

## DS 30: Poster: Organic Thin Films and Thin Oxides

Time: Wednesday 15:00–18:00

Location: P1A

DS 30.1 Wed 15:00 P1A

**Optical and excitonic properties of molecular aggregates on dielectric surfaces** — FULU ZHENG<sup>1</sup>, XING GAO<sup>1,2</sup>, SIDHARTA NAYAK<sup>1</sup>, and ALEXANDER EISEFELD<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Strasse 38, D-01187 Dresden, Germany — <sup>2</sup>Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055, USA

Aggregates of fluorescent dye molecules on dielectric surfaces are of great interest for various technological applications. Due to strong interactions between the molecular transition dipoles, the excitonic eigenstates are coherently delocalized over many molecules [1]. These eigenstates and the corresponding optical transitions are determined by the molecular arrangement. We discuss the dependence of dark and bright states on the molecular arrangement and the spatial shape of the electromagnetic radiation used to probe the aggregate [2]. Strongly inhomogeneous fields can be generated via radiation from the apex of a metallic tip, which allows also scanning across the aggregate. Resulting spatially resolved spectra provide extensive information on the eigenenergies and wave functions [2, 3]. We also found that these delocalized eigenfunctions can be directly reconstructed from spatially resolved near field spectra using convolutional neural networks [3].

[1] A. Eisfeld, C. Marquardt, A. Paulheim, and M. Sokolowski, *Phys. Rev. Lett.* 119, 097402 (2017).

[2] X. Gao and A. Eisfeld, *J. Phys. Chem. Lett.* 9, 6003 (2018).

[3] F. Zheng, X. Gao and A. Eisfeld, *Phys. Rev. Lett.* 123, 163202 (2019).

DS 30.2 Wed 15:00 P1A

**Exploring charge transfer in a Protoporphyrin IX - Semiconductor Model System** — KEN LIM, FELIX ECKMANN, and MARTIN STUTZMANN — Walter Schottky Institut, Technische Universität München, 85748, Garching, Germany

Photocatalytic reduction of  $CO_2$  into carbon neutral solar fuels that can be easily stored are to date typically achieved by either homogeneous (in solution) or heterogeneous (on metal and semiconductors) catalysis techniques. This work investigates a simple model system of semiconductor substrates covered with Protoporphyrin IX (PPIX) monolayers in order to explore the possibility of combining heterogeneous and homogeneous catalysis approaches, benefiting from the advantages of both. To that end, PPIX monolayers were deposited onto various semiconductor substrates via the Langmuir-Blodgett process. Monolayer morphology was studied using atomic force microscopy revealing closely packed molecules on the surface with a tilted orientation. Fluorescence spectroscopy was used to evaluate the model system whereby quenching of monolayer fluorescence due to charge transport to the substrate suggests a decrease in efficiency for a photocatalytically reducing device. Our data shows a dependence of fluorescence peak position and intensity on the excitation wavelength and underlying substrate, especially when exciting at the Soret Band for AlN and GaN. Additionally, experiments with AlGaN substrates demonstrate a positive correlation between substrate bandgap and PL intensity, indicating fluorescence quenching due to electron transfer between excited S2 states and conduction band of the semiconductor.

DS 30.3 Wed 15:00 P1A

**Photoelectron spectroscopy on characterisation and phosphonic** — ADRIANA SALAZAR<sup>1,2</sup>, VALENTINA ROHNACHER<sup>1,2</sup>, MARKUS FRERICKS<sup>2,4</sup>, WOLFRAM JAEGERMANN<sup>4</sup>, and WOLFGANG KOWALSKY<sup>1,2,3</sup> — <sup>1</sup>Kirchhoff Institute for Physics, Uni Heidelberg, Germany — <sup>2</sup>InnovationLab, Heidelberg, Germany — <sup>3</sup>Institute for High-Frequency Technology, TU Braunschweig, Germany — <sup>4</sup>Materials Science Department, TU Darmstadt, Germany

Hole and electron transport layers (HTL /ETL) are necessary for stable and efficient perovskite solar cells (PSCs). Tin Oxide (SnOx) is a promising candidate as ETL due to its suiting electron affinity which leads to an excellent interface with the perovskite absorber material. Further, SnOx owns a high electron mobility, high transmittance and high chemical stability, essential criteria for efficient PSCs.

In these studies, solution processed tin oxide thin films were investigated. Using photoelectron spectroscopy different states of the thin film preparation could be investigated. Here, this surface sensitive technique allows for a chemical analysis while also providing

information about the electronic structure. To tune the work function and to reduce the surface reactivity, SnOx thin films were modified by self-assembled monolayers (SAMs) of 4'-(Dimethylamino)-3,5-difluoro-[1,1'-biphenyl]-4-yl)phosphonic acid (XFPA). Together with results from contact angle measurement, atomic force microscopy and infrared spectroscopy, a better understanding about the SAM formation and surface modification was achieved.

DS 30.4 Wed 15:00 P1A

**Nanoscale Polarization-Resolved Surface Photovoltage of a Pleochroic Squaraine Thin Film** — FRANK BALZER<sup>1</sup>, OLIYA S. ABDULLAEVA<sup>2</sup>, ANGELIKA MADERITSCH<sup>2</sup>, MATTHIAS SCHULZ<sup>3</sup>, ARNE LÜTZEN<sup>3</sup>, and MANUELA SCHIEK<sup>2</sup> — <sup>1</sup>University of Southern Denmark, Sønderborg, Denmark — <sup>2</sup>University of Oldenburg, Germany — <sup>3</sup>University of Bonn, Germany

Local polarized surface photovoltage (SPV) and UV-vis spectroscopy are used to characterize a squaraine:fullerene (SQIB:PCBM) photovoltaic layer blend, which has shown potential to act as neurostimulating platform. The molecular model squaraine donor material SQIB is known to crystallize into two polymorphs upon thermal annealing with distinct polycrystalline thin film texture. For the orthorhombic polymorph, the anisotropic optical response is dominated by the Davydov-split J-type absorption into an upper (UDC) and lower (LDC) Davydov component within the deep red. Kelvin probe force microscopy (KPFM) maps the differential SPV of the active layer on the nanoscale without complications by interfaces, which is spatially correlated with the pleochroic optical response of the thin film. The SPV shows a wavelength-dependent, bichromatic change upon rotating the polarization axis of the illuminating light. With that, subtler nanoscaled optoelectronic sensing platforms become possible.

DS 30.5 Wed 15:00 P1A

**Analyzing the Influence of Doped Organic Semiconductor Interlayers on the Electronic Structure of Intrinsic Hole Transport Materials** — MARKUS FRERICKS<sup>1,2</sup>, CHRISTOF PFLUMM<sup>3</sup>, ERIC MANKEL<sup>1,2</sup>, THOMAS MAYER<sup>1</sup>, and WOLFRAM JAEGERMANN<sup>1,2</sup> — <sup>1</sup>Technische Universität Darmstadt, Darmstadt — <sup>2</sup>InnovationLab GmbH, Heidelberg — <sup>3</sup>Merck KGaA, Darmstadt

The electronic structure at the interfaces of layered electronic devices plays an important role in understanding and improving device properties. In organic light emitting diodes, often a doped layer is placed between the contact and the transport layer to improve the charge injection. While the interface towards the contact is widely studied, less focus is laid on the influence on the intrinsic transport layer. We examined layer systems of doped and undoped hole transport materials. To analyze the electronic structure of the organic semiconductors, photoelectron spectroscopy is used. The organic layers are stepwise deposited by thermal evaporation in an ultra-high vacuum system. In between each deposition step the sample is measured. This allows for the study of the energy level evolution with increasing distance from the interface. The rather difficult interpretation of these organic-organic interfaces is supported by computer modeling. It is found, that the Fermi level position in the intrinsic layer is strongly influenced by the doped layer below. It lies about 1 eV lower compared to a sample without doped layer.

DS 30.6 Wed 15:00 P1A

**Sum-frequency generation vibrational spectroscopy of nHexadecanethiol on oxidised zinc** — ROBERT RAMEKER, DETLEF DIESING, and ECKART HASSELBRINK — Universität Duisburg-Essen, Universitätsstr. 5, 45141 Essen, Germany

Due to its interesting electronic properties, self-assembled organic monolayers are frequently investigated in semiconductor technology for the production of electrodes with tailor made electronic properties. Vibrational sum frequency spectroscopy (vSFS) is a powerful method for characterization of interfaces. From  $2800\text{ cm}^{-1}$  to  $3100\text{ cm}^{-1}$ , symmetric and antisymmetric vibrational modes of the methyl- and methylene groups were observed. Thermal and electrochemical methods were tried to make zinc oxide, which is a semiconductor with a band gap of 3.3 eV, from zinc by oxidation. A better vibronic signature of the adsorbed molecule is obtained for highly oxidised zinc substrates. X-ray photoelectron spectroscopy was used to quantify the

coverage with organic molecules and to gain information about the binding between the organic molecules and the metal oxide surface. For characterisation, electrochemical impedance spectroscopy (EIS) is an important method to analyze anticorrosion effects in different electrolytes.

DS 30.7 Wed 15:00 P1A

**Predicting Organic Thin-Film Structures with DFT and Machine Learning** — ●FABIO CALCINELLI and OLIVER T. HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria

The properties of a material depend on its structure, which for organic thin films often substantially differs from the bulk structure. A theoretical prediction of the most stable thin film structures through traditional, exhaustive first-principle studies is unfeasible due to the combinatorial explosion in the number of possible polymorphs.

The machine-learning based SAMPLE approach [1] can already circumvent this problem for monolayers, by using a few hundred DFT calculations to evaluate the energy of millions of polymorphs through Bayesian Linear Regression. It is our intention to extend the applicability of SAMPLE from monolayers to (meta)stable thin films.

As first step, we predict the best monolayers of a simple organic molecule on graphene, to verify SAMPLE's effectiveness in describing adsorption on organic substrates. Subsequently, we study thin film structures of pentacenequinone or -trone, for which experimental results are available. On this basis we develop a representation for intermolecular interactions in three dimensions and improve our methodologies for local optimization. With this functionality SAMPLE will provide valuable insight into the packing geometries of thin films and into the forces that drive their formation.

[1] Hörmann et al., Computer Physics Communications 244, 143-155, 2019

DS 30.8 Wed 15:00 P1A

**Self-assembled monolayers of triptycene tripods** — FUMITAKA ISHIWARI<sup>1</sup>, ERIC SAUTER<sup>2</sup>, GIULIA NASCIBENI<sup>3</sup>, HIROMU TAGO<sup>1</sup>, YOSHIKI SHOJI<sup>1</sup>, SHINTARO FUJII<sup>4</sup>, MANABU KIGUCHI<sup>4</sup>, TOMOFUMI TADA<sup>1</sup>, EGBERT ZOJER<sup>3</sup>, ●MICHAEL ZHARNIKOV<sup>2</sup>, and TAKANORI FUKUSHIMA<sup>1</sup> — <sup>1</sup>Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, Yokohama 226-8503, Japan — <sup>2</sup>Applied Physical Chemistry, Heidelberg University, Heidelberg 69120, Germany — <sup>3</sup>Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Graz 8010, Austria — <sup>4</sup>Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan

We designed 1,8,13-trimercaptomethyltriptycene (T1) and 1,8,13-trimercaptotriptycene (T2) as potential tripodal precursors for self-assembled monolayers (SAMs) and investigated their adsorption behavior on Au(111). Both SAMs adopt dense, nested hexagonal structures but differ in their adsorption configurations and structural uniformity. While the T2 SAM exhibits a low degree of order and noticeable deviation from the desired tripodal anchoring, all three anchoring groups of T1 are equally bonded to the surface as thiolates, resulting in an almost upright orientation of the benzene rings and large-area structural uniformity. These superior properties are attributed to the effect of conformationally flexible methylene linkers at the anchoring groups, absent in the case of T2. Since the triptycene framework can be functionalized by tail groups in various positions and with high degree of alignment, especially T1 appears as an ideal docking platform for complex and highly functional molecular films.

DS 30.9 Wed 15:00 P1A

**A novel approach for fabrication of photochromic organic thin films via initiated Chemical Vapor Deposition (iCVD)** — ●MAXIMILIAN HEIKO BURK<sup>1</sup>, STEFAN SCHRÖDER<sup>1</sup>, DANIEL LANGBEHN<sup>2</sup>, WIDUKIND MOORMANN<sup>2</sup>, THOMAS STRUNSKUS<sup>1</sup>, STEFAN REHDE<sup>1</sup>, RAINER HERGES<sup>2</sup>, and FRANZ FAUPEL<sup>1</sup> — <sup>1</sup>Christian-Albrechts University Kiel, Institute for Materials Science, Kaiserstr. 2, 24143 Kiel, Germany. — <sup>2</sup>Christian-Albrechts University Kiel, Otto-Diels-Institute for Organic Chemistry, Otto-Hahn-Platz 4, 24118 Kiel, Germany.

Initiated Chemical Vapor Deposition (iCVD) is a solvent-free, cost efficient technique to synthesize highly conformal organic thin films from the vapor phase. The underlying free radical polymerization can be specifically tuned by the deposition parameters and enables furthermore co-polymerization of manifold functional monomers.

In this work we demonstrate the first synthesis of photochromic organic thin films via iCVD deposition. The underlying concept is repre-

sented by sublimation of a solid photoswitchable styrenediazocine in a tailor-made steel unit and transportation into the reactor chamber via an inert carrier gas. The photochromic compound was co-polymerized with V3D3, a triple-functional cyclic compound to guarantee maximum rotational freedom of the azo-group after covalent bonding. Due to a high controllability of the uniform film formation, topography preservation and manifold choice of potential substrates it is possible to equip surfaces with photoswitchable properties in the nano-range without losing the characteristic properties of the material.

DS 30.10 Wed 15:00 P1A

**Preparation and characterisation of spin-coated TiO<sub>2</sub> thin films** — ●ANURAG PANDEY, SANDRA OMORAGBON, LU HE, TERESA MADEIRA, and DIETRICH R.T. ZAHN — Chemnitz University of Technology, Chemnitz, Germany

TiO<sub>2</sub> thin films were synthesized by the sol-gel method using titanium tetraisopropoxide (TTIP) as a precursor under basic conditions to promote formation of thin nanoparticle films. After preparation, the solutions were dried and aged by stirring for 24 hours at room temperature. The thin films were deposited by the spin coating technique with 500/1000/2000/3000/4000 rpm for t=30 seconds on intrinsic, n-doped, and p-doped silicon substrates. The various spin-coated samples were annealed for 2h each at different temperatures of 200, 300, 400, 500, 600, 700, and 800°C.

The TiO<sub>2</sub> thin films were characterised using mainly Raman and SEM for crystal phase determination, film thickness, surface and cross section homogeneity, and porosity. In this work we present and discuss the preliminary results obtained and conclude about the conditions that lead to the best photocatalytic performances of the prepared thin films.

DS 30.11 Wed 15:00 P1A

**Preparation of thin TiO<sub>2</sub> films by DC magnetron sputtering for photocatalytic applications** — ●OSADEBAMWEN SANDRA OMORAGBON, ANURAG PANDEY, LU HE, TERESA I. MADEIRA, and DIETRICH R. T. ZAHN — Semiconductor Physics, Chemnitz University of Technology, Reichenhainer Str. 70, 09126, Chemnitz, Germany

Fossil fuels have been massively burnt in order to keep up to the augmenting energy demands of the world. This has triggered the ever-increasing carbon dioxide (CO<sub>2</sub>) emission. Photocatalytic reduction of CO<sub>2</sub> into solar fuels and chemicals is a promising technology to contemporaneously curb the global warming and partially fulfill the energy requirements. Therefore, significant efforts are being put into the design and development of visible-responsive photocatalysts. Also TiO<sub>2</sub> thin films are promising in this application even though they harvest light only in the ultraviolet range of the solar spectrum [1].

Here we report on preliminary studies of TiO<sub>2</sub> thin films deposited on intrinsic, n-type and p-type silicon substrates by DC pulsed magnetron sputtering using a titanium metal target at room temperature and Ar and O<sub>2</sub> as working gases. Thin films were deposited with different O<sub>2</sub> gas flow rates (1, 3, 9, 12, 20 sccm) while keeping the Ar gas flow rate constant at 30 sccm. X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Raman Spectroscopy techniques were used to characterize the films. The main goal is to determine the conditions that lead to the best photocatalytic performance. [1] N. Shehzad, M. Tahir, K. Johari, T. Murugesan, A critical review on TiO<sub>2</sub> based photocatalytic CO<sub>2</sub>, J. CO<sub>2</sub> Util. 26 (2018) 98-122

DS 30.12 Wed 15:00 P1A

**Magnetism and Phonon Transport in (La<sub>0.6</sub>Pr<sub>0.4</sub>)<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> Thin Films** — ●KAREN P. STROH, VITALY BRUCHMANN-BAMBERG, DANIEL METTERNICH, HENNING ULRICH, and VASILY MOSHNYAGA — I. Physikalisches Institut, Georg-August-Universität Göttingen

Perovskite oxides represent an excellent example of correlated electron systems with strong coupling of electron, spin, and lattice degrees of freedom. They possess rich magnetic, electric, and structural phase diagrams. An example for this intriguing class of materials is the bandwidth-controlled and A-site-substituted manganite (La<sub>1-y</sub>Pr<sub>y</sub>)<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub> (LPCMO). Heteroepitaxial LPCMO thin films were prepared by metalorganic aerosol deposition (MAD) on MgO(100) substrates and were investigated by various local and global techniques with a focus on the magnetic properties.

LPCMO is characterised by relatively strong electron-phonon coupling (EPC) and is well known as a classical colossal magnetoresistance (CMR) material. Not only magnetism but also thermal transport in manganites is substantially influenced by contributions of the lattice including Jahn-Teller distortions mediating EPC. This involves the

question whether it may be used to manipulate thermal transport. Thermal conductivity in LPCMO films was studied by the  $3\omega$  technique and by means of transient thermal reflectance (TTR).

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DS 30.13 Wed 15:00 P1A

**Multiscale modeling of VCM-based ReRAMs** — •NILS SOMMER<sup>1</sup>, KRISTOF LANGE<sup>2</sup>, SOEKKI SON<sup>1</sup>, ALEXANDER ZURHELLE<sup>2</sup>, RAINER WASER<sup>1,2</sup>, and STEPHAN MENZEL<sup>1</sup> — <sup>1</sup>Peter Grünberg Institute (PGI-7), Forschungszentrum Jülich, Jülich, Germany — <sup>2</sup>Institute for Materials in Electrical Engineering II (IWE2), RWTH Aachen University, Aachen, Germany

Memristive elements enable the development of special, completely new hardware for neuromorphic systems. A promising class of memristive elements are redox-based resistive cells (ReRAMs), e.g. based on the valence change mechanism (VCM). In VCM cells, the primary switching mechanism is based on the movement of oxygen vacancies. However, the details of the switching process remain unclear. Our goal is to gain a deeper understanding of switching dynamics and limitations with a multiscale modeling approach. Using atomistic and con-

tinuous model simulations, we investigate the formation and dynamics of oxygen vacancies in the VCM cells as a function of the voltage, time, temperature and boundary effects such as oxygen exchange at the electrodes. Our results are the basis for physics based compact models that can be used for circuit designs.

DS 30.14 Wed 15:00 P1A

**Emergence of a surface 2DEG in Anatase (001) thin films** — •MARIUS FUCHS<sup>1</sup>, CHIARA BIGI<sup>2,3</sup>, ALESSANDRO TROGLIA<sup>2,3</sup>, PASQUALE ORGIANI<sup>2</sup>, JUN JUJII<sup>2</sup>, IVANA VOBORNIK<sup>2</sup>, GIANCARLO PANACCIONE<sup>2</sup>, GIORGIO ROSSI<sup>2,3</sup>, DOMENICO DI SANTE<sup>1</sup>, and GIORGIO SANGIOVANNI<sup>1</sup> — <sup>1</sup>Institut für Physik und Astrophysik, Universität Würzburg, 97074 Würzburg, Germany — <sup>2</sup>CNR-ION TASC laboratory, c/o Area Science Park - Basovizza, Strada Statale 14 km 163,5 - 34149 Trieste, Italy — <sup>3</sup>University of Milano, 20133 Milano, Italy

We report the emergence of a surface 2DEG in Anatase (001) thin films above a threshold thickness. DFT reveals the subsurface Ti dxy orbitals to nourish the 2DEG. The mechanism of formation is further analyzed by using Wannier functions. Additionally we investigate the phononic influence on the electronic dispersion.