

## CPP 1: Interfaces and Thin Films I

Time: Monday 9:30–13:15

Location: C 130

## Topical Talk

CPP 1.1 Mon 9:30 C 130

**Local anodic oxidation nanolithography on alkyl-terminated silicon surfaces: Chemical routes towards functional nanostructures** — ●HARALD GRAAF<sup>1,2</sup>, MAIK VIELUF<sup>1</sup>, and THOMAS BAUMGÄRTEL<sup>1</sup> — <sup>1</sup>Chemnitz University of Technology, Institute of Physics, Germany — <sup>2</sup>Kassel University, Institute of Chemistry, Germany

The structuring of surfaces on a nanometer scale is one of the demands that have to be fulfilled in order to advance the design and to aspire to miniaturisation in semiconductor technologies. Besides further development of conventional optical lithography, alternative lithography techniques are in the focus of recent research to achieve lateral structures on the nanometer scale. Here scanning probe based lithography (SPL) is one of the emerging fields. One SPL approach is the local anodic oxidation (LAO) where a voltage is applied between scanning probe microscopy (SPM) tip and sample surface leading to an electrochemical oxidation reaction. In the case of an (alkyl-terminated) silicon sample, the silicon is oxidized locally at the tip apex forming silicon oxide structures. The chemically different oxide can afterwards be altered through the attachment of molecules or nanoparticles in order to give the structures a defined functionality. In this talk, basics of the LAO technique will be introduced and an overview will be given of the research in that field both regarding the understanding of the process itself as well as possible applications to generate functionalized structures. This contribution will thereby deal on the optical properties of prepared functional nanostructures.

CPP 1.2 Mon 10:00 C 130

**Low temperature route to nano-structured crystalline titania thin films** — ●MONIKA RAWOLLE<sup>1</sup>, CHRISTIAN GEBBE<sup>1</sup>, ERIK V. BRADEN<sup>1</sup>, MARTIN A. NIEDERMEIER<sup>1</sup>, DAVID MAGERL<sup>1</sup>, Kuhu SARKAR<sup>1</sup>, VOLKER KÖRSTGENS<sup>1</sup>, THOMAS FRÖSCHL<sup>2</sup>, NICOLA HÜSING<sup>2</sup>, JAN PERLICH<sup>3</sup>, ADELIN BUFFET<sup>3</sup>, STEPHAN V. ROTH<sup>3</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik Department, LS Funktionelle Materialien, James-Frank-Str. 1, 85748 Garching, Germany — <sup>2</sup>Universität Salzburg, Materialforschung und Physik, 5020 Salzburg, Austria — <sup>3</sup>HASYLAB at DESY, 22603 Hamburg, Germany

A low temperature route to crystalline titania thin films is presented, which is interesting for inorganic-organic hybrid photovoltaics due to lower costs, easy producibility and the possibility of using organic flexible substrates. An ethylene glycol modified titanate (EGMT) precursor yields crystalline titania already at low temperatures, where the crystal phase (anatase or rutile) depends on the pH value.[1] We use this precursor to prepare thin films with well-defined nanostructures. The nano-structure is controlled with a diblock copolymer as templating agent combined with sol-gel chemistry. The nano-morphology is investigated with SEM, XRR and GISAXS. Crystallinity is determined with GIWAXS and related to optical properties as probed with UV/Vis spectroscopy. Solar cells prepared with titania derived from EGMT are characterized electronically under illumination with a solar spectrum (AM 1.5).

[1] Denkwitz et al., J. Appl. Catal. B:Environ. (2009) 91, 470.

CPP 1.3 Mon 10:15 C 130

**Imaging of carbon nanomembranes with helium-ion microscopy** — ●ANDRE BEYER, ANDREY TURCHANIN, and ARMIN GÖLZHÄUSER — Physics of Supramolecular Systems, University of Bielefeld, 33615 Bielefeld, Germany

Helium-ion microscopy (HIM) is similar to scanning electron microscopy but it employs helium ions for scanning a sample instead of electrons. The resulting images are more surface sensitive with a higher resolution as compared to scanning electron microscopy. Here we present a study about imaging extremely thin nano-scale objects: carbon nanomembranes which consist exclusively of atoms near the surface. Such freestanding nanomembranes with a thickness of 1 nm are made from self-assembled monolayers (SAMs) by cross-linking and subsequent transfer to transmission electron microscopy (TEM) grids or other suitable substrates. We show that these nanomembranes exhibit a substantially higher contrast in helium-ion microscopes as compared to electron microscopes. Cross-linking of SAMs is performed by large area exposures with electrons or photons which yield extended

nanomembranes. On the other hand, patterned exposures allow the fabrication of nanosieves, i.e. perforated nanomembranes. Advantages in imaging such patterned cross-linked SAMs as well as freestanding nanosieves with the helium-ion microscope will be discussed.

CPP 1.4 Mon 10:30 C 130

**Improvement of Adsorption Stability of Indoline Sensitizers in Dye-Sensitized Solar Cells by Additional Binding Groups** — ●JANE FALGENHAUER<sup>1</sup>, HIDETOSHI MIURA<sup>2</sup>, and DERCK SCHLETTWEIN<sup>1</sup> — <sup>1</sup>Justus-Liebig-Universität Gießen, Institut für Angewandte Physik, Heinrich-Buff-Ring 16, D-35392 Gießen — <sup>2</sup>Tsukuba Research Center, Chemicea Inc., D-142-1-6, Sengen, Tsukuba, Ibaraki 305-0047, Japan

Dye-sensitized solar cells often suffer from desorption of sensitizer molecules during operation and in contact to a redox electrolyte. In particular for ZnO as active semiconductor material, an optimal dye has still to be found. In this study, novel indoline dyes with additional binding groups to the semiconductor surface were investigated. Their adsorption stability on ZnO was studied in comparison with the established indoline dye D149. The dyes were adsorbed on nanoporous electrodeposited ZnO with a co-adsorbent, chenodeoxycholic acid. The amount of dyes adsorbed to the films was measured by optical absorption spectroscopy. Under operation in contact to a typical redox electrolyte, the dyes showed different desorption probability. The amount of desorbed dyes in such a solution containing the electrolyte additive *N* - Methylbenzimidazole (NMBI) was also investigated by optical absorption spectroscopy, as well as the absorption of the films following these desorption experiments. The stability of the dyes in dependence on the number of binding groups at the sensitizer molecules will be discussed.

CPP 1.5 Mon 10:45 C 130

**Stretchable metal films on ultrathin substrates** — ●MICHAEL DRACK, MARTIN KALTENBRUNNER, INGRID GRAZ, and SIEGFRIED BAUER — Soft Matter Physics, Institute Experimental Physics, J. Kepler University, Altenbergerstraße 69, 4040 Linz, Austria

Today's electronic devices are rigid, tomorrow's electronics is expected to be used everywhere. Conformability will be the key to use electronics everywhere: electronic textiles, ultra-conformable solar panels and stretchable sensor skins are just a few potential applications. Unfortunately most electronic materials are brittle and fracture at 1% strain. Metals are ductile but plastically deform and break. So the question arises how to make such brittle or plastically deformable materials mechanically stretchable.

Here we present an approach to make thin metal electrodes mechanically highly compliant. The metal electrodes are fabricated by thin film processing techniques onto an ultrathin and ultra-flexible polymer substrate. A 1.4 micron thick PEN polymer foil is used as the substrate for the metal films. On a pre-stretched and relaxed elastomer, the metal electrodes on the thin PEN substrate form wrinkles. We have found that such 100nm thick aluminium, copper, gold and silver electrodes can be reversibly stretched uniaxially to 50% for 1000 cycles without failure. Their electrical resistance does not change significantly with cycling, paving ways for making any metal film mechanically stretchable.

CPP 1.6 Mon 11:00 C 130

**Light-induced wrinkling and moving gratings in low-molecular azo films** — PHILIPP GRUNER, MICHAEL ARLT, and ●THOMAS FUHRMANN-LIEKER — Makromolekulare Chemie und Molekulare Materialien, Universität Kassel

The dynamics of mass transport in thin layers of a low molecular glass containing azo chromophores are studied in two experiments.

First, spinodal wrinkling of a multilayer system consisting of the azo glass confined by a rigid substrate and an elastic cover layer is induced by light. The time evolution of the wrinkle structures is measured and compared to thermal wrinkling. Application of theoretical models allows the determination of the viscoelastic properties in the non-equilibrium fluid.

Second, in a dynamic holographic experiment surface corrugation gratings are shifted by phase control of the generating beams. The relaxation timescale in which the corrugation pattern can follow the

moving light field is measured.

With these experiments, fundamental properties of photofluidic thin films such as irradiation-dependent viscosity are addressable.

## 15 min break

CPP 1.7 Mon 11:30 C 130

**Self-assembled membranes from bionanoparticle-polymer conjugates** — ●PATRICK VAN RIJN, NATHALIE MOUGIN, CHRISTINE KATHREIN, and ALEXANDER BÖKER — DWI an der RWTH Aachen e.V., IPC RWTH Aachen University, Germany

New bionanoparticles have been prepared by using Horse spleen Ferritin (HSF) as a scaffold for the grafting from of thermo-responsive poly(N-isopropyl acrylamide) and photo-cross-linkable (2-(dimethyl maleinimido)-N-ethyl-acrylamide. The amino-groups on the exterior of HSF were modified to form a macro-initiator from which sequentially atom transfer radical polymerization was performed.[Mougin, et. al. Adv. Funct. Mater. 2011, 21, 2470] The newly formed bionanoparticles-polymer composites are excellent candidates for the stabilization of polar/apolar interfaces.[van Rijn, et. al., Langmuir, submitted] and oil-in-water and water-in-oil emulsions have been prepared and stabilized by cross-linking, forming soft capsules which are stable enough to be collected, transferred and are able to endure co-solvents like ethanol.[van Rijn, et. al. Chem. Commun., 2011, 47, 8376] A similar process can also be used for the formation of 2-D membranes which display interesting properties. Here the protein is used as a sacrificial template which creates defined pores after denaturation. The membranes are highly stable, easily formed and used for the separation of various nano-sized species.

CPP 1.8 Mon 11:45 C 130

**Stimuli-responsive surfaces based on triblock terpolymer micelles** — ●JULIA GENSEL<sup>1</sup>, EVA BETTHAUSEN<sup>2</sup>, INNA DEWALD<sup>1</sup>, JOHANN ERATH<sup>1</sup>, FOUZIA BOULMEDAIS<sup>3</sup>, AXEL H. E. MÜLLER<sup>2</sup>, and ANDREAS FERY<sup>1</sup> — <sup>1</sup>Physical Chemistry II, University of Bayreuth, Germany — <sup>2</sup>Macromolecular Chemistry II, University of Bayreuth, Germany — <sup>3</sup>Institut Charles Sadron, Université de Strasbourg, France

The surface adsorption of stimuli-responsive block copolymer micelles on a solid substrate leads to stimuli-responsive coatings with well defined thickness and morphology. In this contribution we present a novel approach for the design of stimuli-responsive surfaces based on the deposition of charged pH-responsive core-shell-corona micelles.[1]

The adsorption of these micelles on silica is adequately described by the Random Sequential Adsorption model. By variation of the solution pH, it is possible to reversibly switch the surface micelles' charge density, swelling state and composition.[2] These switchable surfaces can be used as active surfaces for bio-applications for example for the controlled self-regulated bacteria release.

Using the layer-by-layer approach, the micelles are included within multilayer films with tailored nanostructure and integrated pH-responsive properties. The film swelling degree, morphology as well as the mechanical properties of the coatings are tunable by the solution pH. These systems are potentially interesting as nano-actuators.

[1] E. Betthausen et al., Soft Matter, 2011, 7, 8880-8891.

[2] J. Gensel et al., Soft Matter, 2011, 11144-11153.

CPP 1.9 Mon 12:00 C 130

**Guiding block copolymers into sequenced patterns via inverted terrace formation** — ●SUNGJUNE PARK<sup>1</sup>, LARISA TSARKOVA<sup>1</sup>, STEPHANIE HILTL<sup>1</sup>, STEFAN ROITSCH<sup>2</sup>, JOACHIM MAYER<sup>2</sup>, and ALEXANDER BÖKER<sup>1</sup> — <sup>1</sup>DWI an der RWTH Aachen e. V., Lehrstuhl für Makromolekulare Materialien und Oberflächen, RWTH Aachen University, D-52056 Aachen, Germany. — <sup>2</sup>Gemeinschaftslabor für Elektronenmikroskopie, RWTH Aachen University, Ahornstr. 55, D-52074 Aachen, Germany.

We present a facile one-step route to achieve sequenced patterns from microphase separated structures in asymmetric polystyrene-*b*-polybutadiene (PS-*b*-PB) diblock copolymer films. For the guided block copolymer assembly we used topographically corrugated SiCN ceramic substrates which were fabricated by a facile replication process using non-lithographic PDMS masters. Homogeneous block copolymer films have been floated onto the corrugated substrate without significant changes to the corrugations topography. During thermal annealing of PS-*b*-PB diblock copolymer, the material transport was guided by a wrinkled substrate to form regular modulations in the film

thickness. As a consequence of the thickness-dependent morphological behavior, the film surface appears as sequenced patterns of alternative microphase separated structures. The ordering process is attributed to a newly observed phenomenon of inverted terrace formation which is induced by the corrugations on substrate, so that the resulting surface patterns are free from the surface relief structures within macroscopically large areas.

CPP 1.10 Mon 12:15 C 130

**Influence of interface interactions on the inner structure of pressure sensitive adhesive films** — ●MARKUS SCHINDLER<sup>1</sup>, ARMIN KRIELE<sup>2</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, LS Funktionelle Materialien, James-Frank-Str.1, 85748 Garching, Germany — <sup>2</sup>TU München, Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II), Lichtenbergstr.1, 85748 Garching, Germany

Pressure sensitive adhesives (PSAs) are widely used in everyday applications, industries and medicine, although surprisingly still lacking fundamental understanding on molecular scale. Individually tailored compounds exist for almost every possible environment, in which they still allow for reversible adhesion. Previous studies on our model system consisting of the statistical copolymer poly(ethylhexylacrylate-*stat*-methylmethacrylate) have shown that the two components of the polymer establish enrichment layers at the top surface that significantly affect the tack performance. We present insights into the internal reorganization of the solution cast adhesive films' inner structure upon different interface interactions which makes it possible to apply the same adhesive for higher and lower tack applications. The timescale on which these changes of the inner structure take place also provides information about the durability of established adhesive bonds. We present a study on the influence of an unpolar nitrogen atmosphere on the internal reorganization with time of adhesive films showing a complete inversion of the layering installed during the sample preparation.

CPP 1.11 Mon 12:30 C 130

**Decelerating dewetting by shining light on a thin polymer film containing conjugated molecules** — ●IOAN BOTIZ<sup>1,2</sup>, NATALIE STINGELIN<sup>3</sup>, and GÜNTER REITER<sup>1,2</sup> — <sup>1</sup>Freiburg Research Institute for Advanced Studies — <sup>2</sup>Institute of Physics, University of Freiburg — <sup>3</sup>Imperial College London

We use an induced dewetting process as a method to control polymer conformations by stretching molecules within an ultrathin residual layer in the dewetting direction. Varying physical parameters like temperature, substrate type, light intensity, film thickness and age, we control the dewetting velocity, the final patterns (droplets and the residual thin layer), including the degree of molecular stretching. We show that, under nitrogen conditions, light intensity decelerates by two folds the dewetting velocity of a thin film of conjugated Poly[2-methoxy-5-((2'-ethylhexyl)oxy)-1,4-phenylenevinylene] (MEH-PPV) molecules embedded in an optically inert polystyrene matrix. No light effect is observed in thin films of polystyrene alone. Switching the light on and off leads to deceleration and acceleration of dewetting respectively, indicating a reversible effect of light. We attempt to explain our experimental observations suggesting that light induces new electronic states in MEH-PPV molecules (most probably long lived triplet states) leading to a change in molecular conformation characterized by a higher chain rigidity and therefore a higher polymer viscosity, i.e. lower dewetting velocity.

CPP 1.12 Mon 12:45 C 130

**In-situ study of structural changes in lamellar diblock copolymer thin films during heat treatment** — ●ALESSANDRO SEPE<sup>1</sup>, DORTHE POSSELT<sup>2</sup>, JAN PERLICH<sup>3</sup>, DETLEF-M. SMILGIES<sup>4</sup>, and CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>TU München, Physikdepartment, Physik weicher Materie, Garching, Germany — <sup>2</sup>Institute for Science, Systems and Models, Roskilde University, Denmark — <sup>3</sup>HASYLAB at DESY, Hamburg — <sup>4</sup>Cornell High-Energy Synchrotron Source (CHESS), Ithaca, U.S.A.

Diblock copolymer thin films are prominent candidates for a range of applications requiring nanostructured surfaces, such as nanoporous films. Thermal annealing has frequently been applied to remove defects and to improve the long-range order. Annealing temperature is a key parameter because it influences both, the interfacial tension between the two blocks and the polymer mobility. We investigate the mechanisms of structural changes induced by thermal treatment of thin films of poly(styrene-*b*-butadiene) having initially the perpendicular lamellar

orientation. In-situ grazing-incidence small-angle X-ray scattering and VIS interferometry as well as ex-situ atomic force spectroscopy and X-ray reflectivity were used to monitor the changes. We have found that for annealing temperatures below the glass transition temperature of the PS block and subsequent cooling to room temperature, the lateral order is improved, whereas above, a random lamellar orientation and subsequent severe changes of the film structure are observed.

CPP 1.13 Mon 13:00 C 130

**Stability and Orientations of Lamellae in Confined Block Copolymer Films** — •VANESSA WEITH, ALEXEI KREKHOV, and WALTER ZIMMERMANN — Theoretische Physik I, Universität Bayreuth, 95440 Bayreuth, Germany

The study of self-assembly of block copolymers offers substantial op-

portunities to control the morphology of the evolving patterns. This is of considerable fundamental and technological importance for developing new materials to achieve specific properties.

Microphase separation in block copolymers is described by a two-dimensional mean-field model and its stationary, spatially periodic solutions are investigated for unconfined systems and for systems confined between two parallel boundaries having either equal or different wetting properties.

We determine the different stability and existence ranges of the periodic solutions in one and two spatial dimensions as well as the effects of confinement and of the block copolymer surface interaction on the free energy of lamellar solutions. This helps to determine which orientation of the lamellae is selected depending on the input parameters.

Furthermore the spatio-temporal behavior of the phase separation process of confined block copolymers is characterized.