

## DS 20: Focussed Session: In-situ optical spectroscopy

Time: Wednesday 9:30–13:00

Location: H 0111

**Invited Talk** DS 20.1 Wed 9:30 H 0111  
**Differential Optical Spectroscopy for Surface Science** — ●PETER ZEPPENFELD — Institut für Experimentalphysik, Johannes Kepler Universität Linz, Austria

Conceptually very simple optical methods, namely Reflectance Difference Spectroscopy (RDS/RAS) and Differential Reflectance Spectroscopy (DRS), can provide valuable insight into the structure and growth of ultrathin films in straight correlation with their electronic, optical and other physical or chemical properties. Notably, differential optical spectroscopies can achieve sub-monolayer sensitivity and are capable of monitoring kinetic processes on surfaces in real time. This will be illustrated in selected examples dealing with the fabrication and optical characterization of functional layers, such as reconstructed surfaces [1,2], graphene nanoribbons [3], and ultrathin molecular films [4,5]. While the spatial resolution in the UV-VIS range is naturally limited, microscopic information on the structure and electronic properties can be obtained with complementary surface science techniques such as STM and Photoemission Electron Microscopy (PEEM). As an outlook, I will describe how optical spectroscopy and PEEM can be combined into a single experiment, thus enabling truly parallel optical and photoelectron spectroscopy at a local scale.

- [1] L.D. Sun et al., Phys. Rev. B 69, 045407 (2004)
- [2] M. Bachmann et al., Appl. Surf. Sci. 258, 10123 (2012)
- [3] R. Denk et al., Nat. Commun. 5:4253 (2014)
- [4] L.D. Sun et al., Phys. Chem. Chem. Phys. 14, 13651 (2012)
- [5] L.D. Sun et al., Phys. Rev. Lett. 110, 106101 (2013)

**Invited Talk** DS 20.2 Wed 10:00 H 0111  
**In situ Raman monitoring of Potassium intercalation in Manganese Phthalocyanine** — ●OVIDIU D. GORDAN<sup>1</sup>, MICHAEL LUDEMANN<sup>1,2</sup>, FRANZISKA LÜTTICH<sup>1</sup>, DMYTRO SOLONENKO<sup>1</sup>, PHILIPP SCHÄFER<sup>1</sup>, and DIETRICH R.T. ZAHN<sup>1</sup> — <sup>1</sup>Semiconductor Physics, Technische Universität Chemnitz, D-09107 Chemnitz — <sup>2</sup>now at Anface Instruments AG, D-08606 Oelsnitz (V)

Charge redistribution in the molecular orbitals of organic molecules can be used to adjust their optical, electrical, and magnetical properties. In the case of metal phthalocyanines (MPc) this can be done by e.g. potassium intercalation. However, the effects of additional charges on the molecule geometry and the corresponding rearrangement of the molecular orbitals as well as the question whether the charge is electrically active or not are theoretically hard to predict. The entire picture gets more complicated by the formation and coexistence of several charged states between the organic molecule and dopant. Here the intercalation process is studied by *in situ* Raman monitoring. The corresponding Raman spectra reveal extremely strong changes when ultra-thin layers of MnPc prepared by organic molecular beam deposition in ultra-high vacuum are exposed to potassium. These changes can directly be related to the formation of distinct charged phases. The results presented thus beautifully illustrate that *in situ* Raman spectroscopy is a powerful tool for monitoring the dynamics of the intercalation process. Moreover, using organic field effect structures in the Raman experiment the different charged stages can be related to changes in the conductivity.

**Invited Talk** DS 20.3 Wed 10:30 H 0111  
**Infrared surface and interface studies - vibrational analysis and beyond** — ●ANNEMARIE PUCCI — Kirchhoff-Institut für Physik der Universität Heidelberg

Various excitations can be studied in the infrared, vibrational spectra, low-energetic electron transitions, and plasmonic behaviour. With careful referencing, such excitations can be observed also on surfaces and in ultrathin layers. The excitation spectra deliver information on the atomic level and, furthermore, on collective behaviour. In the talk examples for ultra-high vacuum studies will be presented, for example, charge transfer at organic-inorganic interfaces and plasmonic excitations in low-dimensional systems.

**Invited Talk** DS 20.4 Wed 11:00 H 0111  
**Correlation of IR spectra with thin film structure at solid-water interfaces** — ●KARSTEN HINRICHS — Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., 12489 Berlin, Germany

A crucial point for infrared characterizations at solid/liquid interfaces

in electrochemistry, polymer science and biosensing is the understanding of spectra-structure correlations. Optical layer calculations are required for quantitative conclusions on the structure from measured infrared spectra, in particular in the range of water vibrational bands. For infrared measurements of thin films in a flow cell spectroscopic ellipsometry was adapted. Exemplarily the stimuli-responsive properties of polymer brushes will be discussed, e. g. swelling degree, water content, and molecular interactions and dissociation of functional groups within an ultrathin polymer layer as well as the pH- and temperature-responsive adsorption and desorption of proteins. Current work is related to reduce the needed volume of liquids by use of microfluidic cells, to increase the lateral resolution by infrared microscopy, to enhance the detection limit by nano/microstructured substrates and to complement the optical layer simulations by optical calculations (e.g. using rigorous coupled-wave analysis (RCWA), finite-difference time-domain method (FDTD)).

**Invited Talk** DS 20.5 Wed 11:30 H 0111  
**In-situ characterization of electronic materials by optical second-harmonic generation** — ●MICHAEL DOWNER — University of Texas at Austin, USA

Optical second-harmonic generation (SHG) uniquely enables sensitive, noninvasive, in-situ monitoring of centrosymmetry-breaking features of electronic materials, including surface and buried interface discontinuities, and bulk strain gradients and other bond distortions. I will describe several emerging applications of SHG that exploit these unique diagnostic capabilities, and that can be implemented with a compact, single-wavelength femtosecond light source. These include sub-micron imaging of anti-phase boundary defects in GaAs films on Si substrates, detection of "improper" ferroelectricity in advanced double-perovskite materials, detection of strain gradients in 3D integrated circuit structures, and non-spectroscopic fingerprinting of surface bonds during epitaxial film growth. Tunable femtosecond light sources add spectroscopic capability to SHG. I will describe applications of spectroscopic SHG to measurement of band offsets of ultrathin high-K dielectric films with silicon substrates, and to the characterization of unique bond structures at the interfaces of silicon nanocrystals.

DS 20.6 Wed 12:00 H 0111  
**Microfluidic cells in IR-microscopy for biosensing** — ●CHRISTOPH KRATZ<sup>1</sup>, TOM W. H. OATES<sup>1</sup>, DIRK JANASEK<sup>2</sup>, and KARSTEN HINRICHS<sup>1</sup> — <sup>1</sup>Leibniz-Institut für Analytische Wissenschaften -ISAS- e.V., 12489 Berlin, Germany — <sup>2</sup>Leibniz-Institut für Analytische Wissenschaften -ISAS- e.V., 44139 Dortmund, Germany

A novel flow cell platform system for investigations of solid/liquid-interfaces combining expertise in the fields of in situ IR-spectroscopy, enhancement substrates and microfluidics will be presented.

The versatile investigation technique of in situ IR spectroscopy which has been applied in various studies of technologically relevant thin films as e.g. smart polymer brushes will be supported by surface enhanced methods (surface enhanced infrared absorption, SEIRA) to increase sensitivity for biosensing. The high potential of the presented technique lies in a label-free investigation with the possibility e.g. to monitor chemical and structural changes of molecules and proteins via the interpretation of absorption bands of specific molecular vibrations using adequate optical.

DS 20.7 Wed 12:15 H 0111  
**in-situ-ATR-FTIR characterization of thin films deposited from dopamine solutions** — ●MARTIN MÜLLER<sup>1,2</sup> and BIRGIT URBAN<sup>1</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, — <sup>2</sup>Technische Universität Dresden, 01062 Dresden, Germany

in-situ-ATR-FTIR data on reactive deposition of catecholamines like dopamine (DA) at model surfaces aiming at structure and deposition mechanism of such bioinspired melanin like films are presented. The process initially observed by Lee is related to mussel adhesion via L-DOPA rich proteins and caused by a sequence of reaction steps suggesting transformation of DA into indole like moieties followed by polymerization to PDA. An ATR-FTIR pseudo-double-beam device and a thermostatable homebuilt flow cell were used. Germanium (Ge)

internal reflection elements (IRE) were contacted with DA solutions allowing presence or absence of oxygen to certain degree. DA deposition was followed in dependence of either time or concentration. Via significant increases of characteristic IR bands from phenolic and aromatic species the formation of thin PDA films (SFM: 50 nm) at Ge could be followed in-situ. These bands revealed similar thermodynamic and kinetic adsorption behavior with rate constants of  $k=0.013 \text{ min}^{-1}$ . The comparison of ATR-FTIR and transmission-FTIR data on PDA films, on the blackish PDA phase above and on original melanin suggested, that surface and bulk phase initiated PDA material is different. Furthermore, application oriented studies revealed sustained release of model drugs and low protein adsorption at PDA films.

DS 20.8 Wed 12:30 H 0111

**Correlation Between Structure and Optical Properties in Organic Mixtures: A Real-Time Study During Thin Film Growth** — ●ALEXANDER HINDERHOFER, KATHARINA BROCH, ALEXANDER GERLACH, CHRISTOPHER LORCH, JOHANNES DIETERLE, JIŘÍ NOVÁK, and FRANK SCHREIBER — Universität Tübingen, Institut für Angewandte Physik, Auf der Morgenstelle 10, 72076 Tübingen

An understanding of the structure-property relation in binary blends of organic semiconductors is relevant for device optimization as well as for fundamental research [1]. Due to transient effects, post growth studies are often not sufficient for a detailed characterization of these complex systems [2,3]. Using grazing incidence X-ray diffraction simultaneously with optical spectroscopy techniques we follow the growth of binary blends of perfluoropentacene and diindenoperylene in situ and in real-time. Comparing the results obtained for the different mixing ratios, we find significant differences in the structure formation during growth of the mixed films as well as pronounced transient effects in the absorption spectra. We discuss these observations in the context

of the competing effects of favorable intermolecular interaction and steric incompatibilities [4].

[1] A. Hinderhofer and F. Schreiber, *ChemPhysChem* 13, (2012), [2] U. Heinemeyer et al., *Phys. Rev. Lett.* 104, (2010), [3] R. Forcker and T. Fritz, *Phys. Chem. Chem. Phys.* 11, (2009), [4] K. Broch et al., *J. Chem. Phys.* 139, (2013).

DS 20.9 Wed 12:45 H 0111

**Space and Time Resolved Transmission Spectroscopy of Tungsten Oxide Thin Films** — ●SIMON BURKHARDT, SABRINA DARMAWI, MATTHIAS T. ELM, and PETER J. KLAR — I. Physikalisches Institut, Justus-Liebig-Universität, Heinrich-Buff-Ring 16, 35392 Gießen

Tungsten-IV oxide ( $\text{WO}_3$ ) is of great interest for numerous applications due to its electrochromic behavior, where the intercalation of ions results in a change of the optical properties. Although the electrochromism of  $\text{WO}_3$  has been studied intensively during the last decades, the details of the ion intercalation mechanism and the corresponding coloration are still under discussion. In order to provide some new insights,  $\text{WO}_3$  thin films were investigated by a combination of electrochemical and optical measurement techniques. The thin films were obtained by the depositions of  $\text{WO}_3$  powder onto TCO-coated glass substrates via electron beam evaporation. Using transmission spectroscopy the coloration was monitored during the intercalation of hydrogen ions. The results obtained are correlated with structural changes of the thin films during the intercalation, which were investigated using XPS and XRD. Furthermore, similar measurements on laterally patterned  $\text{WO}_3$  thin films are presented, which were performed in order to investigate and simulate the diffusion of the ions during the intercalation process.