DS 25: Symposium: Real Time Growth Studies III

Time: Thursday 15:00-18:30

Invited TalkDS 25.1Thu 15:00H32Pentacene thin film growth — •GEORGE MALLIARAS — CornellUniversity, Ithaca, NY, USA

Organic thin film transistors (OTFTs) are being developed in academic and industrial labs for "disposable" plastic electronics such as radio-frequency identification tags. Among the most promising organic semiconductors is pentacene, which yields transistors with performance similar to that of amorphous silicon. The interfaces of pentacene films with dielectric materials (gate oxide) and conductors (electrodes) play a major role in determining OTFT performance. X-ray scattering has proved to be superb tool for the study of crystalline organic films such as pentacene. My talk will focus on the interface of pentacene films with dielectric materials. Recent studies of growth of pentacene films on silicon oxide has revealed interesting new physics: For example, layer-by-layer growth can be obtained despite the fact that the interaction of pentacene with itself is stronger that that with the substrate. I will discuss our current understanding of how the kinetics of growth affects film morphology. A second topic that will be overviewed is the evolution of structure of organic films with film thickness. As organics are highly polymorphic, they usually adopt a *thin-film* phase at the substrate, with the bulk phase not seen until film thickness has exceeded a certain thickness. I will show that the nucleation of the bulk phase begins at the substrate, but it remains undetected due to the fact that bulk crystallites scatter incoherently. Implications of this phase co-existence on the electrical properties of organic films will be discussed.

DS 25.2 Thu 15:45 H32 Real-time and in-situ study of organic semiconductor growth: using X-ray growth oscillations beyond the anti-Bragg point — •STEFAN KOWARIK^{1,2}, ALEXANDER GERLACH^{1,2}, STEFAN SELLNER¹, FRANK SCHREIBER¹, LEIDE CAVALCANTI³, and OLEG KONOVALOV³ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany — ²Physical and Theoretical Chemistry Laboratory, University of Oxford, Oxford OX1 3QZ, United Kingdom — ³ESRF, 6 Rue Jules Horowitz, Boîte Postale 220, 38043 Grenoble Cedex 9, France

In-situ and real-time X-ray scattering experiments during organic molecular beam deposition (OMBD) have been performed at the ESRF. Using an optimised setup and the high X-ray photon flux at a synchrotron, we show that a wide region in reciprocal space (i.e. many Fourier components of the real-space structure) can be monitored in real-time. In particular we manage to simultaneously acquire X-ray growth oscillations not only at the anti-Bragg condition but in a broad q-interval and in particular at the 2/3, 3/4, 4/5 etc. Bragg points. We will also discuss a simplified scheme for direct data analysis. The real-time measurements allow studying the growth kinetics of organic semiconductors such as pentacene, perfluoropentacene, and dindenoperylene in great detail. We find marked transitions from layer-by-layer growth to roughening, changes in molecular orientation during the growth process, as well as transient strain [1].

[1] S. Kowarik, et al. PRL 96, 125504 (2006).

DS 25.3 Thu 16:00 H32 **Real-Time Observation of Organic Growth on metals** - a SMART Investigation — •PIERRE LEVESQUE¹, HELDER MARCHETTO¹, ULLRICH GROH², FLORIAN MAIER², THOMAS SCHMIDT², RAINER FINK³, TOMÁŠ SKÁLA¹, EBERHARD UMBACH², and HAJO FREUND¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany — ²Universität Würzburg, Experimentelle Physik II, 97074 Würzburg, Germany — ³Universität Erlangen-Nürnberg, Physikalische Chemie II, 91058 Erlangen, Germany

The growth of two similar molecules - PTCDA and NTCDA - on Ag(111) and Au(111) surfaces has been studied in situ by the SMART, using PEEM with UV-light and polarized monoenergetic synchrotron radiation and LEEM. Above room temperature both systems grow in the Stranski-Krastanov mode: first two closed layers of molecules are formed, followed by three dimensional (3D) growths of islands. Strong differences are observed in the molecular orientations: whereas the PTCDA molecules are always flat-lying on the substrate, the NTCDA behaves differently: the molecules are also flat-lying in the double layer but tilted by about 45° in the islands. We report on surprising ob-

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servations like reduced sticking coefficient, metastable layers, internal crystal structures, and dynamic changes within the layers. Differences in the growth and the temperature dependence of the two systems are discussed. Contrast mechanisms leading to the presented results will also be addressed. Project funded by BMBF under contract no. 05 KS4WWB/4.

Invited TalkDS 25.4Thu 16:15H32Growth, Interface Formation and Electron Dynamics of Pen-
tacene Thin Films — •FRANK MEYER ZU HERINGDORF — Univer-
sität Duisburg-Essen, Lotharstrasse 1, 47048
 Duisburg

Pentacene has attracted significant attention lately, as it is an extremely promising candidate for organic field effect transistors in organic displays and radio frequency identification (RFID) tags. We studied the growth and interface formation of Pentacene on various Si surfaces. The initial interaction between the molecule and the substrate is covalent and the molecules are forced to "lie down" on the substrate. Subsequent layers stand upright on top of this flat lying layer and exhibit a fractal shape. As the flat layer remains between the interface and the standing-up molecules, it shields the film from the surface. Consequently, the growth behaviour is independent of the orientation, reconstruction or symmetry of the initial Si surface. The combination of PEEM with pulsed fs-laser sources allows the observation of the decay of electronic excitations in the films with spatial resolution via two photon photoemission. Here, a first photon is used to generate an excitation in the film, while a second photon initiates photoemission. The time-delay between the two (pump- and probe-) photons then allows observation of the decay of the excited intermediate state. The change in the molecular orientation between the initial layer and the fractal islands is also reflected in the decay of electronic excitations in the thin films.

DS 25.5 Thu 17:00 H32 Real-time growth investigations by means of reflectance difference spectroscopy — •MICHAEL HOHAGE, LIDONG SUN, RICHARD DENK, GÜNTHER WEIDLINGER, JOSE MANUEL FLORES-CAMACHO, and PETER ZEPPENFELD — Institut für Experimentalphysik, Johannes Kepler Universität Linz, A-4040 Linz, Austria

Reflectance difference spectroscopy (RDS) has been proven to be a versatile tool to study growth processes on crystalline substrates in-situ and in real-time. RDS measures the difference in the reflectivity of light polarized along two orthogonal directions. Since RDS uses light with normal incidence, it measures the in-plane anisotropy of a sample. For crystals with cubic symmetry the bulk is not contributing to the optical anisotropy, so that the RDS signal is only introduced by an anisotropic surface. The growth on an anisotropic substrate may influence the optical anisotropy signal either by changing the anisotropy of intrinsic surface transitions (e.g. scattering of surface states), by modifying substrate transitions due to anisotropic strain fields beneath the growing structures, or by introducing specific transitions of the deposited material (e.g. HOMO-LUMO transitions of orientated organic molecules). Simultaneously to the investigation of the morphology, the out of plane magnetization of a growing film may be studied by RDS via the polar magneto-optical Kerr effect (MOKE). The capabilities of RDS regarding the real-time investigation of growth will be demonstrated by introducing growth systems where the mentioned effects have been identified.

DS 25.6 Thu 17:15 H32 Optical Spectroscopy of Ultrathin Stacked Nanolayers Grown by Multiple Organic Heteroepitaxy — •ROMAN FORKER¹, THOMAS DIENEL¹, KLAUS MÜLLEN², and TORSTEN FRITZ¹ — ¹Institut für Angewandte Photophysik, TU Dresden, 01062 Dresden, Germany — ²MPI für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

Highly ordered quaterrylene (QT) films in the (sub-) monolayer regime were examined by means of differential reflectance spectroscopy (DRS) while being epitaxially deposited on various substrates. This *in situ* technique provides unsurpassed sensitivity for the thickness-dependent optical analysis *during* film growth. From the DR spectra, the optical constants were extracted using a novel numerical algorithm [1]. Rather broad and structureless spectra were obtained on Au(111). This behaviour changes drastically by depositing a closed monolayer of hexabenzocoronene (HBC) on the Au(111) surface before growing the QT film on top: Well-resolved QT-monomers become visible up to one QT-monolayer, followed by a physical monomer-dimer transition [2, 3] indicated by the appearance of isosbestic points in the spectra. The results are discussed in terms of the different molecular orbital hybridization on Au(111) and on HBC. Structural characterization was done by means of STM and LEED showing closed layers of flat lying molecules.

[1] R. Nitsche et al., Phys. Rev. B 70 (2004), 195432.

- [2] H. Proehl et al., Phys. Rev. Lett. 93 (2004), 097403.
- [3] H. Proehl et al., Phys. Rev. B 71 (2005), 165207.

Invited Talk

DS 25.7 Thu 17:30 H32 Charge Injection across Self-Assembly Monolayers in Organic Field Effect Transistors: Odd-Even Effects - • FABIO

BISCARINI¹, PABLO STOLIAR¹, RAJENDRA KSHIRSAGAR¹, MASSIMILIANO MASSI¹, PAOLO ANNIBALE¹, CRISTIANO ALBONETTI¹, and DAGO DE $LEEUW^2 - {}^1CNR$ -Istituto per lo Studio dei Materiali Nanostrutturati, Bologna, Italy — ²Philips Research Labs, Eindhoven, The Netherlands

We investigate the role of self-assembly monolayers of chain length n, with n ranging between 3 and 18, in modulating the charge injection in pentacene field effect transistors.

The charge carrier mobility exhibits large fluctuations correlated with odd-even n. For n < 8, increases by one order of magnitude. For n > 8, charge mobility decays exponentially with an inverse decay length $\beta = 0.6 \, \mathring{A}^{-1}$.

Charge injection across the interface occurs by tunneling of holes mediated by the alkanethiol layer. At short chain length, decreasing of both interfacial morphological disorder and pentacene-surface interactions dominates over the increasing thickness of the alkanethiol monolayer. At long chain length, the charge injection across the alkanethiol monolayer governs the transistor response.

The odd-even effect is ascribed to the anisotropic coupling between the alkanethiol terminal sigma bond and the HOMO level of ordered pentacene molecules. Our results show that the pentacene transistor is a sensitive gauge for probing charge transport across single monolavers.

DS 25.8 Thu 18:15 H32

In- situ measurements to analyze the intermolecular coupling and film growth of organic semiconductor thin films •DERCK SCHLETTWEIN, CHRISTIAN KELTING, HARRY BRINKMANN, $\operatorname{Wilfried}$ Michaelis, and Karsten Hesse — Institut für Angewandte Physik, Justus-Liebig-Universität Gießen, 35392 Gießen

Intermolecular coupling of electronic pi-systems in thin films of organic semiconductors is of fundamental relevance for both the understanding of physical characteristics and their utilization in electronic devices. Optical absorbance is well- suited to probe them already during film growth, in particular when backed up by electron diffraction studies. Subtle changes in the film structure can be detected in changes of the observed band splitting. Thin films of modified phthalocyanines are a good example since spectra could already be obtained in the monolayer thickness range. Also, the average orientation relative to the substrate surface was extracted from relative intensities and the conclusions are supported by independent measurements of (ex-situ) spectral ellipsometry [1]. Aside from intermolecular coupling but not independent from it, microscopic growth characteristics of the films are of high relevance for technical applications. Measurements of the electrical conduction during film growth turned out very useful to discuss the formation of conduction pathways and hence the growth mode of films. Thus we could distinguish between layer vs. island growth. In a number of cases we observed the formation of ultrathin conductive channels in the monolayer range, interesting for technical application. [1] cooperation with the group of D.R.T. Zahn, TU Chemnitz.