

2023 Quantsol Winter Workshop

European Society for Quantum Solar Energy Conversion

March 19-25, 2023

Welcome Address

Welcome to the 33rd Workshop on Quantum Solar Energy Conversion

Our workshop continues a long tradition of successful meetings, which were only interrupted during the Covid crisis. What makes the Quantsol workshops so special is a view on solar energy conversion from different aspects and technologies with time and space for fruitful and intense discussions.

This year again, the program covers solar cells, electrochemical cells, and a range of established and emerging materials. I personally look forward to the talks and discussions that touch on the fundamental limitations of solar energy conversion.

A very warm thank you to Ute and Omer for taking so well care of the organization and putting a great program together! And thanks to all of you for contributing your latest results and sharing your thoughts on solar energy conversion.

We can also look forward to the warm hospitality of Rauriser Hof and the great landscape of the Rauris valley. I look forward to a week of inspiring talks, intense discussions, and meeting old and new friends.

Susanne Siebentritt

Contents

Welcome Address	3
Perspective on self-trapped excitons (<i>Omer Yaffe</i>)	7
Why should we care that chalcogenide perovskites are highly-polarizable semiconductors? (<i>Rafael Jaramillo</i>)	8
Ionic composition and dynamic disorder in halide perovskites (<i>David Egger</i>)	9
The impact of anisotropy and anharmonicity on the magneto-optical properties of bulk 3D and 2D lead halide perovskites (<i>Efrat Lif- shitz</i>)	10
The influence of ions on capacitance and photoluminescence in per- ovskite devices (<i>Bruno Ehrler</i>)	11
The Role of Active Encapsulation in Perovskite Solar Cells (<i>Shaibal K Sarkar</i>)	12
The role of interfaces in perovskite solar cells (<i>Selina Olthof</i>)	13
Electronic Structure of 2D Metal Halide Perovskites: Ligands, Oc- tahedral Twists, Energy Gaps and Exciton Binding Energies (<i>Antoine Kahn</i>)	14
Electronic properties of hybrid metal halide perovskites: Contempora- ry understanding and future challenges (<i>Norbert Koch</i>)	15
Perovskite interfaces for solar cells investigated with photoelectron spectroscopy (<i>Ute Cappel</i>)	16
Colloidal Bi_2Se_3 platelets with helical quantum channels at the edge (<i>Daniel Vanmaekelbergh</i>)	17
Ternary nitrides - disorder tunable materials? (<i>Susan Schorr</i>)	18
Reconceptualizing flashy approaches: non-equilibrium syntheses as a pathway to break chemical boundaries of photoabsorber mate- rials (<i>Ronen Gottesman</i>)	20
Photoelectrochemical cells with epitaxial tandem absorber structures for highly efficient solar fuels production (<i>Thomas Hannappel</i>)	21
Imaging of Bandtail States in Silicon Heterojunction Solar Cells: Nanoscope Current Effects on Photovoltaics (<i>Klaus Lips</i>)	22
Tailored Colloidal Nanocrystals for Luminescent Solar Concentrators (<i>Celso de Mello Donega</i>)	23
Power-law density of states in organic solar cells (<i>Carsten Deibel</i>)	24
Charge transfer and structural control in block co-polymer OPVs (<i>Jolanda Muller</i>)	25

Relationship between exciton and charge dynamics in organic blends through nano-morphology (<i>Ardalan Armin</i>)	26
Materials and Interfaces in Solid State Tandem Dye-sensitized Solar Cells (<i>Elizabeth Gibson</i>)	27
From Müser to Shockley-Queisser and beyond (<i>Tom Markvart</i>)	28
Generalization of Kirchhoff's Law: The inherent relations between quantum efficiency and emissivity: $\epsilon=\alpha(1-QE)$ (<i>Carmel Rotschild</i>)	29
Operando characterization of charge extraction and recombination profiles in solar cells with nanoscale resolution (<i>Gideon Segev</i>)	30
Polaron transport and light-induced structural dynamics in BiVO ₄ photoanodes (<i>Ian Sharp</i>)	31
Accurate prediction of electronic and optical excitations from density functional theory (<i>Leeor Kronik</i>)	32
Quantifying Charge Extraction and Recombination Using the Rise and Decay of the Transient Photovoltage of Perovskite Solar Cells (<i>Thomas Kirchartz</i>)	33
Revealing Hidden Phases and Self-Healing in Antimony Trichalcogenides and Chalcogenides (<i>Eran Edri</i>)	34
SEMI-TRANSPARENT Sb ₂ S ₃ SOLAR CELLS WITH FLUORENE-BASED ENAMINE AS HOLE TRANSPORT MATERIALS (<i>Nimish Juneja</i>)	35
A hole transport layer for CIGS solar cells (<i>Susanne Siebentritt</i>)	36
Defect Healing and Defect Metrology of WSe ₂ by Gate-Modulated Photoluminescence (<i>Doron Naveh</i>)	37
Surface defects can determine carrier densities of Pb-halide perovskite films (<i>David Cahen and Antoine Kahn</i>)	38
Coordination complexes and polymers for emerging molecular devices (<i>Marina Freitag</i>)	39
Doping soft semiconductors: Opportunities and challenges (<i>Pabitra Kumar Nayak</i>)	40
Single-particle heralded spectroscopy as a tool to reveal puzzling observations in perovskite NCs (<i>Miri Kazes</i>)	41
On the photostability of electron acceptor materials: from fullerene to non-fullerene acceptors (<i>Cleber Marchiori</i>)	42
On the role of mid-gap trap states in organic (perovskite?) photovoltaic devices (<i>Oskar Sandberg</i>)	44
Modelling light-induced charge-separation in photosystems to understand the limits to solar photochemical energy conversion (<i>Daniel Garcia Medranda</i>)	45
Author Index	47

Perspective on self-trapped excitons

Monday, 08:30

Omer Yaffe

Weizmann Institute of Science

The formation of self-trapped excitons in halide perovskite crystals is trending. Intrigued by the concept of a self-trapped exciton in a semiconductor, I decided to prepare a perspective talk. First, I will briefly review its theoretical framework and discuss how self-trapped excitons differ from polarons. Then, I will review experimental evidence for self-trapped excitons in dielectrics. Finally, I will discuss the implications of self-trapped excitons' formation in semiconducting halide perovskites. I based my talk primarily on a book (DOI: 10.1007/978-3-642-85236-7) by K.S. Song and R.T. Williams, published in 1992 and devoted to self-trapped excitons.

Monday, 09:00

Why should we care that chalcogenide perovskites are highly-polarizable semiconductors?

Rafael Jaramillo

Massachusetts Institute of Technology

Chalcogenide perovskites have, like their oxide counterparts, high dielectric polarizability associated with low-energy polar phonons that carry large effective charge. However, unlike oxides, chalcogenide perovskites are natural-born semiconductors, with band gap in the visible-to-near-infrared.

Chalcogenide perovskites are, like halide perovskites, semiconductors with band gap in the visible-to-near-infrared. However, unlike halides, chalcogenide perovskites have a strong component of covalent bonding. This makes their electron-phonon interactions (maybe also their defect chemistry) more like tetrahedrally-bonded semiconductors. Also unlike the halides, chalcogenide perovskites are stable and non-toxic.

Chalcogenide perovskites are therefore an interesting model system to understand the role of dielectric polarizability on semiconductor performance. In particular, we want to understand the role of large low-frequency dielectric constant, large Pekar factor, and a tendency towards polaron formation on rates of phonon-assisted excited-state decay.

I will present measurements that address this issue, including impedance spectroscopy, Raman spectroscopy, photoluminescence spectroscopy, and X-ray absorption spectroscopy. I will also present on enabling advances in chalcogenide gas-source MBE, such as the growth of alloys including the first reported selenide perovskite (with band gap 1.4 eV). I will end with an outlook on the prospects for chalcogenide perovskite solar cell technology.

Ionic composition and dynamic disorder in halide perovskites

Monday, 09:30

David Egger

TU Munich

Halide perovskites are appealing for an array of optoelectronic applications because their properties can be tuned by ionic composition. At the same time, these materials exhibit a plethora of peculiar dynamic effects at finite temperatures. In particular, we and others have shown that the atoms can deviate strongly from the average, ideal crystal structure when we inspect their local geometry at any given time. These pronounced local structural fluctuations induce changes in the optoelectronic properties and were found to transiently modulate the electronic coupling, an effect also occurring in small-molecule, organic crystals and is known as a dynamic disorder. In this presentation, I will discuss our theoretical efforts to capture the consequences of dynamic disorder for carrier dynamics in halide perovskites. This is a challenging task for theorists because it forces us to leave aside several foundational assumptions that do not apply to the case of dynamic disorder. To tackle it, we combine a tight-binding model that is parametrized by density functional theory with molecular dynamics to extract charge-carrier mobilities and their temperature dependencies, which are key observables informing about the pertinent carrier-scattering mechanisms. With our multi-scale model, we rationalize the effect of halide composition on carrier dynamics in halide perovskites through the lens of the dynamic disorder picture.

The impact of anisotropy and anharmonicity on the magneto-optical properties of bulk 3D and 2D lead halide perovskites

Efrat Lifshitz

Technion—Israel Institute of Technology

The renaissance of interest in halide perovskites, triggered by their unprecedented performance in optoelectronic applications, elicited worldwide efforts to uncover various intriguing physical properties, with a particular interest in spin-orbit effects. The current work presents magneto-optical experimental evidence for anisotropic electron-hole interactions in the 3D orthorhombic MAPbBr₃ and the 2D (PEA)₂PbI₄ bulk single crystals. The evidence was seen in the magneto-photoluminescence spectra while monitoring several different crystallographic directions. The observations exposed a highly non-linear response to a magnetic field and asymmetry to the influence of the sign of the magnetic field. A theoretical model implementing anisotropy in the electron-hole interaction, Rashba effect, Landé g-factors, and a lesser contribution from an Overhauser effect corroborated the experimental results.

A continuation of the work involved the investigation of the anharmonic ground-state of the (PEA)₂PbI₄ compound, using complementary information from low-temperature x-ray diffraction (XRD) to the photoluminescence spectroscopy, which was also supported by density functional theory (DFT) calculations. The study extrapolated four crystallographic configurations from the low-temperature XRD. These configurations imply that the ground state has an intrinsic disorder stemming from two coexisting chiral sub-lattices, each with a bi-oriented organic spacer molecule (see scheme). We further show evidence that these chiral structures form unevenly populated ground states, portraying uneven anharmonicity, where surface effects may tune the state population. Our results uncover a disordered that may be associated with a dynamic Rashba effect. The current efforts include using a unique pump-probe experiment to follow a dynamic Rashba effect. Also, preliminary magneto-photoluminescence of (F-PEA)₂PbI₄ uncovered two opposing chiral structures alone through the entire temperature range under investigation. This result was already corroborated by XRD measurements, confirming the locking of the F-PEA degree of freedom. Further study is ongoing regarding the relation between anharmonicity, the Rashba effect, and the dependence on structure and composition.

The influence of ions on capacitance and photoluminescence in perovskite devices

Monday, 11:00

Bruno Ehrler
AMOLF

Mobile ions appear to determine the electric field distribution in a perovskite-based device. However, it is not clear what this means for device operation. I will discuss the influence of field screening on capacitance and photoluminescence measurements. The capacitance value measured for a perovskite device depends on the doping level of the perovskite and the adjacent transport layers, and the ion distribution within the perovskite layer. The latter changes with voltage, temperature, and time, so that mobile ions influence all kinds of voltage, temperature, and time-dependent measurements in non-trivial ways. With capacitance measurements, many properties of mobile ions can be accessed, but only if we understand the way the transport layers and doping levels influence these measurements. I will present drift-diffusion simulations that explore this parameter space. Photoluminescence measurements are also influenced by the local electric field. The presence of a field can lead to drift out of the PL collection zone, or change the local trap filling. Again, mobile ions determine the field, and the local photoluminescence is hence strongly influenced by their presence. I will show lateral device measurements that we use to attempt an understanding of the changes in photoluminescence in the presence of mobile ions.

Monday, 11:30

The Role of Active Encapsulation in Perovskite Solar Cells

Shaibal K Sarkar
IIT Bombay

From a perovskite photovoltaic device standpoint, the Al₂O₃ ALD can be thought of as a thin film encapsulate to protect the underlined material from the extrinsic entities. However, as per the literature is concerned, the role of Al₂O₃ ALD in the perovskite photovoltaic devices is much beyond a mere passive component. This raises a severe ambiguity over the choice of surface (or interface) on which ALD needs to be done for optimized device performance, in terms of the device efficiency and stability.

In my presentation, I would like to elucidate the characteristic differences between the surface limited and substrate enhanced ALD processes which is important to perovskite devices. The objective here is to discuss a unified correlation between the role of the Al₂O₃ ALD mechanism with the perovskite device performance by excluding popular overestimated assumption about the conformality on non-ideal surface, like perovskite or organic thin films. In addition, I would like to emphasize on the fact that how the ALD process can be used to passivate the buried interfacial defect and enhancing the VOC, PL and ELQE.

The role of interfaces in perovskite solar cells

Monday, 17:00

Selina Olthof

University of Cologne

Solar cell devices are typically multi-layer stacks in which the absorber layer is sandwiched between metal oxides and/or organic transport layers in order to facilitate charge extraction or block unwanted charge carriers. In perovskite-based devices, the role that these resulting interfaces play on the device performance as well as its stability are currently poorly understood. One would expect that energetic barriers, arising between the transport levels of the various layers in the device, will affect the overall performance. However, our own results as well as reports in literature often show no clear correlation of the performance and energy level offsets. Therefore, the question arises what the design criteria for ideal charge extraction layers could be.

While the role of energetics remains elusive, it is becoming more and more obvious that chemical interactions between the perovskite and the adjacent layers play a crucial role. We have shown that materials employed in other thin film technologies (such as organic semiconductors) cannot straight forward be transferred to perovskite devices, as the direct contact, in particular to metal oxides, will trigger chemical reactions that lead to a partial or even complete decomposition of the perovskite film. Post treatment of the substrate, or the insertion of thin organic interlayers, can be necessary to stabilize the interface. Overall, I will show how photoelectron spectroscopy measurements can help to analyze these perovskite solar cell related interfaces. Hopefully, such observations will help to better understand processes taking place inside the device and can lead to further improvements.

Electronic Structure of 2D Metal Halide Perovskites: Ligands, Octahedral Twists, Energy Gaps and Exciton Binding Energies

Monday, 17:30

Antoine Kahn
Princeton University

Metal halide perovskites (MHP) come in many flavors, from all inorganic to hybrids, from single to mixed cations and halides, and from 3D to various shades of 2D structures. As for any class of semiconductor, the electronic structure of interfaces between MHPs and adjacent electron and hole transport layers is of paramount importance, and depends in significant ways on the frontier energy levels of all materials involved. This talk addresses the determination of hole and electron transport states in 2D metal halide perovskites via direct and inverse photoemission spectroscopy aided by density functional theory calculations, looking specifically at band gap and exciton binding energy as a function of structure. We investigate a number of different issues. First, we relate energy gap and exciton binding energy in a series of Ruddlesden-Popper (RP) structures ($\text{BA}_2\text{MA}_{n-1}\text{PbI}_{3n+1}$) to the number of Pb-I octahedral layers ($n = 1 - 5$) in the quantum well, and demonstrate a type-I band alignment across the series [1]. Second, we look at Dion-Jacobson (DJ) 2D perovskites with asymmetric organic ligands (butane and dimethylpropane diammonium ligands). We show how the bonding of these ligands affects the structure of the inorganic plane, i.e. twist of the Pb-I octahedra, and the impact of these distortions on the materials energy gap and exciton binding energy [2]. Finally, we extend the latter study to a series of RP structures with CH_3 -, $-\text{COOH}$, $-\text{CN}$, and PEA-based monoammonium ligands [3]. Hydrogen bonding between the functional group and the ammonium terminus influences the inorganic-organic interactions and consequently, the octahedral tilting and the Pb-I-Pb bond angle in the 2D plane. We show that, here again, the electronic bandgap and exciton binding energy increase monotonically as the Pb-I-Pb bond angle distortion increases, exhibiting a strong correlation with an $R^2=0.9370$.

[1] X. Zhong, X. Ni, S. Sidhik, H. Li, A. D Mohite, J.-L. Brédas and A. Kahn, *Adv. Energy Mater.* 2202333 (2022) [2] S. Silver, S. Xun, H. Li, J.-L. Brédas and A. Kahn, *Adv. Energy Mater.* 10, 1903900 (2020) [3] X. Zhong, X. Ni, H. Li, Y.-L. Loo, J.-L. Brédas and A. Kahn, (in preparation)

Electronic properties of hybrid metal halide perovskites: Contemporary understanding and future challenges

Monday, 18:15

Norbert Koch

Humboldt-Universität zu Berlin

Metal halide perovskites are semiconductors that exhibit the rich electronic phenomena known from their more established counterparts, such as interface- and dopant-induced band bending, surface states and surface band bending, and surface photovoltage. But they feature even more complexity due to moderate stability under optical excitation in vacuum that can induce surface states, and reversible p-doping by (ambient) oxygen. The simultaneous occurrence of all these phenomena has initially retarded progress towards a comprehensive understanding of their electronic properties, because the most direct experimental method to assess these properties – photoelectron spectroscopy – has been insufficiently adapted to the needs of the perovskites. Now that several important fundamental questions are resolved, such as those discussed here, we can look forward to obtaining deeper insight into even more complex properties and processes of this fascinating material class. In addition, novel interfacial phenomena have been identified, such as photo-induced energy level re-alignment at charge-selective contacts. This necessitates careful photoelectron spectroscopy studies under operando conditions, in order to reliably link interface energetics and solar cell performance.

Perovskite interfaces for solar cells investigated with photoelectron spectroscopy

Ute Cappel
KTH

Lead halide perovskites have drastically changed the solar cell research field due to their ease of synthesis and high power conversion efficiencies, which now reach over 25%. Improving stability and understanding degradation pathways in these devices is of high importance for their further development and potential commercialisation. X-ray based techniques such as photoelectron spectroscopy (PES) are powerful tools for obtaining chemical and electronic structure information of material surfaces as well as interfaces. By combining measurements with visible illumination and/or dosing of atmospheric gasses, photo-induced reactions and therefore the stability of materials can be studied in-situ. However, the X-rays themselves used for measurement can also cause changes in the perovskite materials. In this presentation, I will show how we were able to establish the mechanism and kinetics of X-ray induced changes in perovskite materials [1]. When taking these effects into account, it is possible to investigate the electronic and chemical structure of perovskite surfaces and interfaces by photoelectron spectroscopy. By studying clean surfaces of perovskite single crystals, it was possible to establish the electronic structure of pure perovskites [2]. Furthermore, I will show results of studies of the interface formation and interface degradation of a perovskite active layer with metals such as silver [3] and copper [4]. Reactions with these metals can lead to a degradation of the perovskite materials. Finally, I will discuss how hard X-ray photoelectron spectroscopy can be used for operando measurements of the interfaces in complete perovskite devices. Such measurements make it possible to study the electric fields at the back contact of a solar cell under bias and illumination.

References: 1 Svanström et al. PCCP 23, 12479-12489, (2021). 2 Garcia-Fernandez et al. Small, accepted. 3 Svanström et al., ACS Appl. Mater. Interfaces 12, 7212-7221 (2020). 4 Svanström et al., ACS Materials Au, accepted.

Colloidal Bi_2Se_3 platelets with helical quantum channels at the edge

Tuesday, 08:30

Daniel Vanmaekelbergh
University of Utrecht

Colloidal nanocrystals underwent a tremendous development with full control over dimensions and surface chemistry, resulting in vast opto-electronic applications. Can they also form a platform for quantum materials, in which electronic coherence is key? Here, we use colloidal, two-dimensional Bi_2Se_3 crystals, uniform in thickness and with limited lateral dimensions, to study the evolution of a three-dimensional topological insulator to the technologically important case of two-dimensions and limited crystal domains. We have studied individual Bi_2Se_3 platelets with diameter in the 100-200 nm range and well-defined thickness (3-6 quintuple layers) with cryogenic scanning tunneling microscopy and spectroscopy. For 4-6 Bi_2Se_3 quintuple layers, we observe an edge state, 8 nm wide, around the entire crystal. The edge state is faint or absent for thinner Bi_2Se_3 platelets. The edge states are resilient under a perpendicular magnetic field. Ab-initio calculations confirm that crystals with more than 3 QLs have a non-trivial band structure with a one-dimensional quantum channel at the edge. The quantum channel consists of 2 counter propagating states with momentum-spin locking. Such states are key for non-dissipative information transfer and quantum computing. The processability and dimensional control of topological insulator colloidal nanocrystals opens a unique window to devices with a large density of addressable quantum states.

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Ternary nitrides - disorder tunable materials?

Susan Schorr

Helmholtz-Zentrum Berlin fuer Materialien und Energie

Zinc-group IV-nitrides (ZnMN_2 with $M = \text{Ge, Sn}$) are being considered as promising candidates for photovoltaic absorber materials, containing uniquely elements of low toxicity and low resource criticality [1]. Further to band gap tuning by alloying group IV elements (Si, Ge, Sn), it has been postulated based on DFT calculations that these compounds possess a second mechanism for bandgap tuning through cation disorder [2].

Zn-group IV-nitrides are structural analogues to group III-nitrides (e. g. GaN), where the group III element is replaced by Zn and a group IV element. Having two different cations raises the question of their ordering. Computational studies show that the $\beta\text{-NaFeO}_2$ type crystal structure (space group $Pna21$), with the two cations ordered on two different 4a Wyckoff sites, is thermodynamically stable [2, 3]. Nonetheless, a certain degree of cation disorder, such as ZnIV and IVZn anti-sites, is possible as an intrinsic disorder of the material. In case of full cation disorder, the material crystallises in the wurtzite-type structure (space group: $P63mc$). Herein, cations share one 2b Wyckoff site, similar to the binary group III-nitrides [4]. Utilising a variable degree of intrinsic disorder is being investigated as a novel strategy to engineer material properties [5].

We performed a systematic study of the crystal structure and structural disorder in ZnGeN_2 as well as ZnSnN_2 . Both materials have been synthesized as powder material: ZnGeN_2 was produced through ammonolysis of Zn_2GeO_4 [6, 7], whereas ZnSnN_2 was synthesized from binary sulphide precursors. A certain oxygen content, which was unavoidable, results in off stoichiometric Zn-rich compositions ($\text{Zn}/\text{MIV} > 1$).

We are using diffraction techniques to investigate the crystal structure and structural disorder of these ternary nitrides. While X-ray powder diffraction gives us already a hint to the crystal structure and allows to determine accurate lattice parameters, neutron diffraction permits to distinguish between the isoelectronic cations Zn^{2+} and Ge^{4+} . Whereas ZnGeN_2 crystallizes under certain synthesis conditions (temperature, reaction time) in the orthorhombic $\beta\text{-NaFeO}_2$ -type crystal structure allowing an ordering of Zn and Ge on the two cation sites of the structure, ZnSnN_2 adopts the hexagonal wurtzite-type structure where the two cations are randomly distributed on the single cation site.

The cation site occupancy factors determined by Rietveld analysis of neutron diffraction data of ZnGeN_2 allowed us to investigate the distribution of Zn and Ge on the two cation sites of the $\beta\text{-NaFeO}_2$ -type crystal structure. In this way, we can distinguish between intrinsic and compositional cation disorder. While both types of disorder depend directly, but different on the synthesis conditions, there is no correlation between oxygen content and intrinsic disorder. Finally, we combine our findings concerning structural disorder and band gap energy determined by UV-VIS spectroscopy to enlighten the relationship

between the disorder mechanisms and an optoelectronic materials property. In this way can conclude that ZnGeN_2 is a disorder tunable material, whereas ZnSnN_2 is not.

References [1] P. Narang, et al., *Adv. Mater.* 26 (2014) 1235–1241. [2] D. Skachkov, et al., *Phys. Rev. B.* 94 (2016) 205201. [3] S. Lany, et al., *Phys. Rev. Mater.* 1 (2017) 035401. [4] J. Breternitz, et al., *Acta Crystallogr. A* 77 (2021) 208-216. [5] R. R. Schnepf, et al., *ACS Energy Lett.* 5 (2020) 2027-2041. [6] J. Breternitz, et al., *Phys. Status Solidi (a)* 216 (2019) 1800885. [7] Z. Wang, et al. *Chem. Sci.* , 2021. DOI: 10.1039/D1SC00328C.

Reconceptualizing flashy approaches: non-equilibrium syntheses as a pathway to break chemical boundaries of photoabsorber materials

Tuesday, 09:30

Ronen Gottesman

The Hebrew University of Jerusalem

A unique approach to exploring non-equilibrium synthesis parameter spaces of oxide and oxynitride thin film photoelectrodes will be presented, broadening the pathway toward discovering new chemical spaces of photoabsorber materials inaccessible through conventional solid-state reactions. At present, only a fraction of the possible chemical combinations is known, making it likely that the best materials are still awaiting discovery. Unfortunately, designing controlled synthesis routes of single-phase materials with low defects concentration will become more difficult in rarefied chemical systems and multi-elemental systems. These challenges demand an initial focus on synthesis parameters of novel non-equilibrium synthesis approaches rather than chemical composition parameters. The well-to-do scheme to achieve that is by high-throughput combinatorial investigations of synthesis-parameter spaces, opening new avenues for stabilizing metastable materials, discovering new chemical spaces, and obtaining photoabsorber with enhanced properties to study their physical working mechanisms in photoelectrochemical energy conversion. Using two non-equilibrium synthesis tools: (plasma-enhanced)-pulsed laser deposition and flash photonic sintering, can form gradients in synthesis parameters without modifying composition parameters, which enables reproducible, high-throughput combinatorial synthesis over large-area substrates and high-resolution observation and analysis. Even minor changes in synthesis significantly impact material properties, physical working mechanisms, and performances, demonstrated by the relationship between synthesis conditions, crystal structures of α -SnWO₄, and properties over a range of thicknesses of CuBi₂O₄, both emerging light-absorbers for photoelectrochemical water-splitting used as model multinary oxides. In the final part of my talk, I will briefly overview my current research of heteroanionic perovskite oxynitrides for photoelectrochemical applications.

Photoelectrochemical cells with epitaxial tandem absorber structures for highly efficient solar fuels production

Tuesday, 10:30

Thomas Hannappel

Technische Universität Ilmenau

Epitaxial semiconductors involving III-V compounds, germanium, and silicon provide highest performance levels in optoelectronic applications such as in solar cells and photoelectrochemical cells. However, highest performance in solar energy conversion can only be achieved, when using optimum absorber layers and sophisticated contact formation for electronic and chemical passivation, i.e. for the protection of the solid-liquid interface against corrosion as well as providing interfacial non-radiative recombination. In order to address the surface and interface properties of III-V semiconductor layer structures in relation to their performance, we present the synthesis, theoretical modelling and properties of critical and well-defined interfaces such as GaInP/AlInP. Lattice-matched n-type AlInP(100) charge selective contacts are commonly grown on n-p GaInP(100) top absorbers in highest-efficiency photoelectrochemical cells, where the cell performance can be greatly limited by missing electron selectivity and detrimental valence band offsets. Hence, understanding of the atomic and electronic properties of the GaInP/AlInP hetero-interface, for instance, is crucial for the reduction of photocurrent losses in III-V multijunction devices. Latest progress on the important III-V/Si interface and modifications by fine-tuning of the preparation as well as experimental model experiments on the surface reactivity of III-phosphide surfaces to H₂O exposure, essential considerations on the properties of critical interfaces in relation to photoelectrochemical cells from a conceptual and from a theoretical modelling point of view assuming mostly idealized surface conditions will be discussed.

Imaging of Bandtail States in Silicon Heterojunction Solar Cells: Nanoscopic Current Effects on Photovoltaics

Tuesday, 11:00

Klaus Lips

Helmholtz-Zentrum Berlin, Department ASPIN

We report the study of atomic scale current percolation at state-of-the-art a-Si:H/c-Si heterojunction (SHJ) solar cells under ambient operating conditions, revealing the profound complexity of electronic SHJ interface processes. Using conduction atomic force microscopy (cAFM) and DFT calculations it is shown that the macroscopic current-voltage characteristics of SHJ solar cells is governed by the average of local nanometer-sized percolation pathways associated with bandtail states of the valence band of the doped a-Si:H contact, leading to above bandgap Voc [1]. We show that the percolation paths are inhomogeneously distributed and strongly cluster which is the consequence of dense ordered domains that form in the amorphous silicon as has recently been found [2]. The observation of above bandgap Voc is not in violation of device physics but a consequence of the nature of the percolation pathways which originate from trap-assisted tunneling causing dark leakage current. We show that the broad distribution of local Voc is a direct consequence of randomly trapped charges at a-Si:H dangling bond defects which lead to strong local potential fluctuations and induce random telegraph noise of the dark current. Applying electrical detection of electron spin resonance (EDMR) [3], we are able to directly detect the localized states that are the origin of the tunneling currents by their magnetic fingerprint. The experimental g tensor is predicted from the DFT calculations used to simulate the cAFM data. We will discuss the detailed microscopic picture of the a-Si:H/c-Si interface and its consequences for the electronic processes.

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Tailored Colloidal Nanocrystals for Luminescent Solar Concentrators

Tuesday, 11:30

Celso de Mello Donega

Debye Institute for Nanomaterials Science, Utrecht University

Luminescent solar concentrators (LSCs) consist of transparent thin sheets in which luminescent species (luminophores) are dispersed. The luminophores absorb sunlight and reemit the energy as down-shifted photons that are partially trapped in the LSC by total internal reflection and are waveguided to the edges where they are absorbed by solar cells. LSCs have attracted increasing attention as building integrated photovoltaic elements since they offer the prospect of adding energy-harvesting functionality to windows. However, their development has been hindered by the lack of suitable luminophores. Colloidal semiconductor nanocrystals (NCs) are promising luminophores for LSCs, due to their very broad absorption spectra, large absorption cross-sections, narrow emission spectra, and potentially high photoluminescence quantum yields and photostability. Moreover, they are coated by organic molecules, which makes solution processing and incorporation in transparent matrices straightforward. Nevertheless, most semiconductor NC compositions lead to low device efficiencies due to reabsorption losses. In our group, we have been investigating novel semiconductor nanocrystal compositions characterized by small reabsorption cross-sections. In this contribution, I will provide an overview of our work, with particular emphasis on compound copper chalcogenide NCs (e.g., CuInS₂), which are ideally suited for LSCs, as they combine low toxicity with large absorption coefficients across a broad spectral range, small reabsorption cross-sections, and unparalleled PL tunability, spanning a spectral window that extends from the blue to the NIR (470 – 1100 nm), depending on their exact composition and size. I will also briefly discuss the results of a long-term (1-year) outdoor test comparing the performance of 50x45 cm² LSC devices of four different luminophores (InP/ZnSe NCs, CdSe/CdS NCs, CuInS₂/ZnS NCs, and an organic dye, Lumogen Red).

Power-law density of states in organic solar cells

Carsten Deibel

Chemnitz University of Technology, Germany

The density of states (DOS) is fundamentally important for understanding physical processes in organic disordered semiconductors, yet hard to determine experimentally. We evaluated the DOS by considering recombination via tail states and using the temperature and open-circuit voltage (Voc) dependence of the ideality factor in organic solar cells. By performing Suns-Voc measurements, we find that gaussian and exponential distributions describe the DOS only at a given quasi-Fermi level splitting. The DOS width increases linearly with the DOS depth, revealing a power-law DOS in these materials.

Charge transfer and structural control in block co-polymer OPVs

Tuesday, 17:30

Jolanda Muller

Imperial College London

The efficiencies of organic photovoltaics (OPVs) - while lower than the conventional silicon solar cells - have seen a sharp increase in recent years thanks to the development of new non-fullerene acceptors. However, achieving long-term performance stability in the higher efficiency OPVs is still challenging. This is because best performing bulk heterojunction devices are based on blends of different materials that demix when exposed to light and heat, leading to a strong reduction in conversion efficiency after as little as a few hours in some cases (Mateker McGehee, 2017). A promising approach to tackle the stability issue is the use of single-component macromolecular semiconductors (Review by Roncali, 2021), which have recently showed significant improvements in conversion efficiency reaching 11% in a block co-polymer system while maintaining good performance stability (Wu et al., 2021b). By combining the state-of-the art polymer donors and non-fullerene acceptors into block co-polymers, we hope to gain a deeper physical understanding of how charge generation and transport works in those systems. For this we are investigating block co-polymer systems based on the PBDB-T and PYT material groups. On the one hand we are using chemical modifications to the building blocks of the polymers to tune the energetics in the system in order to understand the interplay between through-space and through-bond charge transfer. On the other hand, we are modifying the large-scale structure of the polymers by tuning the length of the donor and acceptor segments to make a comparison to the polymer-polymer bulk heterojunction. These new material systems are analysed using optoelectronic measurements and modelling to better understand the morphological ordering in block co-polymers and the impact the morphology has on the device properties. Combining the advances in efficiency thanks to novel chemical design of donors and acceptors with the long-term stability of the block co-polymer structure will hopefully lead to more industrially viable alternatives to the popular bulk heterojunction devices (He et al., 2022).

Relationship between exciton and charge dynamics in organic blends through nano-morphology

Ardalan Armin
Swansea University

Exciton diffusion plays a vital role in determining the power conversion efficiency in organic semiconductor based solar cells through controlling the efficiency of exciton splitting [1]. However, measurements of diffusion length in organic semiconductors requires specialized equipment and expertise [2, 3]. Measurements of exciton splitting efficiencies rely upon quenching experiments prone to erratic errors and large uncertainties. In this presentation I will introduce a quasi-steady state technique to measure exciton diffusion lengths in organic semiconductors, named pulsed-PLQY [4]. Further, I will show how this technique can be utilized in bulk heterojunctions to measure the efficiency of exciton splitting and, also the difficult-to-measure-domain-size. Finally, I will discuss the relationships between nanoscale exciton dynamics and the enhanced charge carrier dynamics seen in state-of-the-art non-fullerene organic solar cells.

The long diffusion lengths measured in non-fullerene acceptor based organic solar cells [3, 4] support large domain sizes while maintaining high exciton splitting efficiencies. These increased domain sizes can lead to large reductions in bimolecular recombination [5, 6], further impacting the efficiency of devices. Lastly, I will discuss the relationship between the enhanced charge carrier dynamics seen in state-of-the-art non-fullerene organic solar cells [7] and improved exciton dynamics, enabled by the nano-morphology of the bulk heterojunction.

References:

[1] D. B. Riley, P. Meredith, A. Armin and O. J. Sandberg, "Role of Exciton Diffusion and Lifetime in Organic Solar Cells with a Low Energy Offset," *The Journal of Physical Chemistry Letters*, vol. 13, pp. 4402-4409., 2022. [2] P. Shaw, A. Ruseckas and I. Samuel, "Exciton diffusion measurements in poly (3-hexylthiophene)," *Advanced Materials*, vol. 20, no. 18, pp. 3516-3520, 2008. [3] Y. e. a. Firdaus, "Long-range exciton diffusion in molecular non-fullerene acceptors," *Nature communications*, vol. 11, no. 1, pp. 1-10, 2020. [4] D. B. Riley, O. J. Sandberg, W. Li, P. Meredith and A. Armin, "A quasi steady-state measurement of exciton diffusion in organic semiconductors," Submitted, 2021. [5] M. C. e. a. Heiber, "Encounter-limited charge-carrier recombination in phase-separated organic semiconductor blends," *Physical review letters*, vol. 114, no. 13, 2015. [6] A. Armin, J. Subbiah, M. Stolterfoht, S. Shoaee, Z. Xiao, S. Lu, D. J. Jones and M. P. , "Reduced recombination in high efficiency molecular nematic liquid crystalline: fullerene solar cells," *Advanced Energy Materials*, vol. 6, no. 22, 2016. [7] W. e. a. Li, "Organic solar cells with near-unity charge generation yield," *Energy Environmental Science*, vol. 14, no. 12, pp. 6484-6493, 2021.

Materials and Interfaces in Solid State Tandem Dye-sensitized Solar Cells

Tuesday, 18:45

Elizabeth Gibson
Newcastle University

One way of improving the efficiency of dye-sensitized solar cells is to use two photoelectrodes in a tandem device, one harvesting the high energy photons, and the other harvesting the low energy photons. This enables the photovoltage to be increased, whilst maximizing light harvesting across the solar spectrum. Despite their promise, a tandem cell with a higher efficiency than the state-of-the-art “Grätzel” cell has not yet been achieved. This is because the performances of photocathodes are significantly lower than TiO₂-based anodes, and the p-type concept has been largely unexplored since the first device was prepared in 1999. The small potential difference between the valence band of the NiO, p-type semiconductor, and the redox potential of the electrolyte and the faster charge-recombination reactions compared to the TiO₂ system limit the efficiency. In recent years, we have made progress by developing new photosensitizers. In parallel we have investigated the charge-transfer processes to determine the mechanism and limitations to efficiency. This has increased our understanding of the redox processes at the dye/electrolyte and NiO/electrolyte interfaces. The fundamental limitation of these devices arises from the NiO material itself and we have re-focussed our efforts on finding a replacement transparent p-type semiconductor. Finally, solid state charge-transport layers have been employed. This presentation will summarise our progress so far and challenges and opportunities for the future.

From Müser to Shockley-Queisser and beyond

Tom Markvart

Centre for Advanced Photovoltaics, Czech Technical University

”The advent of modern photovoltaics in early 1950s was soon followed by theoretical estimates of the maximum possible solar cell efficiencies. Several notable attempts emerged, not all equally remembered today. More than 60 years later, it seems appropriate to review progress in this field, with a view towards the next generation of solar cells. We shall discuss how thermodynamics can expand the Shockley-Queisser detailed balance framework, and provide a link to another popular limit, due to Trivich and Flinn. We shall also show how dusting off Müser’s view, bringing together photovoltaics with thermoelectricity, can point to new clues as to possible paths towards hot carrier solar cells.

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Generalization of Kirchhoff's Law: The inherent relations between quantum efficiency and emissivity:
 $\epsilon = \alpha(1 - \text{QE})$

Wednesday, 09:00

Carmel Rotschild

Technion Israel Institute of Technology

Planck's law of thermal radiation depends on the temperature, T , and the emissivity, ϵ , of a body, where emissivity is the coupling of heat to radiation that depends on both phonon-electron nonradiative interactions and electron-photon radiative interactions. Another property of a body is absorptivity, α , which only depends on the electron-photon radiative interactions. At thermodynamic equilibrium, nonradiative interactions are balanced, resulting in Kirchhoff's law of thermal radiation that equals these two properties, i.e., $\epsilon = \alpha$. For non-equilibrium, Quantum efficiency (QE) describes the statistics of photon emission, which like emissivity depends on both radiative and non-radiative interactions. Past generalized Planck's equation extends Kirchhoff's law out of equilibrium by scaling the emissivity with the pump-dependent chemical-potential μ , obscuring the relations between the body properties. Here we theoretically and experimentally demonstrate a prime equation relating these properties in the form of $\epsilon = \alpha(1 - \text{QE})$, which is in agreement with a recent universal modal radiation law for all thermal emitters. At equilibrium, these relations are reduced to Kirchhoff's law. In the presentation I will go over the analytic proof for the 2-level case, the numerical results for the 3-level case, and the experimental results on Er emission supporting our claims. Our work lays out the fundamental evolution of non-thermal emission with temperature (figure 1), which is critical for the development of lighting and energy devices.

Operando characterization of charge extraction and recombination profiles in solar cells with nanoscale resolution

Wednesday, 09:30

Gideon Segev

Tel Aviv University

The next generation of solar energy conversion systems requires design and integration of new semiconductor materials. Detailed understanding of the opto-electronic properties of these materials, their driving forces and the loss mechanisms that limit device performance is essential to the development of high efficiency systems. However, these materials and systems are difficult to model and only few experimental methods are available for direct characterization of dominant loss processes under relevant operating conditions. To this end, empirical extraction of the spatial collection efficiency (SCE) and the spatial external luminescence efficiency (SELE) are operando, analytical tools that provide functional depth profiles of the active regions in the device.

By coupling external quantum efficiency (EQE) measurements and optical modeling, SCE extraction allows quantifying charge transport properties and loss mechanisms across the device depth profile under real operating conditions with very few assumptions. Similar to SCE, combining optical modeling with wavelength dependent photoluminescence quantum yield (PLQY) measurements enables extracting the SELE - the probability that an electron hole pair photogenerated at a specific point will contribute to photoluminescence from the device. In this contribution we will introduce the SELE concept and will show a first demonstration of the SELE extraction method applied to GaAs samples. Extracting the SELE enables simple distinction between different losses such as surface recombination and self-absorption. The quantification of surface recombination losses makes this an excellent tool for characterizing the effect of surface passivation layers. Furthermore, since the PLQY is directly related to the obtainable photovoltage from the device, the SELE also maps the contribution of different regions in the device to the photovoltage. As a result, combining the SELE and SCE profiles at specific operating points provides detailed spatial information on charge extraction, contribution to the photovoltage, and discrimination between radiative and non-radiative recombination processes at the surface and in the bulk of the device.

Polaron transport and light-induced structural dynamics in BiVO_4 photoanodes

Wednesday, 10:30

Ian Sharp

Technical University of Munich

Monoclinic scheelite bismuth vanadate (BiVO_4) stands as one of the best performing thin film metal oxide photoanodes investigated to date. However, its desirable photoelectrochemical performance characteristics are surprising given the driving force for free charge carriers to self-trap as polarons. For the case of electrons, localization at vanadium sites leads to formation of small electron polarons with a large, thermally activated hopping barrier of several hundred meV. Likewise, for the case of holes, several experimental and theoretical studies have indicated polaron formation. However, significant uncertainties remain regarding the degree of hole localization, the associated structural configurations, and the transport barriers, despite the importance of photogenerated hole extraction for photoanode function. In this work, we present a combined study of polaron transport and recombination on the basis of temperature-dependent (photo)conductivity measurements and transient absorption spectroscopy. While excited states are characterized by large relaxation energies and transport barriers, long excited state lifetimes are also observed. In addition to localized effects associated with polaron formation, preliminary time resolved optical pump/X-ray diffraction probe experiments reveal long-range light-induced structural changes. These non-thermal structural dynamics are associated with increased symmetry and a partial relaxation of the monoclinic distortion within the BiO_8 dodecahedra of BiVO_4 , that play a key role in defining the active state of the illuminated material. Taken together, these observations provide important insights into light-to-chemical energy conversion processes in this promising photoanode material for future application in solar fuels generation.

Accurate prediction of electronic and optical excitations from density functional theory

Wednesday, 11:00

Leeor Kronik

Weizmann Institute of Science

Understanding and ultimately designing useful photovoltaic materials and structures requires an accurate and predictive calculation of their electronic and optical properties. Unfortunately, density functional theory (DFT), which is typically the workhorse of such quantum mechanical calculations, has traditionally struggled in the description of electron and optical excitations. Specifically, research has been fraught for decades with difficult questions as to the extent to which spectroscopic conclusions can be drawn from DFT even in principle, followed by serious concerns as to the reliability of typical DFT approximations in practice. In this lecture, I will explain what the difficulties are, introduce a novel approach to overcoming them rigorously in both the molecular and the solid state, show specific applications to modern photovoltaic materials, and finally discuss limitations and remaining challenges.

Quantifying Charge Extraction and Recombination Using the Rise and Decay of the Transient Photovoltage of Perovskite Solar Cells

Wednesday, 11:30

Thomas Kirchartz
Forschungszentrum Jülich

The efficiency of halide perovskite solar cells has been continuously rising over the past decade to values above 25%. Future technological development will have to deal with issues of device stability but also thrive to further minimize efficiency-limiting loss processes in the bulk and at interfaces within the cell stack. The identification and understanding of electrical losses will require the ability to characterize solar cells and multilayer stacks with a variety of steady-state, time-domain and frequency-domain techniques that are sensitive to the transport and recombination of charge carriers. Especially, time- and frequency-domain techniques offer a large amount of information on dynamic processes in the solar cell, while posing a substantial challenge in terms of the complexity of data analysis.[1]

Here, we show how to use relatively simple analytical solutions to systems of differential equations to extract the key performance-limiting parameters in halide perovskite solar cells from the rise and decay of the transient photovoltage in response to a laser pulse. The results combine the simplicity and comprehensibility of analytical equations with the multiplicity of physical phenomena that occur during a transient experiment on a perovskite solar cell. Transient experiments contain information on phenomena such as recombination and extraction of charge carriers that are difficult to disentangle from each other using traditional approaches.

Furthermore, capacitive charging and discharging of electrodes affects the rise and decay times of transients thereby adding complexity to the data analysis.[2, 3] We solve the problem by creating a numerical model, linearizing it around a bias condition and then solving it analytically by determining the eigenvalues of a 2×2 matrix. The model provides two time constants (the inverse eigenvalues), one for the rise and one for the decay of the voltage after the pulse. These two time constants can be experimentally determined as a function of light intensity. By comparison of model and experimental data, we can then derive a time constant for recombination and one for charge extraction, whereby the ratio of these two time constants is directly correlating with solar cell efficiency.

[1] L. Krückemeier, B. Krogmeier, Z. Liu, U. Rau, T. Kirchartz, *Advanced Energy Materials* 2021, 11, 2003489. [2] D. Kiermasch, A. Baumann, M. Fischer, V. Dyakonov, K. Tvingstedt, *Energy Environmental Science* 2018, 11, 629. [3] L. Krückemeier, Z. Liu, B. Krogmeier, U. Rau, T. Kirchartz, *Advanced Energy Materials* 2021, 11, 2102290.

Revealing Hidden Phases and Self-Healing in Antimony Trichalcogenides and Chalcogenides

Wednesday, 17:00

Eran Edri

Ben-Gurion University of the Negev

The prevalence of self-healing semiconductors is restricted to a few selected cases, which limits the understanding of the phenomenon. Herein, we report self-healing following photoinduced damage in antimony trichalcogenides and chalcogenides—quasi-one-dimensional semiconductors with prospective applications in photovoltaics and other electronic devices. We relate the self-healing to photoinduced phase transition (PIPT) and the ‘damaged’ state to a hidden phase from which the ‘damaged’ semiconductors recover (‘self-heal’). Using vibrational spectroscopy, we elucidated intermediate species in the reaction and reaction dynamics. The comparison of four different materials with a similar crystal structure enabled us to uncover the common structural feature that leads to self-healing in these materials. By analyzing the chemical bonding, we rationalize the chemical reaction and point at bonding states at the bottom of the conduction band as central origins in propelling the hidden phase. Expanding the type and number of self-healing materials, and uncovering the underlying solid-state reactions will facilitate the development of self-healing electronic building blocks for electronic devices.

SEMI-TRANSPARENT Sb_2S_3 SOLAR CELLS WITH FLUORENE-BASED ENAMINE AS HOLE TRANSPORT MATERIALS

Wednesday, 17:30

Nimish Juneja

Tallinn University of Technology

Antimony sulphide (Sb_2S_3) is a promising candidate for semi-transparent solar cells given its appropriate optoelectronic properties [1]. However, expensive hole transport materials (HTMs) are a hindrance in their large-scale commercialization [2]. In this study, we have tested four novel HTMs – V1235, V1236, V1275, and V1461 as an alternative to the conventionally used HTM – P3HT. These novel HTMs are being investigated for the first time in Sb_2S_3 solar cells. Compared to P3HT, fluorene –based enamines are significantly cheaper, optically transparent, and do not require an additional temperature activation. The solar cells are fabricated in glass/FTO/ TiO_2 / Sb_2S_3 /HTM/Au configurations, with TiO_2 and Sb_2S_3 deposited with ultrasonic spray pyrolysis. The as deposited amorphous Sb_2S_3 films are then crystallized by annealing them in N_2 at 260 C for 5 minutes. After that, the HTMs are deposited using spin coating. Thermal evaporation is then used to deposit the Au contacts. The morphological and opto-electronic properties of the fabricated solar cells are analyzed using SEM, UV-visible spectroscopy, current-voltage (IV) characteristics and External Quantum Efficiency (EQE) measurements. Ionization Energy of the functional layers are measured using photoelectron emission spectroscopy method. The energy diagram is analyzed to understand the band edge positions of the HTMs with respect to the absorber for a better understanding of device physics. Further, the impact of the concentration of variations of HTM solutions on the performance of Sb_2S_3 devices has been studied. The solar cells with fluorene unit linked HTMs have yielded higher conversion efficiencies than solar cells fabricated using P3HT. Furthermore, as compared to P3HT devices, the transparency of the solar cell stack with novel HTMs is enhanced by over 20%. The study demonstrates the successful fabrication of solar cells with cost-effective novel fluorene based HTMs in Sb_2S_3 solar cells for semi-transparent applications.

References 1. Versavel M.Y, et al. 2007, Thin Solid Films, 515(18):7171-71762 2. Messina S, et al. 2007, Thin Solid Films, 515(15):5777-5782

A hole transport layer for CIGS solar cells

Susanne Siebentritt

University of Luxembourg

All solar cells suffer from recombination at the metallic contacts. In Si solar cells this issue is solved by a back surface field and by the passivation of surfaces, with holes for the metallic contacts. In CIGS the front-side is rather well passivated by the electron transport layer (or buffer). But the backside is a full area Mo contact with a high recombination velocity. To mitigate back side recombination CIGS solar cells employ a composition gradient that leads to an increased band gap at the back side, which keeps electrons from recombining at the back contact. But this gradient leads to unnecessarily thick absorbers, increased radiative losses and shorter carrier lifetime due to additional non-radiative recombination. We introduce a novel hole transport layer for the back side of CIGS solar cells, that combines a thin CuGaSe₂ layer and an oxide stabilisation layer. Voc is increased by more than 60meV, without reductions in FF. The reduced back side recombination is also demonstrated by an increase in the carrier lifetime by more than a factor of 10.

Defect Healing and Defect Metrology of WSe₂ by Gate-Modulated Photoluminescence

Wednesday, 18:45

Doron Naveh
Bar-Ilan University

Defects in semiconductors have been at the focus of advanced materials research in the past century. Still, it is one of the most vibrant topics in materials research and particularly two-dimensional (2D) semiconductors. Spectroscopy and particularly photoluminescence is one of the main tools for inspecting 2D semiconductors, and in this work we have modulated the spectral measurements with a field effect potential in order to enhance the charge trapping and detrapping from point defects. By performing gate modulated spectroscopy we determined a lower bound for the intrinsic defect density of CVD grown ($6.010^{12} \text{cm}^{-2}$) and exfoliated ($1.310^{12} \text{cm}^{-2}$) WSe₂ samples. We demonstrated that a thin hBN buffer between the device and substrate eliminates hysteresis associated with injected holes. Additionally, we performed a chemical healing process which replaces the oxygen defects with sulfur via adsorption of thiol molecules in solution and trimming of the carbon chains using rapid thermal treatment. We confirmed the efficiency of process in eliminating vacancy defects by XPS, cryogenic photoluminescence and by gate-modulated photoluminescence. Lastly, we showed that the thermal detrapping process can be described as an activated reaction with an energy barrier of $153 \text{pm}97 \text{meV}$, which is an estimate for the defect states' electronic binding energy.

Surface defects can determine carrier densities of Pb-halide perovskite films

Thursday, 08:30

David Cahen and Antoine Kahn
Swansea University

Extrinsic electrical doping (controlled change of bulk carrier densities) of lead halide perovskites (HaPs), is problematic if done as for most semiconductors (SCs). We argue that while HaP doping follows that of Cu-In chalcopyrites, ZnO and other SCs, it is a kind of “turbo” version of such. Development of new SCs always has required meeting two strongly materials-related goals:

- clean the material from electrically active imperfections/impurities to a level of, say 10^{15} cm^{-3} or less, so as to controllably contaminate it with electrically active defects.
- passivate the surfaces so that the effect of -a- will not be swamped by uncontrolled surface effects, and to allow making interfaces that are manageable in terms of defect activity.

To put things in perspective, for Si $10^{15} \text{ cm}^{-3} \sim 0.01$ ppm and a few times that for CdTe or CuInSe₂. For MAPbI₃ $\sim 10^{15} \text{ cm}^{-3}$ corresponds to ~ 1 ppm (ppm is effectively [also] per formula unit). We assume that the bulk defect density of each crystallite, ignoring its surface, will be similar to that of bulk single crystals. Such densities were, for HaPs, deduced from various experiments to be close to or at the thermodynamic limit, 10^{11} cm^{-3} , using estimates for formation enthalpies of likely defects (halide vacancies are common villains). Thus, we need to reconcile the difference between densities of 10^{15} (average of 10^{13} - 10^{17} for polycrystalline films) and 10^{11} cm^{-3} . Here the demonstrated ability to effectively passivate surfaces of HaP polycrystalline films or nanoparticles enters and can be compared to the proven ability to control doping of polycrystalline chalcogenides via their surfaces. This leads to the assertion that if only 0.1% or even 0.005% (50 ppm) of the exposed surface sites are electrically active defect sites, that activity will suffice to have surface doping dominate totally a 10^{15} cm^{-3} volume carrier density of $0.5 \mu\text{m}$ diameter grained films, used in HaP-based PV and LEDs.

Coordination complexes and polymers for emerging molecular devices

Thursday, 09:00

Marina Freitag
Newcastle University

”Current emerging energy conversion (1) and storage technologies are constrained by inefficient and unstable charge transport materials.(2) Charge transfer limitations continue to be a barrier to wider implementation of this solar technology, and this study tackles this issue. Copper(II/I) coordination complexes (CCs) and polymers (CPs) are a novel family of charge transport materials composed of molecular building blocks.(3)

Recently, we demonstrated how dimerization of two-electron polymetallic redox shuttles enhances desirable charge transfer processes, such as Y123 photosensitizer regeneration, rather than charge recombination. Following this electron transfer and furthermore single oxidation of the dimers, our calculations indicate a dynamic transition to Cu(II) monomers through a disproportionation process, with the tetradentate ligands stabilizing the square-planar Cu(II) monomers. Even though their structures are distinctive, their reorganization energy is remarkably low. The 2-electron oxidation process of the Cu(I) dimer creates two Cu(II) monomers, thereby stabilizing both oxidation states. Because Cu(I) monomers are very energetically unfavored, recombination processes in dye-sensitized solar cells are substantially reduced.(4,5)

Also we introduced low-dimensional mixed-valence CPs as hole conducting material in hybrid solar cells. In this CPs CuII dithiocarbamate complexes control the morphology of 1D polymer chains connected by (CuI2X2) copper halide rhombi. The charge transport mechanism at the transition to band-like transport was revealed via combining theoretical and experimental efforts, with a modeled effective hole mass of 6 me. At ambient temperature, the iodide-bridged coordination polymer demonstrated high conductivity of 1 mS cm⁻¹ and hole mobility of 5.8 10⁻⁴ cm²(Vs)⁻¹.(3) Nanosecond photoluminescence of halide perovskite films recorded nanosecond selective hole injection into coordination polymer thin films. Coordination polymers are a long-term, tunable alternative to the existing standard of heavily doped organic hole conductors.

1 Muñoz-García, A. B. et al. *Chemical Society Reviews* 50, 12450–12550 (2021) 2 Morrith, G. H. et al. *Chemical Physics Reviews* 3, 011306 (2022) 3 Michaels, H. et al. *Journal of Materials Chemistry A* (2022) 4 Freitag, M. et al. *Nature Photonics* 11, 372–378 (2017) 5 Benesper, I. et al. *Chem* 8, 439–449 (2022) ”

Doping soft semiconductors: Opportunities and challenges

Thursday, 09:30

Pabitra Kumar Nayak

Tata Institute of Fundamental Research, Hyderabad

Semiconductors based on conjugated organic materials and halide perovskite materials are propelling low-cost optoelectronics forward. Electronic doping of these materials is required for broader applications. For electronic doping in organic materials, molecular and metal complex-based dopants are frequently used. However, the high costs and low doping efficiency, issue of by-products in this class of dopants necessitate alternative approaches. To that end, we have developed dimethyl sulfoxide adducts as an efficient and clean p-type dopant for a wide range of organic semiconductors. Because the byproducts leave the organic semiconductor thin film after doping, this adduct-based doping process produces clean p-type doping. We also demonstrate the use of this novel doping method in metal halide perovskite solar cells, organic thin-film transistors, and organic light-emitting diodes. We will also discuss the application of different types of perovskite and perovskite-like materials for optoelectronic and photo-electrochemical hydrogen production.

Single-particle heralded spectroscopy as a tool to reveal puzzling observations in perovskite NCs

Thursday, 10:30

Miri Kazes

The Weizmann institute of science

Single particle heralded spectroscopy combines the power of the temporal correlation of photon detections with an added information of spectral resolution. In this technique the photoluminescence of a single nanocrystal (NC) is collected through a spectrometer coupled to a single-photon avalanche diode (SPAD) array detector, so that each detected photon is time-stamped according to its arrival time, and energy-stamped according to the array pixel it was detected in. This technique was thus used to determine the controversy regarding the biexciton (BX) binding energy of CsPbBr₃ NCs by unambiguously resolving the BX and 1X emission spectra through post-selection of only photon pair cascades that follow the same excitation pulse. Currently, we extend the technique to the study of triexciton (TX) dynamics through the measurement of a third-order photon correlation. In addition, we aim at elucidating the underlying properties or processes that can lay in the basis of observed differences between CsPbBr₃ and FAPbBr₃ NCs such as the different degree of photon anti-bunching despite similar degree of quantum confinement or the different blinking statistics and try to correlate these with either intrinsic or surface related properties.

On the photostability of electron acceptor materials: from fullerene to non-fullerene acceptors

Cleber Marchiori

Karlstad University - Sweden

Organic photovoltaics (OPV) have reached power conversion efficiencies above 18% thanks to the outstanding performance of novel acceptor materials, often called non-fullerene acceptors (NFA) [1]. The operational lifetime of devices based on NFAs critically depends upon the photochemical stability of the materials and the film morphology. Through the years, lots of knowledge has been acquired on the photodegradation of fullerene derivatives, once considered a universal electron acceptor. For instance, it was shown that the photooxidative process of PCBM promotes the formation of dicarbonyl and anhydride structures on the C60 cage, leading to ring opening [2].

Given the diversity of NFAs available, it is difficult to establish a general description of their photodegradation mechanism as the different building blocks of those complex molecular acceptors can undergo different reactions when exposed to light in the presence of ambient air. Here we report the evolution of the optical properties and electronic structure of a set of NFAs during exposure to one-sun (AM1.5). In particular, we investigate the small-molecule acceptor Y5 [3], and its copolymer counterpart PF5-Y5 [4]. UV-Vis spectroscopy, Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and Near-edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy were employed to assess the thin film properties. The UV-Vis spectra reveal that the copolymer PF5-Y5 undergoes rapid photobleaching, while the spectrum of Y5 film remain, surprisingly, almost intact even after 30 hours of light exposure in air. New carbonyl peaks emerge in the FTIR spectra of PF5-Y5, but are absent in those of Y5, indicating that the bulk of the Y5 film is resistant to photooxidation, while the copolymer containing a Y5-moiety undergoes photochemical degradation reactions. The faster photodegradation of PF5-Y5 compared to Y5 raises the question about the role of the copolymer's BDT moiety in the photooxidation. However, the effect of film packing on the rate of degradation should also be considered. Angle-resolved NEXAFS spectra reveal a stronger linear dichroism in the spin-coated PF5-Y5 films compared to Y5 films, confirming a preferred orientation of the PF5-Y5 polymer backbone, while the random average orientation of Y5 molecules suggests a multi-crystalline Y5 film. These new insights on the effects of intentional photodegradation on donor and acceptor materials properties are a step forward on the understanding of the properties of NFAs, which can contribute to the design of more stable acceptors enabling the development of long-lived OPV devices.

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On the role of mid-gap trap states in organic (perovskite?) photovoltaic devices

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Organic semiconductor-based photovoltaic (OPV) devices have many advantageous properties including tailorable light absorption, low embodied energy manufacturing, structural conformality, and low material toxicity. Apart from solar cells, these properties also make OPVs attractive for applications such as indoor light-harvesting cells and photodetectors. A critical parameter limiting the performance of these diode devices is the dark saturation current which limits the open-circuit voltage of solar cells and the detectivity of photodetectors. For OPV devices, the dark saturation current is strongly limited by non-radiative processes resulting in dark saturation currents several orders of magnitude higher than expected for radiative band-to-band transitions; however, the origin of these non-radiative processes is still debated. Here, we show that the dark saturation current in OPVs is fundamentally mediated by mid-gap trap states. This new insight is generated by a universal trend observed for a large set of organic bulk heterojunction systems and substantiated by sensitive external quantum efficiency and temperature-dependent current measurements. These findings have important implications for OPVs, providing new insight into the origin of non-radiative losses in organic light-harvesting applications such as organic solar cells and photodiodes. Finally, we have also found indications that these results apply for perovskite-based photovoltaic devices as well.

Modelling light-induced charge-separation in photosystems to understand the limits to solar photochemical energy conversion

Thursday, 12:00

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Natural and artificial organic photosystems operate by the same principles. In both types of systems, the absorption of light, diffusion of excitons to locations where charge transfer can occur to electron accepting molecules, and subsequent charge separation and recombination, ultimately control the efficiency of conversion of light into chemical potential energy. However, differences in the structure of the two types of system give rise to different limiting factors. While in organic solar cells it is understood that most of the losses come from non-radiative charge recombination at the large interface between electron donating and electron accepting species, in natural photosystems charge separation and recombination are confined to a tiny reaction centre surrounded by tens or hundreds of light-absorbing pigments, and losses by non-radiative recombination appear to be a reduced route. On the other hand, in the case of photosystems, functionality may be limited, especially at high light intensities, by the kinetics of the sequence of charge transfer events.

In order to investigate photochemical energy conversion in photosystems and organic solar cells in an analogous way, we combine an interacting tight-binding Hamiltonian in an electron-hole basis that accounts for extended excitons and charge transfer states with a kinetic model. This allows to study how the chemical nature and position of pigments influence the free energy landscape, transition rates and ultimately the efficiency of energy conversion. As a first test of the framework we apply it to interpret spectroscopic data for novel versions of PSII that contain different coloured pigments, and show how it can help to define the structure of the photosystem. We also discuss how the approach might be applied to improve the design of artificial photosystems, such as molecular heterojunction devices.

Author Index

- Armin
Ardalan, 26
- Cahen
David, 38
- Cappel
Ute, 16
- de Mello Donega
Celso, 23
- Deibel
Carsten, 24
- Edri
Eran, 34
- Egger
David, 9
- Ehrler
Bruno, 11
- Freitag
Marina, 39
- Garcia Medranda
Daniel, 45
- Gibson
Elizabeth, 27
- Gottesman
Ronen, 20
- Hannappel
Thomas, 21
- Jaramillo
Rafael, 8
- Juneja
Nimish, 35
- Kahn
Antoine, 14
- Kazes
Miri, 41
- Kirchartz
Thomas, 33
- Koch
Norbert, 15
- Kronik
Leeor, 32
- Lifshitz
Efrat, 10
- Lips
Klaus, 22
- Marchiori
Cleber, 42
- Markvart
Tom, 28
- Muller
Jolanda, 25
- Naveh
Doron, 37
- Nayak
Pabitra Kumar, 40
- Olthof
Selina, 13
- Rotschild
Carmel, 29
- Sandberg
Oskar, 44
- Sarkar
Shaibal K, 12
- Schorr
Susan, 18
- Segev

Gideon, 30
Sharp
Ian, 31
Siebentritt
Susanne, 36

Vanmaekelbergh
Daniel, 17
Yaffe
Omer, 7