| | | |
|---|---|---|
| ESRF | **Experiment title:**<br>Time-resolved USAXS investigation of the sedimentation process of colloidal solution onto pre-patterned support | **Experiment number**:<br>Sc-1671 |
| **Beamline**:<br>ID 2 | **Date of experiment**:<br>from: 20.05.05 to: 23.05.05 | **Date of report**:<br>23. 08. 05 |
| **Shifts: 15** | **Local contact(s): M. Sztucki** | *Received at ESRF:* |

Beate Reinhold, Tushar Sant, Ullrich Pietsch

*Institute of Physics, University of Potsdam, Am Neuen Palais 10, 14415 Potsdam, Germany*

**Report:** The 3D-ordering of monodisperse colloidal spheres is of great interest for many kinds of technical applications (e. g. optical and photoelectric devices, photonic crystals, data storage) [1]. Various approaches are described in literature how one can organize colloidal particles to large 3D domains of single crystalline layers [2]. In contrast to AFM X-ray scattering is a tool to get information about the 3D order of colloidal crystals [3]. In case of large colloidal radius the achievable momentum transfer is very small and the scattered beam appears very close to the transmitted primary beam. For this reason we carried out experiments at the USAXS beamline ID02 in GISAXS and transmission geometry.

The aim of the experiment was to perform in-situ deposition experiments in order to find optimum condition for the preparation of large mono-phase domains. Polystyrene particles (PS) with diameter 400 – 1000 nm were deposited onto a substrate that is pre-structured by a surface relief grating or a surface relief dot array. We used Gravity Sedimentation as deposition technique due to its good deposition results in previous experiments and because it can be simply handled for in-situ measurements at a synchrotron radiation beamline. Time-resolved measurements were performed in GISAXS geometry. The sample was illuminated with a parallel beam of 12.4 keV and the scattering signal was observed 10 m upstreams by CCD with a maximum time resolution of about 20 seconds. The experimental setup consisted of a Peltier cell with temperature controller housed in a Plexiglas container. In contrast to former measurements (SC 1381 in 2004) the use of the container provided a stable gas athmosphere above the sample heated to a constant temperature.

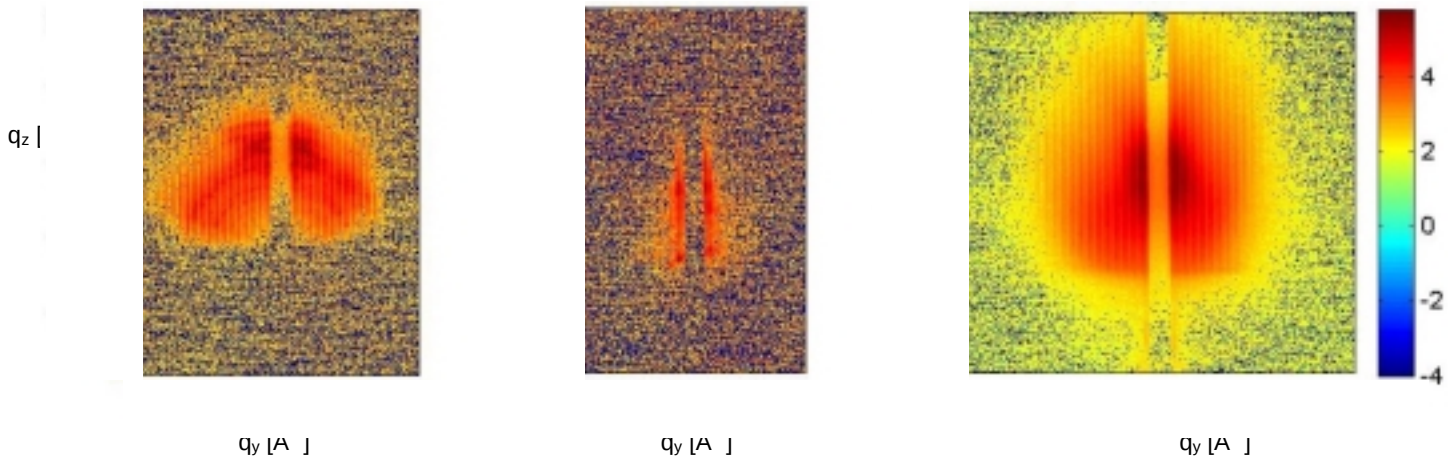


Fig. 1: Scattering image in GISAXS geometry before and after colloidal deposition

The pre-patterned substrate is indicated by the appearance of a series of grating peaks along the $q_y$ direction. These grating peaks disappeared straight after dropping the colloidal solution onto the sample and the weak liquid scattering signal did not change over 4 - 5 hours. Essential changes appeared within a time window of about 5 to 15 minutes (see Fig. 1) where the liquid scattering transforms into scattering of the grating structure again indicating deposition of the colloids. After this time window the scattering pattern kept constant again. The time of solidification, $\tau$, was depending on the temperature used. At $T\text{-}T_{RT}$ = 5 – 7 K, where $T_{RT}$ is the room temperature, $\tau$ was about 6 to 8 minutes. Unfortunately the colloidal ordering was not good enough to create a particular scattering pattern, i.e. the large illuminated sample area did contain several, slightly misaligned domains. Therefore the presence of ordered colloidal domains could be verified only from the increased intensity of the rating peaks measured before and after deposition. Most interesting was the observation that the degree of ordering was higher in the liquid phase right before complete evaporation of solvent compared with the ordering in solid phase.

Ex-situ Atomic Force Microscopy inspections did supply information of the structure of the deposited colloids from the surface of the sample (see fig. 2). X-ray scattering using highly collimated monochromatic synchrotron radiation light was the only tool to get information about 3D order of thin film colloidal crystals.
The achieved colloidal ordering of coated samples could be verified by measurements in transmission geometry (see figure 3). The ring structure is caused by the form factor of individual round-shaped colloids superposed by scattering maxima originated from the underlying grating structure. Verified by ex-situ AFM we found that a picture like fig.2 did appear only if incident beam hit a mono-domain of colloidal ordering (see fig.3). The dot structure in fig.3 is produced if the colloids are exactly arranged along the grooves of the grating (here aligned parallel to $q_x$ axes). Otherwise the dot structure is missing and the colloidal form factor appears only. Unfortunately, in this sense fig.2 can be used as benchmark for perfect colloidal ordering.
The colloidal size did not match exactly the grating period for the present experiment. Therefore we plan to repeat the experiment with better matching between colloids and pre-patterned substrates.

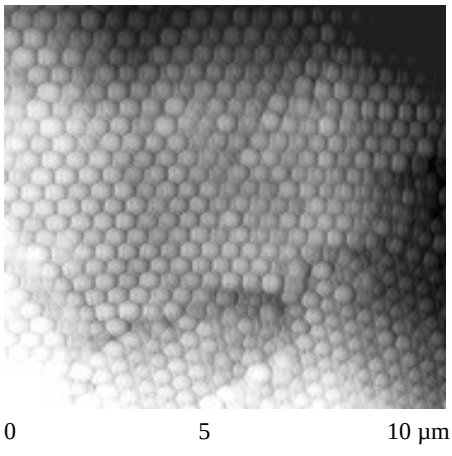


Fig. 2: AFM picture of 420 nm PS colloids on grating (p = 1µm)

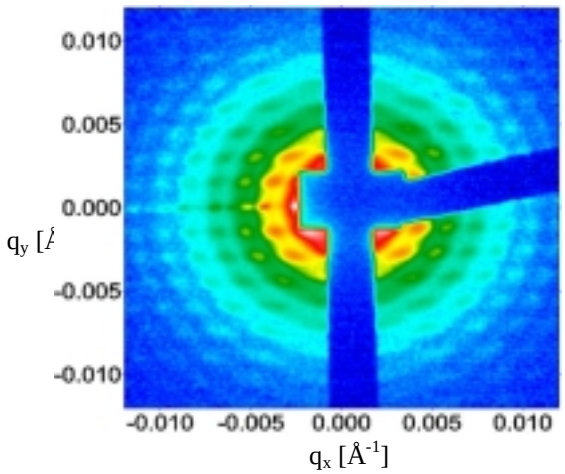


Fig. 3: Scattering image in transmission of 420 nm PS colloids on grating (p = 0,7 µm)

**Acknowledgement :** This work was performed in collaboration with MPI-KFG Golm.

**References**

[1] N. Kobayashi and C. Egami, Opt. Lett., 30 (2005) 299
[2] Y. Xia et. al., Adv. Mater., 12 (2000) 693
[3] S. Narayanan, J. Wang and X.-M. Lin, Phys. Rev. Lett. 93, (2004) 135503