

## CPP 29: Interfaces and Thin Films

Time: Wednesday 9:30–12:45

Location: MER 02

## Invited Talk

CPP 29.1 Wed 9:30 MER 02

**Imaging mineral-water interfaces with atomic force microscopy** — ●ANGELIKA KÜHNLE — Bielefeld University, Bielefeld, Germany

Mineral-water interfaces are omnipresent in nature and technology. Consequently, mineral-water interfaces play a decisive role in many fields, ranging from geochemistry, environmental science and biomineralization to catalysis and electrochemistry. A comprehensive understanding of the interaction of minerals with their surroundings requires the knowledge of the atomic surface structure including the hydration at the interface. In this respect, atomic force microscopy allows for gaining real-space, molecular-level information of the interfacial structure. In this presentation, silver iodide will be discussed as a prototypical example for an ice nucleating material. Silver iodide is a polar material, calling for a stabilization mechanism. So far, however, the stabilization mechanism is unknown. Our atomically resolved atomic force microscopy images reveal no indication for a surface reconstruction at the atomic scale, indicating that another mechanism seems to be at play.

CPP 29.2 Wed 10:00 MER 02

**Template-Induced Growth of Sputter-Deposited Gold Nanoparticles on Ordered Porous TiO<sub>2</sub> Thin Films for SERS Sensors** — ●SUZHE LIANG<sup>1</sup>, TIANFU GUAN<sup>1</sup>, SHANSHAN YIN<sup>1</sup>, EVA KROIS<sup>2</sup>, WEI CHEN<sup>1</sup>, CHRISTOPHER R. EVERETT<sup>1</sup>, JONAS DREWES<sup>3</sup>, THOMAS STRUNSKUS<sup>3</sup>, MARC GENSCHE<sup>1,4</sup>, JAN RUBECK<sup>4</sup>, CHRISTOPH HAISCH<sup>2</sup>, MATTHIAS SCHWARTZKOPF<sup>4</sup>, FRANZ FAUPEL<sup>3</sup>, STEPHAN V. ROTH<sup>4,5</sup>, YA-JUN CHENG<sup>6</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1,7</sup> — <sup>1</sup>TUM School of Natural Sciences, Chair for Functional Materials, Garching — <sup>2</sup>TUM School of Natural Sciences, Chair of Analytical Chemistry and Water Chemistry, Garching — <sup>3</sup>LS Materialverbunde, Institut für Materialwissenschaft, CAU, Kiel — <sup>4</sup>DESY, Hamburg — <sup>5</sup>Department of Fibre and Polymer Technology, KTH, Stockholm, Sweden — <sup>6</sup>Ningbo Institute of Materials Technology & Engineering, CAS, Ningbo, China — <sup>7</sup>MLZ, TUM, Garching

Ordered porous gold/titanium dioxide (Au/TiO<sub>2</sub>) hybrid nanostructured films are specifically interesting in large-scale applications using localized surface plasmon resonances (LSPRs) and surface-enhanced Raman scattering (SERS). We investigate the optical response of sputter-deposited Au/TiO<sub>2</sub> nanohybrid thin films with a focus on the plasmonic response and application as molecular sensors. To elucidate the origin of this behavior, we apply in situ grazing-incidence small-angle X-ray scattering (GISAXS) to investigate the growth kinetics of Au on a TiO<sub>2</sub> template during sputter deposition. The Raman intensity of deposited molecules, probed with rhodamine 6G (R6G), depends on the deposited gold thickness.

CPP 29.3 Wed 10:15 MER 02

**Proteins as stabilizers for foam films: Untangling the different stabilizing effects** — ●KEVIN GRÄFF, SEBASTIAN STOCK, LUCA MIRAU, SABINE BÜRGER, and REGINE VON KLITZING — Soft Matter at Interfaces, Technische Universität Darmstadt, Darmstadt, Germany

Macroscopic foams consist of foam films, which separate the single air bubbles from each other. Investigation of foam films is crucial to understand macroscopic foam properties such as foam stability. In order to untangle electrostatic, steric and network stabilization effects, we study and compare two globular proteins ( $\beta$ -lactoglobulin and bovine serum albumin) and a disordered, flexible protein (whole casein) at low ionic strengths with varying solution pH. Image intensity measurement allows to record spatially resolved disjoining pressure isotherms in a Thin Film Pressure Balance (TFPB). This reveals insights into the structure formation in inhomogeneous protein films. We introduce inhomogeneity tracking (feature-tracking) as a novel method to enable the measurement of interfacial mobility and stiffness of foam films. Around the isoelectric point, Newton Black Films form which are stable for the globular proteins while they are unstable for the disordered flexible one. This difference in film stability is explained by different characteristics of the network structures which is supported by findings in the bulk and at the surface of the respective protein solutions.

[1] Gräff, K. et al, (2022), Untangling effects of proteins as stabilizers for foam films, *Front. Soft. Matter* 2:1035377.

CPP 29.4 Wed 10:30 MER 02

**Anomalous underscreening in concentrated aqueous electrolytes: myth or reality?** — SARAVANA KUMAR<sup>1</sup>, PETER CATS<sup>2</sup>, IGOR SIRETANU<sup>1</sup>, RENÉ VAN ROIJ<sup>2</sup>, and ●FRIEDER MUGELE<sup>1</sup> — <sup>1</sup>Physics of Complex Fluids, Univ. Twente, Enschede, The Netherlands — <sup>2</sup>Institute for Theoretical Physics, Utrecht Univ., Utrecht, The Netherlands

Recent surface forces apparatus experiments that measured the forces between two mica surfaces and a series of subsequent theoretical studies suggest the occurrence of universal underscreening in highly concentrated electrolyte solutions. We performed a set of systematic Atomic Force Spectroscopy measurements for aqueous salt solutions in a concentration range from 1 mM to 5 M using chloride salts of various alkali metals. Experiments were carried out using flat substrates and submicrometer-sized colloidal probes made of smooth oxidized silicon immersed in salt solutions at pH values of 6 and 9 and temperatures of 25degC and 45 degC. While strong repulsive forces were observed for the smallest tip-sample separations, none of the conditions explored displayed any indication of anomalous long range electrostatic forces as reported for mica surfaces. Instead, forces are universally dominated by attractive van der Waals interactions at tip-sample separations beyond approximately 2nm for salt concentrations of 1 M and higher. Complementary calculations based on classical density functional theory for the primitive model support these experimental observations and display a consistent decrease in screening length with increasing ion concentration.

CPP 29.5 Wed 10:45 MER 02

**Layer-by-Layer Spray-deposition of Cellulose and Lignin** — ●SHOUZHENG CHEN<sup>1,2</sup>, CONSTANTIN HARDER<sup>1,3</sup>, IULIANA RIBCA<sup>4</sup>, LUCIANA PLUNTKE<sup>1,5</sup>, MARKUS OBERTHUER<sup>5</sup>, MATS JOHANSSON<sup>4</sup>, JULIEN NAVARRO<sup>2</sup>, and STEPHAN V. ROTH<sup>1,4</sup> — <sup>1</sup>DESY, 22607 Hamburg, Germany — <sup>2</sup>University Hamburg, 20146 Hamburg, Germany — <sup>3</sup>TUM School of Natural Sciences, Chair for Functional Materials, 85748 Garching, Germany — <sup>4</sup>KTH Royal Institute of Technology, 10044 Stockholm, Sweden — <sup>5</sup>HAW, Department Design, 22087 Hamburg, Germany

Cellulose and lignin are the main chemical components of wood and can be further processed and purified into more valuable chemical raw materials such as cellulose nanofibrils (CNF), Kraft lignin and lignosulfonate. Using the idea of a bottom-up approach, CNF-Lignin composite films were prepared by layer-by-layer (LbL) spray-deposition with CNF and different lignins. CNFs provide a three-dimensional porous network structure, and lignin molecules are attached to the structure of CNF to form a homogeneous structure. In addition, Kraft lignin and lignin derivatives contain a large number of phenolic hydroxyl groups, which might be preferential for thermoelectricity. Thus, CNF-Lignin composite film is an ideal template for composite functional materials.

CPP 29.6 Wed 11:00 MER 02

**Growth Kinetics and Molecular Mobility of the adsorbed Layer of Poly(bisphenol-A Carbonate) (PBAC), Polysulfone (PSU), and Poly (2-Vinyl Pyridine) (P2VP)** — ●HASSAN OMAR, PAULINA SZYMONIAK, ANDREAS HERTWIG, and ANDREAS SCHÖNHALS — Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany

Interactions between a polymer and a substrate interface play a vital role in understanding the improvement in thin film material properties as well as serving as a model for nanocomposites. For any non-repulsive polymer-substrate interactions, polymer segments form an irreversibly adsorbed layer and show a slowdown in the glassy dynamics and thus an increase in the thermal glass transition temperature compared to the bulk-like values. The growth kinetics of the adsorbed layer obey a two-step mechanism: formation of immobilized layer with flat segmental conformations and a loosely bound layer with stretched chains pinned to the surface. Here the adsorbed layer was studied for: poly (bisphenol-A carbonate) (PBAC) and polysulfone (PSU), two bulky polymers containing a functional group (phenyl ring) in the backbone and compared to poly (2-vinyl pyridine) (P2VP), where the backbone is a vinyl-derivative and the functional group (pyridine) is in the side chain. The growth kinetics for PBAC and PSU were found to deviate from the well-known mechanism, observed for polymers such as

P2VP. Atomic force microscopy and ellipsometry were used for this investigation and was additionally supported by broadband dielectric spectroscopy.

### 15 min. break

CPP 29.7 Wed 11:30 MER 02

**Influence of heavy chalcogen atoms on structural arrangement and spectroscopic properties in molecular donor/acceptor thin film heterostructures** — ●ELENA CHULANOVA<sup>1</sup>, ANTON PYLYPENKO<sup>1</sup>, ALEXANDER GERLACH<sup>1</sup>, JANNIKA LAUTH<sup>2</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Institute for Applied Physics, University of Tübingen, 72076 Tübingen, Germany — <sup>2</sup>Institute for Physical and Theoretical Chemistry, University of Tübingen, 72076 Tübingen, Germany

Organic semiconductors are widely used in optoelectronics due to their tunable electronic and structural properties. For many applications, the active layers consist of heterostructures and the details of the interaction between an electron donating and accepting moieties are the key factors for enhancing devices' efficiency. The chalcogenadiazole ring is a common acceptor core for organic chromophores and a variety of its condensed derivatives is known and used in this context. The presence of heavy chalcogens in the latter can impact the spin-orbit coupling and affect the optical properties. Here, we present a study on organic binary mixtures in thin films prepared by vacuum deposition, namely of dibenzochalcogenadiazolopyrazines as acceptors and known donors; i.e. diindenoperylene, pentacene,  $\alpha$ -sexithiophene. The bulk heterojunction geometry was used with two materials mixed on the molecular level. We discuss the correlation between the mixing behavior of the molecules, and their structural and optical properties to obtain a systematic understanding of the processes occurring in molecular D-A systems based on 1,2,5-chalcogenadiazoles.

CPP 29.8 Wed 11:45 MER 02

**The influence of increased kinetic energy of gold deposition onto polymers** — ●YUSUF BULUT<sup>1,2</sup>, BENEDIKT SOCHOR<sup>1</sup>, KRISTIAN RECK<sup>3</sup>, JONAS DREWES<sup>3</sup>, SUZHE LIANG<sup>2</sup>, TIANFU GUAN<sup>2</sup>, THOMAS STRUNSKUS<sup>3</sup>, FRANZ FAUPEL<sup>3</sup>, PETER MÜLLER-BUSCHBAUM<sup>2,4</sup>, and STEPHAN V. ROTH<sup>1,5</sup> — <sup>1</sup>DESY, 22607 Hamburg — <sup>2</sup>TUM School of Natural Sciences, Chair for Functional Materials, 85748 Garching, Germany — <sup>3</sup>CAU Kiel, Chair for Multicomponent Materials, Faculty of Engineering, 24143 Kiel — <sup>4</sup>MLZ, TUM, 85748 Garching — <sup>5</sup>KTH Royal Institute of Technology, Department of Fibre and Polymer Technology, SE-100 44 Stockholm

High Power impulse magnetron sputtering (HIPIMS) is a novel industrial relevant deposition technique enabling thin metal layers being coated onto polymers with increased adhesion and density. Compared to conventional direct current magnetron sputtering, no pre- and post-treatment is required to achieve these properties. So far there is no report discussing the nucleation and growth process during HiPIMS deposition. In this study, the polymer templates polystyrene (PS), poly-4-vinylpyridin (P4VP) and polystyrene sulfonicacid (PSS) are studied. Even though the polymers are very similar in their structure, it is expected that the distinct different functional moiety influence the kinetics of the initial growth stages of the gold layer. Results of simultaneous in situ grazing-incidence small angle X-ray scattering (GISAXS) and grazing incidence wide angle X-ray scattering (GIWAXS) are presented.

CPP 29.9 Wed 12:00 MER 02

**Analysis of non-equilibrium thin film growth using X-ray photon correlation spectroscopy** — ●INGRID DAX<sup>1</sup>, IVAN ZALUZHNYI<sup>1</sup>, MICHAEL SPRUNG<sup>2</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Universität Tübingen, Germany — <sup>2</sup>Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

Thin film growth is a classic example of a non-equilibrium process in which a wide variety of functional properties can be obtained depending on the growth kinetics. Understanding the microscopic dynamics

underlying the growth of molecular materials is an essential prerequisite for the rational design of complex structures and morphologies with controlled properties.

We perform in-situ X-ray experiments in grazing incidence geometry to follow the formation of thin film growth in real time, which reveals details of the dynamics during this process. This includes the adsorption of molecules on the substrate and the subsequent formation, realignment and diffusion of resulting molecular islands.

Specifically, we use modern coherent techniques based on X-ray photon correlation spectroscopy (XPCS). This resolves dynamics on the scale of 50-1000 nm, providing an unprecedented level of detail into the growth and diffusion of molecular islands during the growth process. We decompose our measurements into dynamic and kinetic time scales by comparing them to simulations, and interpret the results using established XPCS tools. This allows us to show that the time scales of a few 100 seconds are mainly due to kinetics, i.e., the growth of the islands.

CPP 29.10 Wed 12:15 MER 02

**In situ GISAXS investigation of sputtering IZO thin film for optoelectronic applications** — ●HUAYING ZHONG<sup>1</sup>, LUKAS V SPANIER<sup>1</sup>, CHRISTOPHER R. EVERETT<sup>1</sup>, XINYU JIANG<sup>1</sup>, SHANSHAN YIN<sup>1</sup>, MARLENE SOPHIE HÄRTEL<sup>2</sup>, JIAHUAN ZHANG<sup>2</sup>, BERTWIN BILGRIM OTTO SEIBERTZ<sup>3</sup>, MATTHIAS SCHWARTZKOPF<sup>4</sup>, STEPHAN V. ROTH<sup>4,5</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1,6</sup> — <sup>1</sup>TUM School of Natural Sciences, Chair for Functional Materials, Garching, Germany — <sup>2</sup>HZB, Solar Energy, Berlin, Germany — <sup>3</sup>Department of technology for thin-film components, TU Berlin, Berlin, Germany — <sup>4</sup>DESY, Hamburg, Germany — <sup>5</sup>Department of Fibre and Polymer Technology, KTH, Stockholm, Sweden — <sup>6</sup>MLZ, TUM, Garching, Germany

Transparent conducting oxide (TCO) thin films have been studied intensively for optoelectronic devices, such as photodetectors, photovoltaics and light emitting diodes (LEDs). Among the several TCO thin films, zinc doped indium oxide (IZO) has received much attention as interface layer in optoelectronic devices due to its excellent electrical conductivity, optical transmittance, high thermal/chemical stability, low cost and low deposition temperature. Here, ITO glass and spin coated ZnO on ITO glass are used as the templates for IZO thin film deposition via DC magnetron sputtering technique. The growth dynamics of IZO film on these two templates are respectively investigated via grazing small angle x-ray scattering (GISAXS) characterization, and the morphology and optoelectrical properties of final films are further investigated.

CPP 29.11 Wed 12:30 MER 02

**Investigation of Mg(0001) and Mg(1010) surfaces in Grignard electrolytes by reflection anisotropy spectroscopy** — ●MARIO LÖW<sup>1</sup>, HOLGER EUCHNER<sup>2</sup>, and MATTHIAS M. MAY<sup>1,2</sup> — <sup>1</sup>Universität Ulm, Institute of Theoretical Chemistry, 89081 Ulm, Germany — <sup>2</sup>Universität Tübingen, Institute of Physical and Theoretical Chemistry, 72076 Tübingen, Germany

The high abundance and large volumetric capacity of the metal anode make rechargeable magnesium batteries potential candidates for future battery technologies. While understanding and controlling the electrode-electrolyte interface is essential for battery performance, there is often little known about the underlying atomistic interface structure under operating conditions [1].

To address this issue for the case of Mg, we study single crystalline magnesium surfaces in contact with standard Grignard electrolytes and under applied potential [2]. We employ reflection anisotropy spectroscopy (RAS) as an optical, high-resolution technique for the operando investigation of the interfacial structure as a function of the applied electrode potential. The Mg-crystal surface is studied in various solvents and Grignard electrolytes during voltammetric cycling. Finally, we seek comparison to theoretical spectra obtained within the random phase approximation.

[1] Popovic, Jelena. *Nature Communications* 12.1 (2021): 1-5.

[2] Lu, Z., et al. *Journal of Electroanalytical Chemistry* 466.2 (1999): 203-217.