

CPP 57: Thin Films, Nanostructures and Nanoparticles I

Time: Thursday 10:15–13:00

Location: ZEU 114

CPP 57.1 Thu 10:15 ZEU 114

Nanostructured diblock copolymers as templates for metal sputter deposition — ●MARC GENSCH^{1,2}, BJÖRN BEYERSDORFF¹, WIEBKE OHM¹, MATTHIAS SCHWARTZKOPF¹, CALVIN BRETT^{1,2}, DENIZA CHEKRYGINA², PALLAVI PANDIT¹, ANDREAS STIERLE^{1,2}, and STEPHAN ROTH^{1,3} — ¹DESY, Notkestr. 85, D-22607 Hamburg — ²University of Hamburg, Luruper Chaussee 149, D-22761 Hamburg — ³KTH, Teknikringen 56-58, SE-100 44 Stockholm

Nanostructured polymer metal composites demonstrate great perspective for flexible electronic and plasmonic applications [1]. Therefore, the growth kinetics and optical properties for silver deposition on co- and homopolymers were characterized by GISAXS, specular reflectance spectroscopy (UVVis), AFM and resistivity measurements. As substrates, solvent annealed PS-*b*-PMMA diblock copolymers of different molecular weights and their corresponding homopolymers were used. Thus, the influence of the block length and the diblock domains could be investigated. The study reveals the selective wetting of silver on one of the blocks from the copolymer thin films. The silver layers show a clear plasmon resonance. GISAXS measurements indicate a difference in the embedding of silver clusters depending on the polymer substrate. [1] S. V. Roth et al., ACS Appl. Mater. Interfaces 7, 12470 (2015).

CPP 57.2 Thu 10:30 ZEU 114

In situ GISAXS of gyroid terpolymer films during selective solvent annealing — JAMES A. DOLAN¹, KAROLINA KORZEB², RAPHAEL DEHMEL¹, BODO D. WILTS², KARL C. GÖDEL¹, MORGAN STEFIK³, ULRICH WIESNER³, TIMOTHY D. WILKINSON¹, JEREMY J. BAUMBERG¹, ULLRICH STEINER², and ●ILJA GUNKEL² — ¹University of Cambridge, Cambridge, UK — ²Adolphe Merkle Institute, Fribourg, CH — ³Cornell University, Ithaca, NY, USA

Solvent annealing is an effective means to generate order in polymer systems. When solvent enters a film, the resultant plasticization drastically increases the mobility of the polymer chains. Annealing diblock copolymers in selective solvents has already been shown to induce morphological transitions from spheres to cylinders, gyroids, or lamellae. However, for the next more complicated family of linear block copolymers, triblock terpolymers, the morphological effect of selective solvent annealing is not well understood. Therefore, we present the results of *in situ* GISAXS during selective solvent annealing of gyroid-forming polyisoprene-*b*-polystyrene-*b*-poly(ethylene oxide) triblock terpolymer films. The selectivity was adjusted by using mixed vapor ratios of tetrahydrofuran and methanol. Distinct from diblock copolymers, we found that irrespective of the solvent vapor ratios used for annealing, the gyroid morphology remained. However, the selectivity of the solvent did either increase or decrease the unit cell size of the gyroid in both swollen and dried films.

CPP 57.3 Thu 10:45 ZEU 114

Selective metal deposition on block copolymer nanotemplates: A new perspective — ●EZZELDIN METWALLI¹, YUAN YAO¹, VOLKER KÖRSTGENS¹, MATTHIAS SCHWARTZKOPF², STEPHAN V. ROTH², and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching — ²DESY, Notkestr. 85, 22607 Hamburg

The characteristic metal affinity towards one block of self-assembled block copolymer (BC) templates plays an essential role to fabricate highly-order and well-defined metal nanopatterns. Deposition of inert metal atoms on several BC nanotemplates shows an extreme selectivity towards the glassy polymer nanodomain [1]. An explanation based on a difference in the metal-polymer interaction energy cannot adequately explain such extreme affinity. To better investigate this phenomenon, RF magnetron sputtering system was used to deposit gold metal in its atomic state on glassy poly(methylmethacrylate) and soft poly(ethylhexylacrylate) amorphous homopolymers as well as the corresponding statistical copolymer P(EHA-stat-MMA). At time resolution of 15 milliseconds, the nucleation/growth kinetics of gold nanoparticles on these polymer films was monitored using *in situ* grazing incidence small angle X-ray scattering (GISAXS). The coalescence behavior of the inert metal is mainly dominated by an improved atom mobility within the glassy polymers. This study on polymer thin films provides a new perspective into the long-time debated high selectivity

characteristics of metals towards one block of BC based nanotemplates. [1]S. V. Roth et al., ACS Appl Mater Inter 2015, 7, 12470.

CPP 57.4 Thu 11:00 ZEU 114

In situ GISAXS study of Aluminum thin film growth on PS-*b*-PMMA and its constituent homopolymers — BJÖRN BEYERSDORFF¹, ●MATTHIAS SCHWARTZKOPF¹, WIEBKE OHM¹, ALEXANDER HINZ², THOMAS STRUNSKUS², OLEKSANDR POLONSKYI², FRANZ FAUPEL², VOLKER KÖRSTGENS³, FRANZIKA LÖHRER³, PETER MÜLLER-BUSCHBAUM³, and STEPHAN V. ROTH^{1,4} — ¹Deutsches Elektronen-Synchrotron DESY — ²Christian-Albrechts-Universität zu Kiel — ³Technische Universität München — ⁴KTH Royal Institute of Technology

Installation of nanostructured metal films with tailored optical properties is of high importance in many areas of modern science and technology. Aluminum (Al) nanostructures for instance are very promising for surface-enhanced Raman Scattering (SERS) due to their wide tuneability of the plasmon resonance [1]. When depositing metal by sputter deposition on a nanostructured diblock copolymer substrate, a different adatom mobility on the two polymer blocks leads to selective wetting of one block and thus to an imitation of the polymer structure by the metal atoms [2,3]. We report on the sputter deposition of Al on a PS-*b*-PMMA diblock copolymer thin film and its two constituent homopolymers PS and PMMA by means of grazing incidence small-angle X-ray scattering (GISAXS). Cluster growth kinetics on the diblock and the homopolymer films is analyzed and compared to *ex situ* samples investigated by AFM. [1] Gérard et al., J. Phys. D: Appl. Phys., 48, 184001 (2015), [2] Lopes et al., Nature 414, 735 (2001), [3] Roth et al., ACS Appl. Mater. Interfaces 7 (23), 12470 (2015)

CPP 57.5 Thu 11:15 ZEU 114

Structural evolution of gold-*teflon* nanocomposite multilayer structure — ●PALLAVI PANDIT¹, AJAY GUPTA², SIGRID BERNSTORFF³, MATTHIAS SCHWARTZKOPF¹, DENIZA CHEKRYGINA⁴, and STEPHAN ROTH¹ — ¹DESY, Notkestr. 85, D-22607 Hamburg — ²Amity University, 201313 Noida India — ³Eletra, SS 14, I-34149 Basovizza Trieste — ⁴UHH, Lurup. chaus. 149, D-22761 Hamburg

The combination of metal nanoparticles in polymer metrics has gained sustained research interest as their fine control of size and shape leads to the fabrication of materials with novel electronic, magnetic and catalytic properties. This offers some level of controllable performance. Thermal annealing as well can artificially modify the morphology of embedded metal nanoparticles. In this study the structural evolution of gold/PTFE multilayer nanocomposite has been studied using *in-situ* temperature dependent Grazing incidence Small and wide angle X-ray scattering. Nanoparticles exhibited a lognormal size distribution in multilayer structure. A rather well defined inter-particle correlation is observed in lateral and vertical direction. Linear dependence of the size of nanoparticles on square root of annealing time suggests a diffusion control growth of nanoparticles. After annealing at 573 K the nanoparticles distribution become isotropic in both the directions. UV-Vis reflectance spectroscopy has been used to study the Surface Plasmon Resonance of gold nanoparticles. The SPR frequency exhibits a systematic variation with gold content as well as with thermal annealing.

15 min break

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Printed nanostructured polymer films embedded with magnetic nanoparticles — ●SENLIN XIA¹, EZZELDIN METWALLI¹, MATTHIAS OPEL², PAUL A. STANIEC³, EVA M. HERZIG⁴, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching — ²Walther-Meissner-Institut, Bayerische Akademie der Wissenschaften, 85748 Garching — ³Beamline I22, Diamond Light Source, Harwell, OX11 0DE, United Kingdom — ⁴TU München, Munich School of Engineering, Herzog Group, Lichtenbergstr. 4, 85748 Garching

Nanostructured polymer films containing magnetic nanoparticles (NPs) are promising materials due to their potential applications in the areas of high-density storage and magnetic sensors. Owing to the advantages, like large-scale production and energy saving, print-

ing techniques were employed to fabricate hybrid films composed of maghemite NPs and PS-*b*-PMMA diblock copolymer (DBC). External magnetic fields were applied during the printing process to guide the NPs within the polymer matrix. The mesoscopic structure of PS-coated maghemite NPs within the DBC films was investigated as a function of the NP concentration using optical microscopy, AFM, SEM and GISAXS. The PS-coated NPs were selectively dispersed in the PS domains of the lamella-structured hybrid films. At high NP concentrations, the coalescence of NPs into large micro-sized metal-oxide wires was observed. The superparamagnetic behavior of the hybrid film was proved using a superconducting quantum interference device magnetometer.

CPP 57.7 Thu 12:00 ZEU 114

vinyl-terminated Au nanotriangles as platform for the fabrication of hybrid Au@pNIPAM particles for improved SERS responses. — MIGUEL CASADO-RODRIGUEZ¹, CHRISTIAN KUTTNER², MANUEL LOPEZ-ROMERO¹, ANDREAS FERY^{2,3}, and ●RAFAEL CONTRERAS-CACERES² — ¹Universidad de Malaga, Departamento de Quimica Organica. Facultad de Ciencias. Universidad de Malaga 29071. Malaga. Spain — ²Leibniz-Institut fu*r Polymerforschung, Dresden e.V. Hohe Strasse 6, 01069 Dresden, Germany — ³Physical Chemistry of Polymeric Materials, Technische Universita*t Dresden, 01069 Dresden, Germany

We present a new approach for a water-based seedless synthesis of vinyl-terminated triangular Au nanotriangles. This method enables temperature controllable Au size by using 3-butenic acid as reducing agent. We initially analyze the influence of the temperature on the particle size. Interestingly, the presence of terminal double bonds on the Au nanotriangle surface (coming from 3BA) is exploited for the fabrication of core@shell hybrid systems by free radical polymerization of N-isopropylacrylamide (AuNT@pNIPAM). Additionally, Au overgrowth using AuNTs@pNIPAM as seeds permits the fabrication of Austars@pNIPAM particles. The SERS enhancement capabilities of these two core*shell hybrids demonstrate that Au cores with tips and high curvature sites produced the highest plasmonic responses.

CPP 57.8 Thu 12:15 ZEU 114

Nanostructure tuning of sputter deposited Al layers on polystyrene using bias voltage — ●STEPHAN V. ROTH^{1,2}, MATTHIAS SCHWARTZKOPF², BJÖRN BEYERSDORFF², CALVIN BRETT², MARC GENSCHE², WIEBKE OHM², ANDRE ROTHKIRCH², ALEXANDER HINZ³, OLEKSANDR POLONSKY³, THOMAS STRUNSKUS³, FRANZ FAUPEL³, FRANZISKA C. LÖHRER⁴, VOLKER KÖRSTGENS⁴, ADRIAN HAUSSMANN⁴, LORENZ BIESSMANN⁴, and PETER MÜLLER-BUSCHBAUM⁴ — ¹KTH, Teknikringen 56-58, SE-100 44 Stockholm — ²DESY, Notkestr. 85, D-22607 Hamburg — ³CAU, Kaiserstr.2, D-24143 Kiel — ⁴TUM, James-Franck-Str. 1, D-85748 Garching

Nanostructuring the polymer-metal interface in thin films is crucial for organic photovoltaics, flexible electronics and sensors. Hence, we investigated in real-time the different growth kinetics of nanostructured Aluminum layers on polystyrene thin film substrates during DC sputter deposition at applied bias voltages from 0V to -400V and at industrial coating rates. Using grazing incidence X-ray scattering and UV-Vis spectroscopy, we were able to directly correlate the crystallinity, the nanogranular structure and the optical properties at all growth stages during in situ sputter deposition at the applied bias voltages. Electron microscopy confirmed a transition in the nanogranular structure at a

bias voltage around -300 V from a densely packed via a worm-like transient stage to a large cluster layer. Our results offer a versatile route for fabricating tailored metal arrays, ranging from nanoparticulate layers to full scale electrical contacts.

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In situ GISAXS analysis of spray deposited biopolymer thin films — WIEBKE OHM¹, BJÖRN BEYERSDORFF¹, MATTHIAS SCHWARTZKOPF¹, PALLAVI PANDIT¹, CALVIN BRETT¹, MARC GENSCHE¹, SHUN YU², NITESH MITTAL², DANIEL SÖDERBERG², and ●STEPHAN ROTH^{1,2} — ¹Deutsches Elektronen-Synchrotron Hamburg, Notkestraße 85, 22607 Hamburg — ²KTH Royal Institute of Technology, Department of Fibre and Polymer Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden

Flexible biopolymer substrates based on cellulose nanofibrils (CNFs) are gaining increasing interest for nanotechnology such as organic electronics or solar cells since they present a renewable and sustainable alternative for synthetic polymers. In view of efficient industrial scalable fabrication, both the controlled arrangement of the CNFs during deposition and the use of industrial compatible deposition processes are essential.

We thus applied air-brush spray deposition of aqueous dispersions of CNF/water as a versatile deposition technique for preparing of cellulose thin films [1]. In situ grazing incidence small angle x-ray scattering (GISAXS) and atomic force microscopy measurements revealed the inner structure of these cellulose films. The effect of different types of CNFs was explored, enzymatic cellulose as well as TEMPO oxidized cellulose with different surface charges. The influence of different incidence angles of the spray was studied to reveal the impact on ordering of the CNFs. [1] Roth, J. Phys.: Condens. Matter 28, 403003(2016)

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An in-situ STXM approach to understand soft x-ray induced chemical modification in polymers — ●MARKUS MEYER¹, ANDREAS SPÄTH¹, BENJAMIN WATTS², and RAINER H. FINK¹ — ¹Friedrich-Alexander Universität Erlangen-Nürnberg, Physikalische Chemie II, Erlangen, Germany — ²SwissLight Source (SLS), Paul Scherrer Institut, Villigen, Switzerland

Certain binding motifs in organic molecules are very sensitive to UV or XUV irradiation which induces severe chemical modifications. Scanning transmission x-ray microspectroscopy (STXM) was used to follow the evolution of effects like mass loss (due to bond rupture) and chemical changes of sample in an all but in-situ fashion. In our studies we investigated carbonyl group containing ultrathin free-standing films of PMMA, PLA and polycarbonate. The aim is a comprehensive study on x-ray induced chemical modification of the target for resonant and non-resonant excitations. It is found that the cleavage of chemical bonds does not follow a defined reaction pathway, thus directly leading to the formation of new C=C double bonds. In contrary, our studies provide clear evidence of small molecule fragments leaving the sample, thereby changing the chemical nature of the pristine material. This process is accompanied by deposition of residual gas onto the sample of interest as an unavoidable secondary process. Theoretical considerations are applied in a simulation and are able to retrace and to confirm the findings of the in-situ STXM analysis going well beyond recent publications [1]. [1] Leontowich, A. et al, JElectronSpectrosc, 58-64, 206, 2016