

## DS 22: Interfaces and Thin Films III (joint session with CPP)

Time: Wednesday 9:30–13:00

Location: C 243

DS 22.1 Wed 9:30 C 243

**Patterned Diblock co-polymer Thin Films as Templates for Advanced Anisotropic Metal Nanostructures** — ●STEPHAN V. ROTH<sup>1</sup>, GONZALO SANTORO<sup>1</sup>, JOHANNES F.H. RISCH<sup>1</sup>, SHUN YU<sup>2</sup>, MATTHIAS SCHWARTZKOPF<sup>1</sup>, PENG ZHANG<sup>1</sup>, SARATHLAL KOYILOTH VAYALIL<sup>1</sup>, MICHAEL A. RÜBHAUSEN<sup>3</sup>, NICK J. TERRILL<sup>4</sup>, PAUL STANIEC<sup>4</sup>, YUAN YAO<sup>5</sup>, EZZELDIN METWALLI<sup>5</sup>, and PETER MÜLLER-BUSCHBAUM<sup>5</sup> — <sup>1</sup>DESY, Notkestr. 85, 22607 Hamburg — <sup>2</sup>KTH, Teknikringen 56-58, 10044 Stockholm — <sup>3</sup>Inst. f. Nanostruktur- und Festkörperforschung, CFEL, APOG, Univ. Hamburg, Luruper Chaussee 149, 22761 Hamburg — <sup>4</sup>DLS, Harwell Sci. & Innov. Campus, Didcot, Oxfordshire OX11 0QX — <sup>5</sup>LS funkt. Mat., Physik-Department, TU München, James-Franck-Str. 1, 85748 Garching

The tailoring of the metal-polymer interface in hybrid materials plays a crucial role in modern advanced material science. Using glancing angle deposition of gold on a nanostructured diblock copolymer thin film (PS-*b*-PMMA), we are able to fabricate directional hierarchical structures. This approach exploits the selective wetting of Au on the PS block. We prove the asymmetric, localized growth of the gold nanoparticles and are able to extract the different growth laws by in situ scattering methods as well as imaging methods. The optical anisotropy of these hierarchical hybrid materials is probed by angular resolved spectroscopic methods and is correlated to the nanostructure. This approach offers the possibility to tailor functional hierarchical thin films for plasmonics and metamaterials, as nanoantennae arrays, in organic photovoltaics and sensor electronics.

DS 22.2 Wed 9:45 C 243

**Transparent aluminium oxide coatings on polymer substrate** — ●SAMANTHA MICCIULLA<sup>1</sup>, XIAOFEI DUAN<sup>2</sup>, ROBERT N. LAMB<sup>2</sup>, and REGINE VON KLITZING<sup>1</sup> — <sup>1</sup>Technische Universität Berlin — <sup>2</sup>The University of Melbourne

Smart coatings are highly versatile systems, applicable to diverse purposes and finely tunable by proper external stimuli. Polymers are mostly used to create responsive films, however they suffer hard conditions like high temperatures, aggressive chemicals, high mechanical stress, with consequent degradation or irreversible modifications. Therefore the use of a thin inorganic coating enriching the system of high mechanical and chemical stability may be the solution to this limitation. A good candidate to this purpose is aluminium oxide (Al<sub>2</sub>O<sub>3</sub>), which presents anti-corrosion properties, high wear resistance, and high biocompatibility. Moreover, the transparency of alumina ceramics in the UV-Vis range makes it suitable to optical applications. A synthetic route to prepare Al<sub>2</sub>O<sub>3</sub> was developed to reduce the risk of degradation of the underneath polymer, using low temperatures and mild chemicals. The composition of alumina/polymer coatings was studied by X-Rays Photoelectron Spectroscopy and the surface morphology by Scanning Electron Microscopy. The latter showed the achievement of a smooth, cracks-free coating upon hydrothermal treatment (105°C, 38 atm). Our studies focused on the preparation of alumina coatings on polymer substrates having different surface hydrophilicity, charge and structure, and revealed that the wetting properties of the polymer surface play the dominant role for the quality of the coating.

DS 22.3 Wed 10:00 C 243

**Tailoring the mechanics of ultrathin carbon nanomembranes by molecular design** — ●XIANGHUI ZHANG, CHRISTOF NEUMANN, POLINA ANGELOVA, ANDRÉ BEYER, and ARMIN GÖLZHÄUSER — Fakultät für Physik, Universität Bielefeld, 33615 Bielefeld, Germany

Freestanding carbon nanomembranes (CNMs) with a thickness between 0.6 nm and 1.7 nm were prepared from self-assembled monolayers (SAMs) of diverse polyaromatic precursors via low energy electron induced cross-linking. The mechanical properties of CNMs were investigated by applying a pressure difference between the two sides of the membrane and by measuring the resulting deflection with atomic force microscopy. We found a correlation between the rigidity of the precursor molecules and the macroscopic mechanical stiffness of CNMs. While CNMs from rigid and condensed precursors like naphthalene and pyrene thiols prove to exhibit higher Young's moduli of 15–19 GPa, CNMs from non-fused oligophenyls possess lower Young's moduli of ~10 GPa. For CNMs from less densely packed SAMs, the presence of defects and nanopores plays an important role in determining their me-

chanical properties. The finite element method (FEM) was applied to examine the deformation profiles and simulate the pressure-deflection relationships.

DS 22.4 Wed 10:15 C 243

**Covalent modification of large area monolayer graphene towards biosensing.** — ●FELIX RÖSICKE<sup>1</sup>, MARC GLUBA<sup>1</sup>, GUO GUANG SUN<sup>2</sup>, KARSTEN HINRICHS<sup>2</sup>, JÖRG RAPPICH<sup>1</sup>, and NORBERT NICKEL<sup>1</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany — <sup>2</sup>Leibniz - Institut für Analytische Wissenschaften - ISAS - e.V., Department Berlin, Berlin, Germany

We investigated the electrochemical grafting of para-N-maleimidophenyl (pMP) onto graphene from the respective diazonium salt (p-(N-Maleimido)benzenediazonium tetrafluoroborate, pMPDT) by electrochemical quartz crystal microbalance (EQCM), Raman- and infrared spectroscopies.

The p-MP is well known to react with any SH-group present in solution and is therefore a possible candidate to build up bio-sensing devices which, in combination with graphene, are very stable and conductive systems that can be transferred to any substrate. The sample preparation was performed by a transfer of CVD grown large area graphene [1] to an isolating layer of SiN<sub>x</sub> on Au-coated QCM chips. Using graphene as working electrode, the current behavior and the change in the resonant frequency of the EQCM reflect the electrochemical reduction of the diazonium compound. Raman and infrared spectroscopies reveal the binding of pMP onto the graphene layer. The charge used for the reduction of pMPDT correlates to the amount of grafted pMP and the observed defect density of graphene. Finally the pMP functionalized graphene surface was tested by reaction with 4-Nitrobenzenethiol.

DS 22.5 Wed 10:30 C 243

**Light absorption of Ultrathin Gallium Layers during Oxidation** — ●FRANK LAWRENZ<sup>1</sup>, CHRISTIAN A. HELM<sup>1</sup>, and STEPHAN BLOCK<sup>2</sup> — <sup>1</sup>Physik, Uni Greifswald, 17487 Greifswald, Germany — <sup>2</sup>Chalmers University of Technology, 412 96 Göteborg, Sweden

The fabrication of ultrathin metal oxide layers is important for many technological applications. Here we describe a simple method for the formation of 3 nm thick gallium oxide layers which extend up to 1 cm<sup>2</sup>. Liquid gallium is applied onto silica surfaces, leaving thin layers that are immediately oxidized at their surface under ambient conditions, followed by slower oxidation of the remaining layer. This is quantified using UV-Vis absorption measurements, indicating that the oxidation of the entire layer is completed after two weeks. A rate model is developed to describe the oxidation of ultrathin Ga layers.

DS 22.6 Wed 10:45 C 243

**Ambiguous Copolymer Surfaces from Light-Mediated Radical Polymerization** — ●CHRISTIAN W. PESTER<sup>1,2</sup>, JUSTIN E. POELMA<sup>2</sup>, CRAIG J. HAWKER<sup>2</sup>, and EDWARD J. KRAMER<sup>1</sup> — <sup>1</sup>UC Santa Barbara, Department of Materials, Department of Chemical Engineering — <sup>2</sup>Department of Chemistry and Biochemistry, Materials Research Laboratory, Santa Barbara, CA, 93106

We describe the use of visible-light-mediated living radical polymerization of methacrylate-based, anti-fouling relevant monomers, i.e., poly(trifluoroethyl methacrylate) (TFEMA) and poly(ethylene glycol methacrylate) (PEGMA). Resulting ambiguous surfaces are expected to show promising features for marine anti-fouling applications. Light-catalysis affords facile lithographic patterning. In this PEGMA-*b*-TFEMA case study we patterned these diblocks to give topographically and chemically well-defined ambiguous surfaces which combine hydrophilic and hydrophobic properties on the micron length scale. XPS, dynamic secondary ion mass spectroscopy, and scanning x-ray transmission microscopy, allowed us to precisely determine chemical surface composition, whereas AFM afforded precise analysis of topographical features inherent to patterning. The light-activated polymerization method we use was readily coupled to well-established ATRP techniques and afforded expansion of this case study to advanced monomers, e.g. highly fluorinated compounds and zwitterionic acrylates. Polymer backbone functionalization combined with lithography allowed spatial control over brush architecture, adding to the wide chemical and conformational accessible parameter space.

15 min. break

DS 22.7 Wed 11:15 C 243

**Light-Controlled Molecular Zippers based on Azobenzene Main Chain Polymers** — ●CHRISTOPHER WEBER<sup>1</sup>, TOBIAS LIEBIG<sup>1</sup>, ANTON ZYKOV<sup>1</sup>, LINUS PITHAN<sup>1</sup>, SEBASTIAN BOMMEL<sup>1,2</sup>, DAVID BLÉGER<sup>3</sup>, and STEFAN KOWARIK<sup>1</sup> — <sup>1</sup>Institut für Physik, Humboldt-Universität zu Berlin, 12489 Berlin — <sup>2</sup>Deutsches Elektronen-Synchrotron, 22607 Hamburg — <sup>3</sup>Institut für Chemie, Humboldt-Universität zu Berlin, 12489 Berlin

We report that thin films of azobenzene main chain polymers with interdigitating dodecyl side chains (molecular zippers) can be switched reversibly with light between a semicrystalline and an amorphous state, corresponding to a closed and open state of the molecular zippers. Simultaneous time-resolved x-ray diffraction and optical spectroscopy measurements show that the kinetics of the amorphization of the crystalline domains is about 12 times slower than the photoisomerization of the azobenzene chromophores. Our findings suggest that the amorphization is triggered by *E-Z* isomerization of a small amount of azobenzene chromophores within the polymer film and that the slower kinetics of the photoinduced amorphization is determined by structural and topological constraints and not by a different isomerization mechanism in crystalline domains.

DS 22.8 Wed 11:30 C 243

**Monte Carlo Simulations for Switchable Model Molecules** — ●RAFFAELE TAVARONE<sup>1</sup>, PATRICK CHARBONNEAU<sup>2</sup>, and HOLGER STARK<sup>1</sup> — <sup>1</sup>Institut für Theoretische Physik, Technische Universität Berlin, D-10623 Berlin, Germany — <sup>2</sup>Departments of Chemistry and Physics, Duke University, Durham, North Carolina 27708, USA

Light-switchable molecules are chemical compounds that can undergo a light-induced, reversible *trans-cis* isomerization. They can be used to build functional monolayers with, for example, switchable wetting properties. A typical example of a light-driven *trans-cis* transition is the azobenzene isomerization.

Inspired by the conformational changes of the azobenzene compound, we build a model in which a *trans* isomer is regarded as a straight needle while a *cis* isomer is regarded as a bent needle. First, we determine the phase behavior of such molecules on a planar surface using Monte Carlo simulations. The resulting phase diagram (density versus molecular shape) shows several liquid-crystal mesophases.

Second, we build a kinetic model for a glassy monolayer inspired by a recent experiment [1]. They showed that the spontaneous algebraic relaxation of orientational order, inscribed in the sample with linearly polarized light, is strongly enhanced by illumination with circularly polarized light. In our simulations we allow molecules to switch between the *trans* and *cis* isomers due to the interaction with light. We are able to trace the influence of neighbors hindrance and other microscopic processes on the kinetic of the relaxation reported in the experiment.

[1] Fang, G. J., et al., Nature communications 4, 1521 (2013).

DS 22.9 Wed 11:45 C 243

**Effect of Binary Polymer Mixtures on the Growth of Polyelectrolyte Multilayers** — ●MALTE PASSVOGEL, PETER NESTLER, and CHRISTIANE A. HELM — Physik, Uni Greifswald, 17487 Greifswald, Germany

The buildup of polyelectrolyte multilayers (PEMs) is investigated in solution with multiple angle null-ellipsometry. Polyanion poly(styrenesulfonate) (PSS) and polycation polydiallyldimethylammonium (PDADMAC) are adsorbed sequentially from 0.1 NaCl solution. After  $N_{trans}$  deposited PDADMAC/PSS layer pairs a transition from parabolic to linear growth occurs, then the thickness per layer pair  $d_{BL}$  is constant.  $d_{BL}$  is 12.3 nm, if the molecular weight ( $M_w$ ) exceed threshold values which are specific for each polymer (25 kDa for PSS and 80 kDa for PDADMAC). If either the PDADMAC or the PSS molecular weight is decreased below the threshold values,  $d_{BL}$  either falls (for PDADMAC) or rises (for PSS) suggesting very different growth modes. Binary mixtures of PDADMAC and PSS with  $M_w$  below and above the threshold value are used, while  $M_w$  of the complementary polyanion is kept above the threshold.  $d_{BL}$  depends linearly on the mole fraction of the low-molecular-weight PDADMAC. However,  $d_{BL}$  is only influenced by low-molecular-weight PSS, if its molar fraction exceeds 90%. Always, the same linear relationship between  $N_{trans}$  and  $d_{BL}$  is found. These observations can be explained with an asymmetric growth model of polyelectrolyte multilayers.

DS 22.10 Wed 12:00 C 243

**The Swelling Behaviour of Voids inside Polyelectrolyte Multilayers** — ●MAXIMILIAN ZERBALL<sup>1</sup>, RALF KÖHLER<sup>2</sup>, OLAF SOLTWEDEL<sup>3</sup>, and REGINE VON KLITZING<sup>1</sup> — <sup>1</sup>Institut für Chemie, Technische Universität Berlin, Str. 17.Juni 124, 10623 Berlin — <sup>2</sup>Institut für Weiche Materie und funktionelle Materialien, Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin — <sup>3</sup>Max-Planck-Institut für Festkörperforschung, Lichtenbergstr. 1, 85747 Garching

Polyelectrolyte Multilayer (PEM) are organic films built up via subsequent adsorption of oppositely charged polyions. PEMs are highly sensitive to external parameter like the relative humidity (r.h.) of the ambient atmosphere. This ability makes them to ideal candidates for sensoric applications. In order to use these films as sensors it is important to understand and to control the swelling behavior. The uptaken water of swollen PEMs are subdividable into two contributions; the swelling water, which influences thickness and optical properties, and the void water, which only affects the optical properties of the PEM.

The swelling behavior of voids, i.e. the separated amount of uptaken water inside voids in comparison to the uptaken amount of water inside the PEM with increasing r.h., is rarely researched. For the purpose to understand the swelling behavior of voids more in detail, in this study the void water and swelling water of PEMs in dependence of the relative humidity was investigated by neutron reflectivity. The results suggest that the strongest increase of voidwater proceeds between 0% r.h. and 6% r.h. while beyond, the swelling water dominates the amount of water.

DS 22.11 Wed 12:15 C 243

**Influence of Barrier Layers on Interdiffusion in Polyelectrolyte Multilayers** — ●PETER NESTLER<sup>1</sup>, MALTE PASSVOGEL<sup>1</sup>, OLAF SOLTWEDEL<sup>2</sup>, RALF KÖHLER<sup>3</sup>, and CHRISTIANE A. HELM<sup>1</sup> — <sup>1</sup>Physik, Uni Greifswald, 17487 Greifswald, Germany — <sup>2</sup>MPI FKP 70569 Stuttgart, Germany — <sup>3</sup>Helmholtz-Zentrum Berlin, 14109 Berlin, Germany

Polyelectrolyte multilayers are made from poly(diallyldimethylammonium) (PDADMA), poly(styrenesulfonate) (PSS). Using selective PSS deuteration each film consists of a protonated and a deuterated compartment.

During annealing in 1 M NaCl solution the internal interface between these two compartments broadens due to interdiffusion. The PSS diffusion coefficient  $D_{PSS}$  inside the multilayer film is quantified via neutron reflectivity. Eventually the annealing leads to a uniform distribution of protonated and deuterated PSS inside the film. If one polycation layer in the film centre is branched poly(ethyleneimine) (PEI), then PEI serves as a diffusion barrier. In this case the barrier is impenetrable for up to 70% of PSS molecules. The diffusion behaviour of the remaining 30% can be described using a position-dependent distribution of DPSS inside the multilayer film. The effective PSS diffusion coefficient is reduced by one to two orders of magnitude.

DS 22.12 Wed 12:30 C 243

**Improved Electrolyte-Additive Induced Performance of Graphite Anodes for Lithium-Ion Batteries – Electrochemical and Electrode Surface Studies** — ●ANNA DIMITROVA<sup>1</sup>, ANDRE MÜLLER<sup>2</sup>, SVETLOZAR IVANOV<sup>2</sup>, MARCEL HIMMERLICH<sup>1</sup>, ANJA EISENHARDT<sup>1</sup>, ANDREAS BUND<sup>2</sup>, and STEFAN KRISCHOK<sup>1</sup> — <sup>1</sup>Technische Universität Ilmenau, Institut für Physik und Institut für Mikro- und Nanotechnologien, Germany — <sup>2</sup>Technische Universität Ilmenau, Fachgebiet Elektrochemie und Galvanotechnik, Germany

The electrolyte decomposition is a crucial stage in the formation cycle of Li-ion batteries. It results in the formation of a protective passivation layer on the graphite electrode surface, called *solid electrolyte interphase* (SEI). SEI formation competes with Li ion intercalation and its chemical composition and structure determines the battery cell life time. To control this process we designed a phosphorous enriched electrolyte, which enhances the rate performance and the capacity retention of the Li-ion battery compared to a non-modified electrolyte. In order to study charge-discharge cycles in the batteries and to analyze the SEI composition, we combined electrochemical studies with X-ray Photoelectron Spectroscopy (XPS). In this work the influence of the electrolyte on the SEI composition was investigated and a correlation between chemical structure and electrochemical characteristics of the Li-ion battery will be discussed.

DS 22.13 Wed 12:45 C 243

**Deposition of copper multilayers on Au(111) in sulphuric acid solution: An electrochemical scanning tunneling mi-**

**scopy study** — •BARTOSZ MADRY<sup>1</sup>, KLAUS WANDEL<sup>1,2</sup>, and MAREK NOWICKI<sup>1</sup> — <sup>1</sup>Institute of Experimental Physics, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław, Poland. — <sup>2</sup>Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstr. 12, 53115 Bonn, Germany.

The co-adsorption of submono-, mono- and multi-layers of Cu with sulfate anions on a Au(111) electrode surface was investigated in electrochemical environment (0.1 mM CuSO<sub>4</sub> + 0.1 M H<sub>2</sub>SO<sub>4</sub>) by cyclic voltammetry (CV) and in-situ scanning tunneling microscopy (STM).

Correlated with the STM investigations the CV measurements indicate co-adsorption/-desorption processes of Cu of submono-, mono- and multi-layer coverages with sulfuric acid species on Au(111). The formation of a quasi-hexagonal Moiré superstructure on terraces of copper multilayers was observed in situ by STM. In detail the observed Moiré-structure is similar but not identical to the one observed on the (111) surface of bulk copper. High resolution STM images show the formation of a ( $\sqrt{3} \times \sqrt{7}$ )-like sulfate structure on all multilayer copper terraces.