

DS 3: Organic Thin Films

Time: Monday 15:00–19:30

Location: H 2032

Invited Talk

DS 3.1 Mon 15:00 H 2032

Thin film growth studies using time-resolved X-ray scattering — ●STEFAN KOWARIK — Institut für Physik, Newtonstr. 15, 12489 Berlin

Thin film growth inherently is a non-equilibrium process. This means that the route to the final film structure is determined not simply by a minimization of the free energy, but by a non-trivial competition between thermodynamics and kinetics. For a quantitative understanding one therefore needs information on the nanoscopic surface processes such as molecular binding as well as surface diffusion and step-edge crossing. In situ X-ray scattering is ideally suited for such measurements as it can be used to monitor temporal changes on the atomic scale. We show how real-time in situ Grazing Incidence Small Angle Scattering (GISAXS) can be combined with simultaneous X-ray reflectivity measurements to characterize both in-plane and out-of-plane film structure as a function of time. While GISAXS gives information on nucleation densities and island sizes, reflectivity measurements make it possible to extract the out-of-plane density profile so that both measurements together give a rather complete morphological characterization. We give examples for growth of small-molecule organic semiconductors such as C60, where we determine diffusion barrier, step edge barrier and binding energy, but the techniques are equally applicable to growth of atomic systems. S. Bommel, N. Kleppmann, C. Weber, H. Spranger, P. Schäfer, J. Novak, S.V. Roth, F. Schreiber, S.H.L. Klapp, S. Kowarik, "Unravelling the multilayer growth of the fullerene C60 in real-time", *Nature Communications* 5, 5388 (2014).

DS 3.2 Mon 15:30 H 2032

Epitaxial Growth of a Methoxy-Functionalized Quaterphenylene — ●FRANK BALZER¹, ROLAND RESEL², ARNE LÜTZEN³, HORST-GÜNTHER RUBAHN¹, and MANUELA SCHIEK⁴ — ¹MCI, NanoSyd, University of Southern Denmark, Alsion 2, DK-6400 Sønderborg, Denmark — ²Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria — ³University of Bonn, Kekulé Institute for Organic Chemistry and Biochemistry, Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany — ⁴University of Oldenburg, Energy and Semiconductor Research Laboratory, Institute of Physics, Carl-von-Ossietzky-Str. 9-11, D-26111 Oldenburg, Germany

Thin films from conjugated small molecule semiconductors are important building blocks for organic electronics. Functionalization can control their electrical and optical properties, but also change thin film morphology. Here the epitaxial growth of a methoxy functionalized *para*-quaterphenylene (MOP4) on alkali halides as well as on mica is investigated by a combination of low energy electron diffraction (LEED), polarized (confocal) light microscopy (PLM), atomic force microscopy (AFM), and X-ray diffraction (XRD). On both substrates a thin film phase is present, resulting however in different morphologies: On the alkali halides mainly islands from upright molecules form, whereas on mica clusters and nanofibers from lying molecules grow. LEED even detects an initial wetting layer on mica with a different structure. Especially the fibers show a specific polarization pattern of the emitted blue fluorescence. Clusters and fibers age via Ostwald ripening due to water vapor, resulting in a strong change of morphology.

DS 3.3 Mon 15:45 H 2032

Influencing the growth of *para*-sexiphenyl through chemical tuning — ●ANTON ZYKOV¹, MINO SPARENBERG¹, PAUL BEYER¹, LINUS PITHAN¹, CHRISTOPHER WEBER¹, YVES GARMSHAUSEN², FRANCESCO CARLÀ³, STEFAN HECHT², SYLKE BLUMSTENGEL¹, FRITZ HENNEBERGER¹, and STEFAN KOWARIK¹ — ¹Inst. f. Physik, Humboldt-Universität zu Berlin — ²Inst. f. Chemie, Humboldt-Universität zu Berlin — ³ESRF, Grenoble

We investigate the molecular growth of hybrid organic-inorganic semiconductor systems (HIOS) and show that chemical tuning can be used to optimize the growth mode [1]. We employ fluorination of *para*-sexiphenyl (6P) to drastically alter the growth mode from a rough three-dimensional towards a smooth, crystalline layer-by-layer growth as demanded for efficient opto-electronic devices with advanced properties. Our study combines *in situ* atomic force microscopy and *in situ* real-time X-ray scattering performed at the ID03 beamline at ESRF to monitor the evolution of the molecular thin film structure and morphology on non-polar ZnO (1010) substrates. In contrast to the parent

molecule 6P, we observe for the fluorinated 6P a suppression of the growth of a second crystal phase and an increased molecular diffusivity together with a lower Ehrlich-Schwoebel barrier. As a consequence the interlayer mass transport is increased, which leads to the observed improvement in growth-mode.

[1] M. Sparenberg*, A. Zykov*, P. Beyer, L. Pithan, C. Weber, Y. Garmshausen, F. Carlà, S. Hecht, S. Blumstengel, F. Henneberger and S. Kowarik. *Phys. Chem. Chem. Phys.*, 2014, **16**, 26084-26093.

DS 3.4 Mon 16:00 H 2032

Negative thermal expansion based on collective rotational motions of PTCDI-C8 in a crystalline organic thin film — ●SEBASTIAN BOMMEL^{1,2}, LINUS PITHAN², CHRISTOPHER WEBER², GONZALO SANTORO¹, STEPHAN V. ROTH¹, EDGAR WECKERT¹, and STEFAN KOWARIK² — ¹Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ²Institut für Physik, Humboldt-Universität zu Berlin, Germany

The understanding of the structure-function relationship in molecular thin films for the fabrication of advanced functional nano-materials is still challenging because molecules possess many conformational and rotational degrees of freedom. Here we report on temperature-dependent rotation of the organic semiconductor PTCDI-C8. Highly crystalline organic thin films have been investigated using Grazing Incidence X-ray Diffraction (GIXD), which enables us to determine the temperature-dependent unit cell and the arrangement of molecules within the unit cell. From fitting the intensities of the Bragg reflections at different temperatures we find that the tilt angle of the molecules changes continuously with temperature and does not exhibit hysteresis. A change in molecular tilt of 4° is observed for a 200 K temperature difference. This collective mechanical response of a molecular rotation is connected with a large negative thermal expansion coefficient of the *a*-axis within the thin film unit cell of -135 ppm/K. Such negative thermal expansion offers highly desirable properties for the design of thermo-mechanical devices such as actuators.

DS 3.5 Mon 16:15 H 2032

Shape anisotropy of organic thin films induced by ion-beam irradiated rippled substrates — ●MARKUS KRATZER¹, DOMINIK WRANA², KONRAD SZAJNA², FRANCISZEK KROK², and CHRISTIAN TEICHERT¹ — ¹Institute of Physics, Montanuniversität Leoben, Franz Josef Straße 18, 8700 Leoben, AUSTRIA — ²Institute of Physics, Jagiellonian University, Lojasiewicza 11, 30-348 Krakow, POLAND

Control over thin film growth morphologies of conjugated molecules is a key issue in organic electronics. Here, we investigated the growth of the organic semiconductor *para*-hexaphenyl (6P) on ion bombarded, rippled TiO₂(110) surfaces. Such substrates are highly anisotropic, representing one-dimensionally patterned templates with alternating ascending and descending step trains exhibiting typical step distances smaller 1 nm. 6P islands have been observed featuring clear shape anisotropy and discrete island widths according to the ripple wavelength. These observations are addressed to anisotropic detachment of molecules differently bound to the island rim at ascending and descending steps. A change of the average ripple length from ~11 nm to ~60 nm, resulted in a change of the average islands' length-to-width ratio from ~1.5:1 and ~4.5:1. In addition, strong diffusion anisotropy along and perpendicular to the ripples was found to be responsible for an increasing island density with decreasing ripple length.

15 min. break.

DS 3.6 Mon 16:45 H 2032

Thin film growth analysis of quinacridone on SiO₂ — ●BORIS SCHERWITZL and ADOLF WINKLER — Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria

Quinacridone (C₂₀H₁₂N₂O₂) is part of the group of H-bonded organic dyes with remarkable air stability and attractive semiconducting properties. The combination of inter- as well as intramolecular H-bonding with pi-pi stacking leads to highly crystalline film formations with unique charge transport behaviors. Understanding the initial growth, namely from the sub-monolayer regime up to a few layers, is a key factor in evaluating possible applications in future microelectronic devices. In this contribution, we report our recent efforts and studies

on the initial growth behavior of thin quinacridone films on a silicon dioxide substrate under UHV conditions with respect to sample treatment. After preparing and analyzing the substrate surface with Auger Electron Spectroscopy, thin films were created via physical vapor deposition from a Knudsen cell and subsequently analyzed with Thermal Desorption Spectroscopy, Atomic Force Microscopy and Raman Spectroscopy. Both sputter cleaned samples and samples with a carbon layer on top were investigated and yielded similar results. It could be shown, that quinacridone films tend to form bulk-like structures bound by strong hydrogen bonds, even at sub-monolayer coverages. Furthermore, a comparison between metal Knudsen cell and glass evaporation source deposition was made.

DS 3.7 Mon 17:00 H 2032

Interface dipole and growth mode of partially and fully fluorinated rubrene on Au(111) and Ag(111) — FALK ANGER¹, HENDRIK GLOWATZKI², ANTONI FRANCO-CAÑELLAS¹, CHRISTOPH BÜRKER¹, ●ALEXANDER GERLACH¹, REINHARD SCHOLZ³, YOUICHI SAKAMOTO⁴, TOSHIYASU SUZUKI⁴, NORBERT KOCH², and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany — ²Helmholtz-Zentrum für Materialien und Energie GmbH, Berlin, Germany — ³Institut für Angewandte Photophysik, TU Dresden, 01069 Dresden, Germany — ⁴Institute for Molecular Science, Myodaiji, Okazaki 444-8787, Japan

Thin films of fully and partially fluorinated rubrene deposited on Au(111) and Ag(111) were investigated using ultraviolet and X-ray photoelectron spectroscopy [1]. We demonstrate that fluorination of the molecules is an efficient way for tuning the metal-organic interface dipole and the hole injection barrier [2,3].

Moreover, the results indicate that the pronounced electrostatic dipole moment of partially fluorinated rubrene (F₁₄-Rub) has a strong impact on the growth mode of these molecules. Most notably, we infer that the first layer of F₁₄-Rub on Au(111) and Ag(111) is formed by molecules with alternating orientation of their dipole moments, whereas the second layer shows a nearly uniform orientation.

[1] F. Anger et al., submitted

[2] F. Anger et al., Appl. Phys. Lett. **102** (2013) 13308

[3] M. Kytka et al., J. Chem. Phys. **130** (2009) 214507

DS 3.8 Mon 17:15 H 2032

Small organic molecules for strongly coupled microcavities — ●FELIX LEMKE, VADIM LYSSENKO, and KARL LEO — Institut für Angewandte Photophysik, TU Dresden, Deutschland

Strongly coupled organic microcavities are a promising system to investigate exciton-polaritons. Due to their non-crystalline structure, the phonon-assisted relaxation to the $k = 0$ state is more probable than in inorganic microcavity systems. Even if organic materials are quite promising, small organic molecules showing strong coupling are very rare. The advantages are easier production procedures and long lifetimes.

An estimation of the usability for the investigated materials will be presented. Using absorption spectra and the Kramers-Kronig-Relation, the complex refractive index is calculated. By comparing these results with the cavity mode, already a first statement can be given. Further insight is gained with transfer matrix calculations. These calculations can also be used to optimise the coupling strength and therefore the splitting. The results are then compared to the measured data.

DS 3.9 Mon 17:30 H 2032

Magnetic transition metal phthalocyanine thin films: morphology, ordering, electronic structure and tuning of electronic properties via alkali metal doping — ●OLGA MOLODTSOVA¹, SERGEY BABENKOV¹, KARINA SCHULTE², VOLODYMYR MASLYUK³, INGRID MERTIG³, THOMAS BREDOW⁴, and VICTOR ARISTOV^{1,5,6} — ¹DESY Hamburg, Germany — ²MAX-lab Lund, Sweden — ³Uni Halle, Germany — ⁴Uni Bonn, Germany — ⁵Uni Hamburg, Germany — ⁶ISSP RAS, Russia

Magnetic transition metal phthalocyanines (MTM-Pc*s) are considered as materials for development of low dimensional molecular magnets, quantum computers and hybrid systems for memory devices. To make further progress in development such devices both the understanding and the tailoring of the physical, chemical and transport properties of the organic semiconductor components are required. The evolution of electronic structure of the MTM-Pc*s intrinsic and with potassium doping has been studied by means of photoemission spectroscopy, near-edge X-ray absorption fine structure and DFT calcu-

lations. The DFT calculations and detailed analysis of the core-level spectra permit us to suggest possible lattice sites for the potassium ions. The data disclosed filling of the lowest unoccupied molecular orbital upon doping and associated changes of the core level absorption spectra. None of the films prepared in our studies showed a finite electronic density of states at the Fermi level. Acknowledgements: This work was supported by the RFBR Grant No. 13 -02-00818 and the BMBF-Project No. 05K12GU2, PSP-Element No. U4606BMB1211

DS 3.10 Mon 17:45 H 2032

Cross-linking-induced disappearance of surface-enhanced Raman scattering in aromatic self-assembled monolayers — ●ANDRÉ BEYER¹, MARCEL MAINKA¹, XIANGHUI ZHANG¹, THOMAS HUSER², and ARMIN GÖLZHÄUSER¹ — ¹Physics of Supramolecular Systems, University of Bielefeld, 33615 Bielefeld, Germany — ²Biomolecular Photonics, University of Bielefeld, 33615 Bielefeld, Germany

Surface-enhanced Raman scattering (SERS) spectra from aromatic self-assembled monolayers (SAMs) were recorded with the assistance of gold nanoparticles in different geometries. SAMs on planar gold surfaces with gold nanoparticles on top as well as SAMs on gold nanoparticles yielded comparable spectra with high signal-to-noise ratios. The cross-linking of aromatic SAMs by electron exposure results in the formation of carbon nanomembranes (CNMs). We demonstrate the formation of CNM-shells due to electron exposure of SAM-covered gold nanoparticles. Surprisingly, no Raman scattering in the range between 200 – 3100 cm⁻¹ was detectable from any aromatic SAM after cross-linking in the different SERS detection geometries. This finding was supported by performing SERS measurements on CNM/SAM samples which yielded no signal from the CNM but an intense signal from the SAM. Implications, possible mechanisms, and potential applications of this effect will be discussed.

15 min. break.

DS 3.11 Mon 18:15 H 2032

High-speed confocal Raman imaging of carbon nanotubes — ●MICHAEL LUDEMANN, SUSANNE HARTMANN, ANNE-D. MÜLLER, and FALK MÜLLER — Anfatoc Instruments AG, Melanchthonstr. 28, D-08606 Oelsnitz (V)

Raman spectroscopy is a powerful tool in terms of chemical analysis and determination of physical properties. The ability of scanning the sample during a measurement provides an insight into these properties in a spatially resolved way by converting spectral features into color code images.

Due to a huge number of image points, Raman mapping is seriously affected by long acquisition times. A new Raman spectrometer is designed for excellent coupling to an atomic force microscope (AFM) with the focus of maximized light throughput. Here, the optimum compromise for a sufficiently high signal-to-noise ratio is achieved at 8 ms exposure time per pixel resulting in an image acquisition time of less than 3 minutes, even with a non-cooled CCD. Based on this development, high-speed Raman mapping measurements on carbon nanotube (CNT) bundles on a silver/glass substrate are presented.

Raman mapping of single CNTs enables to distinguish between different types of CNTs. The spatial distribution of the CNT bundles and hot spot induced surface enhanced Raman spectroscopy (SERS) will be presented, as well.

DS 3.12 Mon 18:30 H 2032

Fast IR laser mapping ellipsometry for the study of functional organic thin films — ●ANDREAS FURCHNER¹, GUOQUANG SUN¹, HELGE KETELSEN², JÖRG RAPPICH³, and KARSTEN HINRICHS¹ — ¹Leibniz-Institut für Analytische Wissenschaften – ISAS – e. V., Schwarzschildstraße 8, 12489 Berlin, Germany — ²SENTECH Instruments GmbH, Schwarzschildstraße 2, 12489 Berlin, Germany — ³Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institut für Silizium-Photovoltaik, Kekuléstraße 5, 12489 Berlin, Germany

The infrared spectral range provides information about the structural and chemical properties of functional organic thin films. The need to characterize these properties with high lateral resolution in short measurements times requires a new generation of infrared ellipsometer. A novel laboratory-based infrared laser mapping ellipsometer is presented that allows for measurements with lateral resolutions of 0.12 mm and time resolutions down to 80 ms per spot. The ellipsometer is applied for the optical characterization of inhomogeneous

poly(3-hexylthiophene) and poly(*N*-isopropylacrylamide) organic thin films used for opto-electronics and bioapplications.

DS 3.13 Mon 18:45 H 2032

Characterization of advanced biomaterials for the medical device industry using Synchrotron Radiation-based FTIR microspectroscopy and X-Ray spectroscopic techniques — ●ANDREA HORNEMANN¹, BEATRIX POLLAKOWSKI¹, BONNIE TYLER², GERALD HOLZLECHNER³, ANNA BELU⁴, ARNE HOEHL¹, and BURKHARD BECKHOFF¹ — ¹Physikalisch-Technische Bundesanstalt, Berlin, Germany — ²National Physics Laboratory, London, United Kingdom — ³BAM Federal Institute of Materials Research and -Testing, Berlin, Germany — ⁴Medtronic, Minneapolis, U.S.A.

Since its early development implantable medical devices had tremendous impact on the quality of life. But still today many implants cause inflammations due to incompatibility with human tissues or due to device related infections. Hence, there is a need for exploring new advanced biomaterials that comprise thin film coatings, surface grafted biomolecules, nanoparticle coatings, drug-eluting films, and especially bioresorbable components. Reliable metrological tools for the rapid characterization of medical devices are essential to probe their physicochemical properties. Both vacuum-based and ambient techniques, represented here by X-ray and FTIR spectroscopic techniques, allow for a characterization of surface layers, contaminants on the surface of medical devices in the manufacturing environment, and enable the detection of defects and chemical constituents in the near-surface region. The measurement sequences exhibit the potential of the use of orthogonal methods as FTIR and X-ray spectrometry to significantly contribute to the traceable and reliable characterization of medical devices.

DS 3.14 Mon 19:00 H 2032

Molecular Orientations in Photochromic Layers on Silicon(111) Investigated by X-ray Absorption Spectroscopy — ●DANIEL PRZYREMBEL¹, MICHAEL ÅXMAN PETERSEN^{2,3}, ANDREAS HEBERT², KAROLA RÜCK-BRAUN², CORNELIUS GAHL¹, and MARTIN WEINELT¹ — ¹Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ²Department of Organic Chemistry, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany — ³Department of Chemistry, Danmarks

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Fulgimides are a class of photochromic molecular switches that undergo ring closing and opening upon illumination with UV and visible light, respectively.[1] When coupled to self-assembled monolayers (SAMs) of suitable anchoring molecules they retain the ability to reversibly isomerize and show photostationary states dominated by either a ring-opened *E/Z* mixture or the ring-closed form.[2] We have investigated individual preparation steps towards as well as the resulting densely packed SAMs of a fulgimide on Si(111) single crystal surfaces by X-ray absorption spectroscopy. From the polarization-dependent contrast of the near edge X-ray absorption fine structure (NEXAFS) we deduced mean molecular orientations with respect to the sample surface and we evaluated the changes induced by UV illumination.

[1] Y. Yokoyama *Chem. Rev.* **2000**, *100*, 1717-1739.

[2] K. Rück-Braun, M. Å. Petersen, F. Michalik *et al. Langmuir* **2013**, *29*, 11758-11769.

DS 3.15 Mon 19:15 H 2032

Nucleation of Vaterite-Phase Calcium Carbonate by Poly Glutamic Acid Peptides on Gold — ●HAO LU, MATTHEW A. HOOD, RAFAEL MUÑOZ-ESPÍ, MISCHA BONN, and TOBIAS WEIDNER — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Nature uses proteins and peptides containing acidic residues to control the crystal structure of polymorph materials such as calcium carbonate. Among the three most typical anhydrous polymorphs - calcite, aragonite and vaterite - the latter is the most thermodynamically unstable phase, and occurs rarely as biomineral. However, the vaterite structure can be stabilized in vitro by the presence of soluble biomolecules. Previous studies have focused on nucleation in the solution phase. Here we demonstrate interfacial nucleation: vaterite can be stabilized by specifically designed peptides bound to inorganic substrates. As a model system, we used a thiol-terminated poly glutamic acid sequences attached to a gold surface. The data show that the adsorbed peptides act as effective templates for the crystallization of a vaterite film. Using several complementary surface analytical techniques we follow structural changes of the peptide structure induced by the crystallization, which provides molecular-level insights into the biomineralization process of calcium carbonate.