

CPP 41: Crystallization, Nucleation, Self Assembly II (joint session CPP/DY, organized by CPP)

Time: Wednesday 16:00–18:30

Location: H42

Invited Talk

CPP 41.1 Wed 16:00 H42

From holes to drops to toroids: Transcription of surface patterns into 3D-morphologies by dewetting — ●GÜNTER REITER¹, SAMER AL AKHRASS², and LAURANT VONNA³ — ¹Institute of Physics and Freiburg Materials Research Centre, University of Freiburg, 79104 Freiburg, Germany — ²Université Claude Bernard Lyon 1, Ingénierie des Matériaux Polymères (IMP - UMR CNRS 5223), 15 Boulevard Latarjet, 69622 Villeurbanne Cedex, France — ³Institut de Science des Matériaux de Mulhouse, (IS2M - UMR CNRS 7361), 15, rue Jean Starcky 68057 Mulhouse Cedex, France

Dewetting of thin films is a simple and thus highly convenient process for creating regularly ordered topographical patterns on various length-scales. Here, we present a general pathway, based on dewetting of a thin polymer film, which allows to convert a chemical surface pattern of hexagonally arranged non-wettable circular patches into a sequence of ordered three-dimensional topographies. With increasing thickness of the dewetting film, cylindrical holes, followed by droplets with the shape of a spherical cap and finally toroids were generated. We identified the width w of the rim, where the dewetted fluid was collected, as the crucial parameter which determined the final three-dimensional morphology. Our experiments demonstrate that for a given surface pattern various three-dimensional morphologies can be obtained by simply varying the initial thickness of the thin film.

CPP 41.2 Wed 16:30 H42

Time-resolved characterization of aggregation during printing of thin films — STEPHAN PRÖLLER¹, FENG LIU², CHENG WANG³, THOMAS P. RUSSELL², ALEXANDER HEXEMER³, PETER MÜLLER-BUSCHBAUM⁴, and ●EVA M. HERZIG¹ — ¹Technische Universität München, Munich School of Engineering, Lichtenbergstr. 4, 85748 Garching, Germany — ²Department of Polymer Science and Engineering, University of Massachusetts Amherst, MA 01003, USA — ³Lawrence Berkeley National Laboratory, Advanced Light Source Berkeley, CA 94720, USA — ⁴TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching, Germany

The nanomorphology can strongly influence the physical properties of thin films. For example, polymer:fullerene mixtures used in the application for organic photovoltaics vary significantly in performance depending on the inner film morphology. Tracking the actual crystallization and aggregation processes on length scales ranging from sub-nanometers to several tens of nanometers reveals how the different growth processes compete with each other leading to the final film morphology.[1] We can track solvent removal, fullerene aggregation and polymer crystallization with time for different experimental conditions using grazing incidence x-ray scattering revealing fundamental mechanisms of thin film formation. This information correlated with device performance helps to derive design principles for large scale, industrial thin film fabrication.

[1] Pröller et al, Adv. Energy Mater. DOI:10.1002/aenm.201501580

CPP 41.3 Wed 16:45 H42

Following the crystallization in PEDOT:PSS films during printing — CLAUDIA M. PALUMBINY¹, FENG LIU², THOMAS P. RUSSELL^{2,3}, ALEXANDER HEXEMER⁴, CHENG WANG⁴, and ●PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching, Germany — ²Materials Science Division, LBNL, Berkeley, USA — ³Department of Polymer Science and Engineering, UMass, Amherst, USA — ⁴Advanced Light Source, LBNL, Berkeley, USA

PEDOT:PSS is one of the most promising electrode materials beyond ITO. Printed films of PEDOT:PSS are compared with ethylene glycol (EG)-doped PEDOT:PSS films and films that are treated with EG after printing and annealing, so-called EG-post-treatment. In-situ GIWAXS is used to determine the structure of the molecules in the crystallites during the printing. During film formation, the dependence of different processing conditions on the resulting interchain coupling (characterized by the pi-pi stacking distance), molecular orientation, and crystallite size are determined as a function of film composition. Thus, understanding the film evolution during the printing process allows for directed modification of solutions and printed films for en-

hanced organic electronic device performance.

15 min. break

CPP 41.4 Wed 17:15 H42

Towards a multiscale study of aggregation of PCPDTBT in presence of a solvent — ●NANCY C. FORERO-MARTINEZ¹, TRISTAN BERAU¹, BJOERN BAUMEIER², and KURT KREMER¹ — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²Department of Mathematics and Computer Science and Institute for Complex Molecular Systems, Eindhoven University of Technology, The Netherlands

Conjugated donor-acceptor polymers are excellent candidates as donor materials for organic photo-voltaic devices due to their charge transport properties. In particular, the microstructure of the low-band-gap PCPDTBT polymer is considered to be affected by the change in morphology of side chains and/or by the processing solvents. The performance of PCPDTBT-optimised solar cells is thus intrinsically linked to the initial preparation of the system: out-of-equilibrium conditions influence the equilibrium system. In this work, we perform multiscale simulations to monitor how the initial presence of solvents drives the formation of PCPDTBT aggregates. We propose as a first step a simplified model of the polymer system that takes into account only CPDT monomers, since their crystalline structure is known experimentally. An atomistic description of the potential energy and the corresponding coarse grained representation are used to study the structure and dynamics of CPDT monomers in solution. We intend to characterise the interactions between polymer and solvent to identify the mechanism promoting aggregation.

CPP 41.5 Wed 17:30 H42

Revealing Structure Formation in conjugated polymers such as PCPDTBT by Optical Spectroscopy — ●ANNA KÖHLER¹, CHRISTINA SCHARSICH¹, FLORIAN FISCHER², KEVIN WILMA³, FABIAN PANZER¹, RICHARD HILDNER³, and SABINE LUDWIG² — ¹Experimental Physics II, University of Bayreuth, Bayreuth, Germany — ²IPOC-Functional Polymers, University of Stuttgart, Stuttgart, Germany — ³Experimental Physics IV, University of Bayreuth, Bayreuth, Germany

There is increasing evidence that the performance of conjugated polymers in organic solar cells is strongly affected by the presence of small crystallites or aggregates. However, short-range order is difficult to detect using structural techniques. Here, we show that optical spectroscopy can be employed to reveal the presence of short-range ordered structures as well as their formation mechanism. We present a comprehensive study of the optical properties as a function of temperature for PCPDTBT in solution and in thin films with two distinct morphologies.[1] Using absorption and photoluminescence spectroscopy as well as Franck-Condon analyses, we show that PCPDTBT in solution undergoes a phase transition (critical temperature: 300 K) from a disordered to a truly aggregated state upon cooling. Comparison is made to the formation of aggregates in P3HT.[2] The saturation value of aggregates in solution is reached in PCPDTBT thin films at any temperature. In addition, we demonstrate that a low percentage of thermally activated excimer states is present in the films at temperatures above 200 K.

CPP 41.6 Wed 17:45 H42

Comparing molecules and solids across structural and al-chemical space — ●SANDIP DE — Laboratory of Computational Science and Modelling, Institute of Materials, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Evaluating the (dis)similarity of crystalline, disordered and molecular compounds is a critical step in the development of algorithms to classify structures, search chemical space for better compounds and materials, and drive the next generation of machine-learning algorithms for predicting the stability and properties of atomic systems. In recent years several strategies have been designed [1-3] to compare atomic coordination environments. In particular, the Smooth Overlap of Atomic Positions has emerged as a natural framework to obtain translation, rotation and permutation-invariant descriptors of atomic environments, driven by the design of various classes of machine-learned inter-atomic

potentials. Here we will present few examples showcasing how one can construct a Sketchmap[4-6] representation of databases of both molecular and bulk structures, using (dis)similarity definitions based on such local descriptors that can treat alchemical and structural complexity within a unified framework.

[1] A. P. Bartok, et al, Phys. Rev. B88, 054104(2013) [2] Ali Sadeghi et al, J. Chem. Phys. 139, 184118 (2013) [3] Sandip De et al, Phys. Rev. Lett. 112, 083401(2014) [4] G. A. Tribello et al, Proc. Acad. Natl. Sci. U.S.A. 109 5196 (2012) [5] M. Ceriotti et al, Proc. Acad. Natl. Sci. U.S.A. 108 13023 (2011) [6] M. Ceriotti et al, J. Chem. Theory Comput. 9 1521 (2013)

CPP 41.7 Wed 18:00 H42

Area confined nucleation and position control by vapor deposition — •OLEG BULLER¹, HONG WANG², WENCHONG WANG², LIFENG CHI², and ANDREAS HEUER¹ — ¹Institut für Physikalische Chemie, WWU, Münster — ²Physikalisches Institut and Center for Nanotechnology, WWU, Münster

Experimentally it is possible that after vapor deposition of organic molecules on surfaces, prepatterned with a regular gold grid, in basically each cell a single nucleus is formed (defects less than 2%) exactly in the center of each grid. This enormous nucleation and position control can be reproduced for different organic molecules. Via combination of kinetic Monte Carlo simulations and analytical calculations a theoretical explanation for this high quality is provided. In this way it is possible to understand, e.g. that the size of the grid and the external flux simultaneously have to be varied in order to stay in the regime of perfect nucleation and position control. A direct comparison between

the experimental and theoretical results is presented.

CPP 41.8 Wed 18:15 H42

Coverage dependent nucleation of PTCDI-C₈ studied by AFM and *in situ* real time XRR and GISAXS — •ANTON ZYKOV¹, SEBASTIAN BOMMEL², CHRISTOPHER WOLF¹, LINUS PITHAN¹, CHRISTOPHER WEBER¹, PAUL BEYER¹, GONZALO SANTORO³, STEPHAN V. ROTH², and STEFAN KOWARIK¹ — ¹Inst. f. Physik, Humboldt Universität Berlin — ²Deutsches Elektronen-Synchrotron DESY, Hamburg — ³Inst. de Ciencia y Tecnología de Polímeros, CSIC, Madrid

Assembly of molecular building blocks into functional nanomaterials is of great importance for devices however it is difficult to follow molecular scale morphology during growth. Here we show that modern synchrotron small angle X-ray scattering (GISAXS) and X-ray reflectivity (XRR) agree with post growth AFM measurements of roughness and island densities of PTCDI-C₈ on silicon oxide, but additionally offer *in situ* and real time capability. We observe interesting differences in the growth of the 1st and 2nd monolayer (ML) such as different molecular adsorption probabilities and a transition of the island shapes. From the scaling of saturation island densities with substrate temperature and growth rate we evaluate ML dependent nucleation energies and critical nucleus sizes. We discuss our results in the framework of nucleation theories and find that 2nd ML nucleation does not proceed in the often applied diffusion limited aggregation regime. This work shows that X-ray techniques are similarly suited for continuously monitoring multilayer growth and unravel intricate details about sub-monolayer growth.