. This instability is overtaken by means of a structural 1x2 surface reconstruction, characterized by a distinctively more favorable polaron distribution. The calculations are validated by a direct comparison with experimental AFM and STM data. Our study identifies a fundamentally novel mechanism to drive surface reconstructions that enters a long standing issue on the origin of the reconstruction in rutile (110) surface.

C5. Electronic Structure and Defect Physics of Tin Sulfides: SnS, Sn₂S₃, and SnS₂

Lee Burton¹, Yu Kumagai², Aron Walsh³, Fumiyasu Oba²

¹*Université Catholique de Louvain (Belgium)*, ²*Tokyo Institute of Technology (Japan)*, ³*Imperial College London (United Kingdom)*

Abstract

The tin sulfides SnS, Sn₂S₃, and SnS₂ are investigated for a wide variety of applications such as photovoltaics, thermoelectrics, two-dimensional electronic devices, Li ion battery electrodes, and photocatalysts. For these applications, native point defects play important roles, but only those of SnS have been investigated theoretically in the literature. In this study, we consider the band structures, band-edge positions, and thermodynamical stability of the tin sulfides using a density functional that accounts for van der Waals corrections and the GW0 approximation. We revisit the point-defect properties, namely, electronic and atomic structures and energetics of defects, in SnS and newly examine those in SnS₂ and Sn₂S₃ with a comparison to those in SnS. We find that SnS₂ shows contrasting defect properties to SnS: Undoped SnS shows p-type behavior, whereas SnS₂ shows n type, which are mainly attributed to the tin vacancies and tin interstitials, respectively. We also find that the defect features in Sn₂S₃ can be described as a combination of those in SnS and SnS₂, intrinsically Sn₂S₃ showing n-type behavior. However, the conversion to p type can be attained by doping with a large monovalent cation, namely, potassium. The ambipolar dopability, coupled with the earth abundance of its constituents, indicates great potential for electronic applications, including photovoltaics.

C6. Defects in rutile SnO₂

Migle Grauzinyte

University of Basel (Switzerland)

Abstract

Transparent conducting oxides (TCOs) are a class of technologically important materials, that can lead to improved solar cell performance as well as an array of new optoelectronic devices. The high cost of Indium in making a well established TCO (Sn-doped In₂O₃) leads to a continued search for alternative suitable TCO materials. In our work we examine the suitability of different dopants for SnO₂, in view of achieving a n-type low resistivity and high optical transparency TCO. Substitutional atoms of higher valency than Sn (+4) are speculated to act as free electron donors and their formation energies, as a function of the Fermi level, help identify the stable charge state of the defect. In this talk I will show how these defects interact with hydrogen impurities and oxygen vacancies; these are viewed as other potential sources of free electrons in SnO₂ crystals. Finally, we shortlist the most suitable dopants in this material.

I7. Deep level links to device performance in CdTe solar cells

Jon Major

University of Liverpool (United Kingdom)

Abstract

Determining the nature of electrically active defects in thin film solar cells, such as CdTe, is incredibly complex. Due to the use of relatively low purity materials in conjunction with high proportion of grain boundaries and defects compared to single crystal alternatives, the role of defects in determining cell performance is far from clear. In addition to vacancy defects a variety of impurity defects are also expected from the raw material, glass substrate and post-growth processing. Deep level transient spectroscopy (DLTS) is a well-known as a method of characterising such electrically active defects in PV devices. The technique has however been developed in relation to simpler single crystal systems where identified deep levels energies can easily be related to specific defects. For thin film solar cells rather than focusing on the identification of defects with specific associated energy levels, we demonstrate that the observable deep level behavior is modified as a function of cell processing. This talk will present initial results demonstrating the links between observable deep levels via DLTS and CdTe solar cell performance.

C7. Intrinsic charge trapping in amorphous Al_2O_3

Oliver Dicks, Alexander Shluger

University College London - London's Global University (United Kingdom)

Abstract

Thin films of Al_2O_3 , which tend to be amorphous (a- Al_2O_3) rather than crystalline, are currently being investigated for use in electronic applications, including charge-trapping memory devices[1,2] and high-k dielectrics in Ge devices[3]. As charge trapping ultimately effects the performance of these devices we present a comprehensive categorization of intrinsic hole and electron traps in a- Al_2O_3 using DFT calculations with hybrid functionals. Amorphous structures of Al_2O_3 have been generated through the molecular dynamics (MD) melt-quench method, using a Born-Mayer type potential previously used to generate a- Al_2O_3 structures[4]. Using DFT as implemented in the CP2K code and the PBE0-TC-LRC (3.0Å cutoff) hybrid functional we demonstrate shallow polaronic hole traps in crystalline Al_2O_3 and much deeper hole and hole-bipolaron traps in a- Al_2O_3 . Particular attention is paid to minimizing the self-interaction error of the system by adjusting the cutoff of the nonlocal functional. The intrinsic hole traps can be predicted from structural and molecular orbital precursors in the amorphous material, allowing estimates of the trap density and study of the mobility edge in a- Al_2O_3 . We also suggest that the orbital character of the bands in amorphous materials plays a large role in the probability of electron trapping in these amorphous metal oxides, with the delocalized and non-directional s states that form the conduction band minimum of a- Al_2O_3 preventing intrinsic negative charge trapping.

References:

- [1] L. Goux et al. M., VLSI Technology (VLSIT), 2012 Symposium on pp.159-160 (2012)
- [2] Ya Li et al. Electron Devices, IEEE Transactions on 62, no.4, pp.1184-1188 (2015)
- [3] S. Swaminathan et al, J. Appl. Phys. 110 (2011), 094105
- [4] L. Blackberg et al, Nucl. Instr. Meth. Phys. Res. 759 (2014), 10

C8. Oxygen vacancies as electron traps in wide gap semiconducting oxides: a hybrid QM/MM study

John Buckeridge¹, Richard C. Catlow¹, Alexey Sokol¹, Aron Walsh²

¹University College London - London's Global University (United Kingdom), ²Imperial College London (United Kingdom)

Abstract

The formation of oxygen vacancies, their electron-trapping properties and hence effect on the n-type conductivity of transparent conducting oxides (TCOs) has remained a controversial topic. They have been determined to be deep donors in SnO₂ and ZnO, while it has been proposed that their formation on the surface of In₂O₃ would lead to intrinsic n-type conduction. Numerous computational studies on this subject have correlated the calculated defect properties with available experimental spectroscopic data (luminescence etc.), but, notably, contradict each other in the defect assignment. We use state-of-the-art hybrid quantum mechanical/molecular mechanical solid state embedding to determine the formation energy, electronic and optical properties of the oxygen vacancy in the three archetypal TCOs In₂O₃, ZnO and SnO₂. To ensure a high level of accuracy in our simulations, we employ three hybrid exchange and correlation density functionals (PBE0, B97-2 and BB1k) and compare their predictions with previous plane-wave pseudopotential based calculations and experiment. For ZnO and SnO₂, our results using the PBE0 functional are in excellent agreement with calculations done using a plane-wave basis set (which predict the oxygen vacancy to be a deep donor in all three systems). In bulk In₂O₃ we find, in contrast to previous studies, that the oxygen vacancy is a resonant shallow donor. Using BB1k, which has been developed specifically to treat both reaction energies and kinetic barriers accurately, for the cases of SnO₂ and ZnO we show that the vacancy is indeed a deep donor, but shallower than previously proposed. Our results are in excellent agreement with available deep level transient spectroscopy measurements and other relevant experimental data.

C9. Mn impurities in CaZnOS: insight from luminescence spectroscopy and density functional theory

Jonas Joos¹, Kurt Lejaeghere², Katleen Korthout¹, Dirk Poelman¹, Philippe Smet¹

¹*LumiLab, Department of Solid State Sciences, Ghent University (Belgium),* ²*Center for Molecular Modeling, Ghent University (Belgium)*

Abstract

Manganese is a well-known optical dopant. It can adapt different charge states of which the divalent, Mn²⁺, featuring a 3d⁵ electron configuration, and the tetravalent, Mn⁴⁺, featuring a 3d³ electron configuration are most abundant in luminescence literature. Both these charge-states of Mn can show efficient luminescence, originating from intraconfigurational 3d transitions, having the emission in the visible spectral range. Excitation of the luminescence can be achieved by exciting the 3dN manifold directly or sensitized by exciting the host compound with subsequent energy transfer. This study concentrates on the oxysulfide CaZnOS [1]. This polar compound is built of alternating monolayers of ZnS and CaO, and forms a peculiar host for Mn²⁺. It has been proposed as LED phosphor as well as mechanoluminescent pressure gauge [2, 3]. This material was synthesized by a solid-state reaction and the luminescent properties were characterized in detail. The ability of this material to store energy through the trapping of charge carriers is assessed from thermoluminescence measurements. To get a thorough understanding of the properties of this phosphor, the electronic structure of the doped and undoped compound is analyzed in detail. First principles calculations on charged supercells within the framework of density functional theory (DFT) are combined with semi-empirical crystal field theoretical (CFT) calculations to obtain the multiplet structure of the 3d⁵ manifold, phonon energies of the Mn defect and the location of the impurity levels in the single-particle energy gap of the CaZnOS host. This particular phosphor is used as an example to demonstrate the complementarity of different types of energy level schemes [4].

References:

- [1] T. Sambrook et al., *Inorg. Chem.* 46 (2007) 2571-2574
- [2] C. J. Duan, A. C. A. Delsing, H. T. Hintzen, *Chem. Mater.* 21 (2009) 1010-1016
- [3] J.-C. Zhang et al., *Opt. Express* 21 (2013) 12976-12986
- [4] J. J. Joos, D. Poelman, P. F. Smet, *Phys. Chem. Chem. Phys.* 17 (2015) 19058-19078

18. Charge transport, recombination, and defects in solvent-exfoliated semiconducting transition metal dichalcogenides

Kevin Sivula

Ecole Polytechnique Fédérale de Lausanne (Switzerland)

Abstract

Given their established robustness and favorable optoelectronic properties, the semiconducting transition metal dichalcogenides (TMDs, e.g. MoS₂ and WSe₂) are attractive for solar energy application. Recent advances in the solvent-assisted exfoliation of TMDs into 2D nano-flakes suggests that inexpensive roll-to-roll processing can be used to prepare TMD devices inexpensively over large area. However, the high concentration of edge defects in these materials act as recombination sites for photogenerated carriers. In this presentation the challenges with charge transport, separation, recombination and interfacial transfer in these systems will be discussed with respect to the 2D flake size and defect passivation treatments. Our results give insight into the roles of edge and bulk defects and suggest routes for improvement. Overall it is shown that TMDs can achieve internal quantum efficiency for photon harvesting similar to bulk single crystal samples.

C10. Charge traps in carbon nanotube-based field-effect transistors

Jana Tittmann-Otto^{1,2}, Martin Hartmann^{1,2}, Johann Ullrich¹, Stefan Schulz¹⁻³, Sascha Hermann¹⁻³

¹*Chemnitz University of Technology (Germany)*, ²*Center for Advancing Electronics Dresden (Germany)*,
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Abstract

Carbon nanotubes offer a great potential as channel material for future electronics. Like other nanomaterials, they are strongly affected by their environment. Neighboring residual molecules, water, oxide surface states or interface states can act as charge traps, thus inducing hysteresis and a deterioration of the electrical properties. Therefore, special attention needs to be paid on high quality surfaces and the absence of adsorbed molecules when fabricating carbon nanotube-based field effect transistors (CNT-FETs). We present our investigation on the effect of process residues on the performance of wafer-level fabricated CNT-FETs with special emphasize on the reduction of charge traps. An oxygen plasma treatment prior to CNT integration is shown to successfully reduce the amount of contaminations on the gate dielectric surface. This is verified by AFM measurements, revealing a decrease in roughness of the substrate from 2.49 nm to 0.42 nm. Simultaneously the hysteresis in transfer characteristics of the transistor devices is drastically reduced even without a proper passivation layer against the environment. This is remarkable as plasma treatments are known to create a hydrophilic surface, hence increasing the amount of adsorbed water molecules. The transistors were stable for at least 9 weeks under ambient conditions. As these findings contradict former results shown in literature, we further investigated the effects of charge traps present in similar CNT-FETs. An analysis of charging and relaxation times enables a differentiated view on charge trap origins, such as water molecules.

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