Location: H 0111

# DS 18: Optical Analysis of Thin Films (Reflection, Ellipsometry, Raman, IR-DUV Spectroscopy, ...): Session I

Time: Wednesday 9:30–13:00

Invited Talk DS 18.1 Wed 9:30 H 0111 Infrared nanopolarimetric analysis of structure and anisotropy of thin films — •KARSTEN HINRICHS and TIMUR SHAYKHUTDINOV — Leibniz-Institut für Analytische Wissenschaften -ISAS e.V., Schwarzschildstr. 8, 12489 Berlin, Germany

IR spectroscopic techniques can deliver simultaneously high chemical and structural contrast, be coupled with optical models and numerical calculations and typically are non-destructive and label-free. In this contribution recent progress and perspectives in IR spectroscopic nanopolarimetric analysis (30 nm resolution) using an extended version of a photothermal IR nanoscopy (AFM-IR) technique are presented. In particular, several highly sensitive polarization dependent nanoscale studies of anisotropic thin film materials, as polymer, protein and polaritonic films as well as supramolecular aggregates are discussed.[1-4]

[1] T. Shaykhutdinov et al, Supramolecular Orientation in Anisotropic Assemblies by Infrared Nanopolarimetry, ACS Macro Lett. 2017. 6: 598-602.

[2] K. Hinrichs et al, Electrochemical Modification of Large Area Graphene and Characterization by Vibrational Spectroscopy, in K. Wandelt (ed.), Encyclopedia of Interfacial Chemistry, Elsevier (2018).

[3] T. Shaykhutdinov et al, Mid-infrared nanospectroscopy of Berreman mode and epsilon-near-zero local field confinement in thin films, Opt. Mater. Express 2017. 7: 3706-3714.

[4] F. Rösicke et al, Functionalization of any substrate using covalently modified large area CVD graphene, Chem. Comm. 2017. 53: 9308-9311.

### 15 min. break.

DS 18.2 Wed 10:15 H 0111

Investigation on the electric-field-induced switching effect of copper-tetrathianoquinodimethane by polarized Raman spectroscopy — ●YANLONG XING<sup>1</sup>, EUGEN SPEISER<sup>1</sup>, PETRA S. DITTRICH<sup>2</sup>, and NORBERT ESSER<sup>1</sup> — <sup>1</sup>Leibniz-Institut für Analytische Wissenschaften - ISAS - e. V, 12489 Berlin, Germany — <sup>2</sup>Department of Biosystems Science and Engineering, ETH Zurich, CH-4058, Basel, Switzerland

Copper-tetrathianoquinodimethane (Cu-TCNQ) is a kind of important material due to its electric-field-induced reversible switching characteristics in conductivity. However, there is still inconsistency in reported studies regarding the switching effect: one proposed mechanism is the phase/composition changes (from phase II to phase I or between charged and neutral TCNQ molecules); the other mechanism is the Schottky contact between Al electrodes and Cu-TCNQ. To clarify this issue, we performed polarized Raman measurement on Cu-TCNQ crystals upon applying electric field by using a microdevice with Pt electrodes.

The rotational polarized Raman spectra showed the different crytal structures of the two phases of Cu-TCNQ (I and II). When applying an electric field to Cu-TCNQ wire (phase I), only after a threshold voltage, electron transfer between TCNQ0 and TCNQ- could be observed by the Raman signal of TCNQ0. A quantitative study on the Raman intensity and conductivity of Cu-TCNQ was under investigation, as well as the crystal structure changes of Cu-TCNQ.

#### DS 18.3 Wed 10:30 H 0111

Infrared spectroscopic ellipsometry of trapezoidal SiO2 columns and protein coated lamellar gratings — •CORDULA WALDER<sup>1</sup>, ANDREAS FURCHNER<sup>1</sup>, MATTHIAS ZELLMEIER<sup>2</sup>, JÖRG RAPPICH<sup>2</sup>, HELGE KETELSEN<sup>3</sup>, and KARSTEN HINRICHS<sup>1</sup> — <sup>1</sup>Leibniz Institut für Analytische Wissenschaften ISAS e.V., Schwarzschildstraße 8, 12489 Berlin — <sup>2</sup>Helmholtz Zentrum Berlin für Materialien und Energie GmbH, Institut für Silizium Photovoltaik, Kekuléstraße 5, 12489 Berlin — <sup>3</sup>SENTECH Instruments GmbH, Schwarzschildstraße 2, 12489 Berlin

The in-situ ellipsometric characterization of structured surfaces is interesting for applications like light management in solar cells, biotemplates and biosensors. In this work we aim to enhance the understanding of the results for periodic micrometer-sized structures in the infrared spectral regime where the vibrational fingerprints of the investigated materials become visible. Two-dimensional SiO2 trapezoidal columns on silicon with periods from 10 to 20 um in both lateral directions were characterized. The infrared Müllermatrix spectra of these samples were modelled by RCWA for different azimuth angles of sample rotation. Simulations show that the off-diagonal Müllermatrix elements can be particularly sensitive to changes of the lengths of the trapezoids and the azimuth angle. As an example for a structured biohybrid interface SiO2 line gratings on silicon wafers were coated with monolayers of human serum albumin (HSA protein). Analysis of the ellipsometric spectra delivered structural properties as well as the vibrational bands of the nanometer-thin protein layer.

DS 18.4 Wed 10:45 H 0111 Raman spectroscopy study of lattice and electron dynamics in a SIIrO<sub>3</sub> film — •KAUSHIK SEN, KAI KLEINDIENST, DIRK FUCHS, KARSTEN WOLF, ROLF HEID, and MATTHIEU LE TACON — Institute for Solid State Physics, Karlsruhe Institute of Technology, Karlsruhe, Germany

SrIrO<sub>3</sub> has been proposed as a candidate to realize the so-called 'topological insulator' phase due to its strong spin-orbit coupling  $(0.4 \,\mathrm{eV})$ and electron-electron correlations (0.5 eV). The narrow bands and their extreme sensitivity to the rotations of IrO<sub>6</sub>-octahedra place the compound close to a metal-insulator transition. This has motivated us to investigate the lattice dynamics of these systems, which potentially plays an important role in conductivity. We report the lattice and electron dynamics in a 60 nm thick SrIrO<sub>3</sub> film using Raman scattering experiments as a function of temperature and light polarizations. With confocal Raman spectroscopy, we measured the temperature dependence of phonons modes with  $A_g$  and  $B_{2g}$  symmetries. Corresponding atomic displacements are assigned with the help of firstprinciple lattice dynamics calculations. Finally, an electronic continuum could directly be evident. We particularly focus our attention on the anomalous temperature dependence of the frequency of the  $B_{2g}$ phonon around  $390 \,\mathrm{cm}^{-1}$  (arises from the rotation of  $\mathrm{IrO}_{6}$ -octahedra, which is out-of-phase along the direction of c-axis). This indicates an anomalous phonon hardening below 50 K, which deviates from the expected anharmonic phonon decay. It further displays a strong Fano asymmetry attesting the coupling of this mode to the underlying continuum.

DS 18.5 Wed 11:00 H 0111 **Polarization dependent photoluminescence and Raman spec troscopy of single III-nitride nanowires** — •MAXIMILIAN RIES<sup>1,2</sup>, PASCAL HILLE<sup>3</sup>, JÖRG SCHÖRMANN<sup>3</sup>, EUGEN SPEISER<sup>2</sup>, MAR-TIN EICKHOFF<sup>3,4</sup>, and NORBERT ESSER<sup>1,2</sup> — <sup>1</sup>School of Analytical Sciences Adlershof (SALSA), Albert-Einstein-Strasse 5-9, 12489 Berlin — <sup>2</sup>Leibniz Institut für Analytische Wissenschaften - ISAS e.V., Schwarzschildstrasse 8, 12489 Berlin — <sup>3</sup>Physikalisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 16, 35392 Giessen — <sup>4</sup>Institute of Solid State Physics, University of Bremen, Otto-Hahn-Allee NW1, 28359 Bremen

Modern LEDs are frequently made of III-nitride structures, with applications ranging from lightning, optoelectronics to life sciences and health care. To allow excellent performance, complex heterostructures and nanostructures must be fabricated with high precision. Recently, III-nitride nanowires have been employed in sensor devices due to their high surface-to-volume ratio, tunable optical properties and the possibility for surface functionalization. These devices are usually based on arrays of vertically aligned nanowires grown along the c-axis. To suppress ensemble effects and understand the impact of parameters such as alloy composition and morphology on optical properties, we performed polarization dependent measurements of photoluminescence and Raman spectroscopy on single III-nitride nanowires. Combined with transmission and scanning electron microscopy experiments we investigated the nature of defect luminescence and alloy inhomogeneity.

DS 18.6 Wed 11:15 H 0111 In-situ Monitoring of Lateral Hydrogen Diffusion in Amorphous and Polycrystalline Tungsten Trioxide Thin Films — •SIMON BURKHARDT<sup>1,2</sup>, MATTHIAS T. ELM<sup>1,2,3</sup>, BERNHARD LANI-  $\rm WAYDA^4,$  and PETER J.  $\rm KLAR^{1,2}-^1Institute$  of Experimental Physics I, Heinrich-Buff-Ring 16, 35392 Gießen, Germany —  $^2Center$  for Materials Research (LaMa), Heinrich-Buff-Ring 16, 35392 Gießen, Germany —  $^3Institute$  of Physical Chemistry, Heinrich-Buff-Ring 17, 35392 Gießen, Germany —  $^4Mathematical$ Institute, Arndtstrasse 2, 35392 Gießen, Germany

Tungsten trioxide  $(WO_3)$  thin films show remarkable changes of their optical properties upon reversible ion insertion making them essential components in electrochromic devices. The development of such devices demands a fundamental understanding of charge carrier transport in WO<sub>3</sub>. In-situ transmission spectroscopy during locally confined electrochemical hydrogen insertion is used to investigate the lateral diffusion of hydrogen inside amorphous and polycrystalline WO<sub>3</sub> thin films. The absorbance of WO<sub>3</sub> thin films is resolved spatially and temporally at a wavelength of  $(637 \pm 15)$  nm. The results reveal concentration-dependent diffusion processes in both, amorphous and polycrystalline WO<sub>3</sub>. By comparing experimental data with numerical simulations, the dependence of the diffusion coefficient on the hydrogen concentration is investigated. Although amorphous WO<sub>3</sub> thin films are known for their faster coloration kinetics, the diffusivity of hydrogen in polycrystalline  $WO_3$  is found to exceed the diffusivity of hydrogen in amorphous  $WO_3$ .

#### 15 min. break.

physik, WWU Münster

DS 18.7 Wed 11:45 H 0111 A condensed Krypton conversion electron source with ellipsometry monitoring for the KATRIN experiment — •STEPHAN DYBA FOR THE KATRIN-COLLABORATION — Institut für Kern-

The KATRIN (KArlsruhe TRItium Neutrino) experiment will perform an ultra-precise measurement of the endpoint region of the energy spectrum of electrons from tritium  $\beta$ -decay to determine the neutrino mass with a sensitivity of 0.2 eV (90% C.L.). To achieve the required accuracy, the kinetic energy of the decay electrons is measured using a MAC-E filter type spectrometer. To characterize the transmission properties of the KATRIN main spectrometer a movable calibration source has been constructed, using mono-energetic conversion electrons from the decay of the <sup>83m</sup>Kr isomer as a natural standard. For this purpose the radioactive krypton atoms from a <sup>83</sup>Rb generator are frozen onto a HOPG substrate at a temperature below 30 K. This Condensed Krypton Source (CKrS) uses sub-monolayer film thicknesses to provide decay electrons with a narrow line width and stable line position. The substrate is prepared by heating and laser ablation. The substrate with the sub-monolayer <sup>83m</sup>Kr and condensing residual gas are monitored using PCSA type ellipsometry, where analyzer and the light detector are directly mounted near to the substrate under ultra-high vacuum in the cold environment. The whole system is movable to allow to freely position the source within the magnetic fluxtube of the experiment.

This project is supported by BMBF, contract number 05A11PM2.

## DS 18.8 Wed 12:00 H 0111

Electron capture by Sn polaron in Kesterite solar cells — •SUNGHYUN KIM<sup>1</sup>, JI-SANG PARK<sup>1</sup>, and ARON WALSH<sup>1,2</sup> — <sup>1</sup>Thomas Young Centre and Department of Materials, Imperial College London, London, United Kingdom — <sup>2</sup>Department of Materials Science and Engineering, Younsei University, Seoul, Republic of Korea

The kesterite mineral, such as Cu2ZnSnS4 (CZTS), has attracted much attention as a replacement of the commercial Cu(In,Ga)S2 light absorber, consisting of only earth-abundant elements, and thus has the potential to support a Terawatt photovoltaic industry. Non-radiative carrier recombination is the likely origin of large open-circuit voltage deficit which is the primary bottleneck for achieving efficient kesterite solar cells. We have performed first-principles calculations within the framework of density functional theory to search for killer recombination centers in CZTS. The sulfur vacancy in CZTS is electrically benign not producing any donor levels in the band gap. However, we find that the sulfur vacancy can act as an efficient non-radiative site with the aid of an intermediate state involving Sn polaron formation. We point out that trap-assisted recombination does not necessarily accompany

a charge transition level deep in the band gap of a semiconductor.

DS 18.9 Wed 12:15 H 0111 Electroreflectance and photoluminescence of Cu2(Zn1x,Cdx)SnS4 thin film solar cells — •Segiu Levcenco<sup>1</sup> SHREYASH HADKE<sup>2</sup>, LYDIA HELENA WONG<sup>2</sup>, and THOMAS UNOLD<sup>1</sup> <sup>1</sup>Helmholtz Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner Platz 1, 14109 Berlin, Germany — <sup>2</sup>Energy Research Institute @ NTU Nanyang Technological University 637553, Singapore Although Cu2(Zn1-x,Cdx)SnS4 (CZCTS)- absorber layers have demonstrated efficiency of 11.5% in thin film solar cells devices their optical and defect properties are not investigated sufficiently. For instance, the band gap in these materials is often derived from the external quantum efficiency measurements and different reports have provided band gaps that vary for similar compositions of CZCTS. In this work we employ the electroreflectance (ER) and photoluminescence (PL) techniques for characterizing CZCTS devices. The effects of Cd content and Cu/(Zn+Sn) cations ratio on the electronic transitions are investigated. In the near band edge region the ER spectra provide distinct derivative like structures corresponding to transitions near the critical points of the dielectric function, which are used to evaluate the band gap transition energies. In addition, a defect recombination with transition energy in the range of 1.1-1.3 eV has been resolved in PL spectra.

DS 18.10 Wed 12:30 H 0111 Two-Dimensional Optical Transport Measurements in CuInGaSe<sub>2</sub> by Highly Spatially, Spectrally, and Time Resolved Cathodoluminescence Microscopy — •MATHIAS MÜLLER<sup>1</sup>, TORSTEN HÖLSCHER<sup>2</sup>, MATTHIAS MAIBERG<sup>2</sup>, FRANK BERTRAM<sup>1</sup>, ROLAND SCHEER<sup>2</sup>, and JÜRGEN CHRISTEN<sup>1</sup> — <sup>1</sup>Institute of Experimental Physics, Otto-von-Guericke-University Magdeburg, Germany — <sup>2</sup>FG Photovoltaik, Martin-Luther-University Halle-Wittenberg, Germany

To gain a deeper understanding regarding transport of carriers and the influence of inhomegenieties, highly spatially, spectrally, and time resolved cathodoluminescence (CL) measurements have been performed on polycrystalline CuInGaSe<sub>2</sub> (CIGSe) with varying Cu/III-ratios (CGI: 0.8 and 0.87). For this purpose, one-dimensional and twodimensional optical transport measurements are compared, and performed to determine lateral carrier diffusion lengths. The samples are etched with bromine-methanol to smoothen the surface for further processing. 220 nm thick Ti masks of different shapes are applied via photolithography. One-dimensional measurements are carried out in CL-linescans perpendicular to the mask's edge. In a second step for the two-dimensional measurements, the sample is excited by the pulsed e-beam in the center of circular apertures in the Ti-mask with diameters ranging from  $2.5\,\mu\text{m}$  to  $50\,\mu\text{m}$ . Both methods lead to concurrent low temperature (T = 5 K) diffusion lengths of ca. 20  $\mu$ m. Furthermore, a strong spatial dependence of the carrier lifetime is revealed with lifetimes ranging from 17 ns to 50 ns over only a few  $\mu$ m.

 $\begin{array}{c} {\rm DS} \ 18.11 \quad {\rm Wed} \ 12:45 \quad H \ 0111 \\ {\rm Investigating} \ \ {\rm the} \ \ {\rm exitonic} \ \ {\rm interactions} \ \ {\rm by} \ \ {\rm polarization-resolved spectro-microscopy of a textured squaraine thin film} \\ - \ {\rm \bullet Dominik} \ \ {\rm H\ddot{o}weling^1, \ Luca \ Beverina^2, \ Christoph \ Lienau^1, \ Martin \ Silies^1, \ {\rm and} \ \ {\rm Manuela \ Schiek^1 \ - \ }^1 {\rm Institute} \ \ {\rm of \ Physics, \ University \ of \ Oldenburg, \ Germany \ - \ }^2 {\rm University \ of \ Milano-Bicocca, \ Milano, \ Italy \ \ {\rm otherwise} \ \ {\rm otherwise} \ \ {\rm otherwise \ Schiek \ - \ }^2 {\rm University \ of \ Milano-Bicocca, \ Milano, \ Italy \ \ {\rm otherwise \ Schiek \ - \ }^2 {\rm University \ of \ Milano-Bicocca, \ Milano, \ Milano, \ {\rm Italy} \ \ {\rm otherwise \ - \ }^2 {\rm University \ of \ Milano-Bicocca, \ Milano, \ {\rm Italy} \ \ {\rm otherwise \ - \ }^2 {\rm University \ of \ Milano-Bicocca, \ Milano, \ {\rm Italy} \ \ {\rm otherwise \ - \ }^2 {\rm University \ of \ Milano-Bicocca, \ Milano-Bicocca, \ Milano-Bicocca, \ {\rm Milano-Bicocca, \ Milano-Bicocca, \ Milano-Bicocca, \ Milano-Bicocca, \ {\rm Milano-Bicocca, \ Milano-Bicocca, \ {\rm Milano-Bicocca, \ Milano-Bicocca, \ Milano-Bicocca, \ Milano-Bicocca, \ {\rm Milano-Bicocca, \ Milano-$ 

Small conjugated molecules like squaraines are a promising alternative to semiconducting polymers in the field of organic photovoltaics. Understanding the exitonic interaction of these molecules enables us to tailor devices for specific applications. In this study we use a homebuilt linear polarization-resolved spectro-microscope to investigate the molecular packing of crystalline nHSQ nanostructures. A characteristic "double-hump" signature in the absorption spectrum of nHSQ has been ascribed to the excitation of an intermolecular charge transfer band [1]. Our optical measurements show the excitation of these peaks at different angles. When comparing these angles with the known outof-plane crystallographic orientation [2] we can predict the in-plane orientation of the nHSQ molecules. [1] Zheng et al. Sol. Energy Mater Sol. Cells 157, 366 (2014) [2] Brück et al. PCCP 16, 1067 (2014)