| ESRF | **Experiment title:** In situ X-ray reflectometry of growing colloidal crystal on conductive substrate. | **Experiment number**: HS-4083 |
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| **Beamline**: ID10B | **Date of experiment**: from: 16/06/2010 to: 21/06/2010 | **Date of report**: |
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**Introduction**

It is well known that artificial opals (AO) consist of the submicron monodisperse microspheres packed in a face centered cubic structure. AO and materials on their basis are considered as good candidates for the creation of high quality Photonic Crystals (PhC). The latter have recently attracted great attention due to their unusual optical properties and promising applications in optical devices. The basic problem in creating AO is formation of defects at every stage of synthesis, which cause disorder of structure and subsequent deterioration of optical properties. There are several interactions, which leads to the crystal forming – Coulomb interaction between spheres or between substrate and spheres, capillary forces and gravity. Each of these interactions affects the quality of the AO structure. A separate impact of each driving force at different stages of the crystal formation is not really explored.

The vertical deposition technique is at the time being the most effective method for AO creation allowing synthesis of high quality defectless (fault-free) structures with an area of several centimeters. It was supposed that the vertical deposition technique suggests that meniscus moves along a fixed vertical substrate and the crystal is formed in the area under meniscus [1]. We are particularly interested in answering the following question: can the charged spheres form hexagonal layers in a bulk sample far from the meniscus or it is only possible in this triple gas-liquid-solid interface? How ordering of the spheres along the substrate depends on the distance from the gas-liquid interface?

**Samples and experimental techniques**

In our experiments we have used several types of the suspensions of colloidal microspheres and substrates. Microspheres were PMMA, polystyrene and silica with diameters (D) from 90 to 250 nm and dispersion (ΔD) of 5%. The substrates were glass with golden layer of thickness of tens nanometers, or, the plate of Si single crystal with well polished working surface along (100) crystallographic plane.

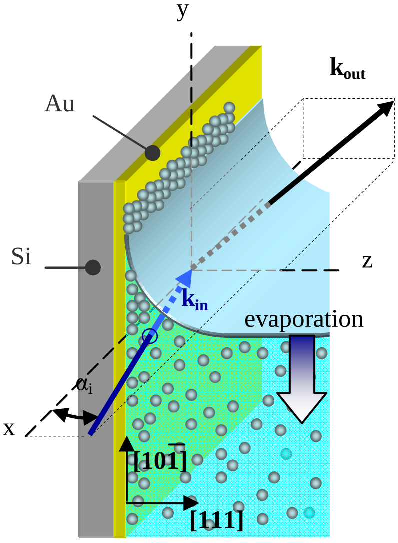

Fig.1. The scheme of the experiment

We have applied grazing incidence x-ray diffraction (GID) method and x-ray reflectometry to study ordering of the charged spheres at the solid-liquid interface. We have used maximum energy available on ID10B (22 keV), which provides both reasonable penetrations through the suspension and angular resolution of the scattering. We used two experimental procedures for the measurements. (i) The container with suspension, the substrate, therefore, the spot irradiated by the X-ray beam were fixed during the experiment (Fig. 1). The suspension evaporates and meniscus moves along a fixed vertical substrate, thus the x-ray reflection is taken from the same spot of the sample. This spot is located (a) deep in suspension at the early stage, (b) exactly under meniscus, (c) above meniscus,

(d) far away from suspension. The second procedure is the y-scan of the sample (along y-direction Fig. 1) after the measurements at the 1 geometry. In this case the sample was moved along the vertical direction and x-ray beam probed the surface of the substrate at different positions: (a) well below, (b) exactly in, (c) just above, and (d) well above the meniscus.

**Grazing incidence x-ray diffraction**

The investigation of the growth during the first experimental procedure had not shown any ordered/disordered structure formed on the substrate. This occurred because of the necessary experimental

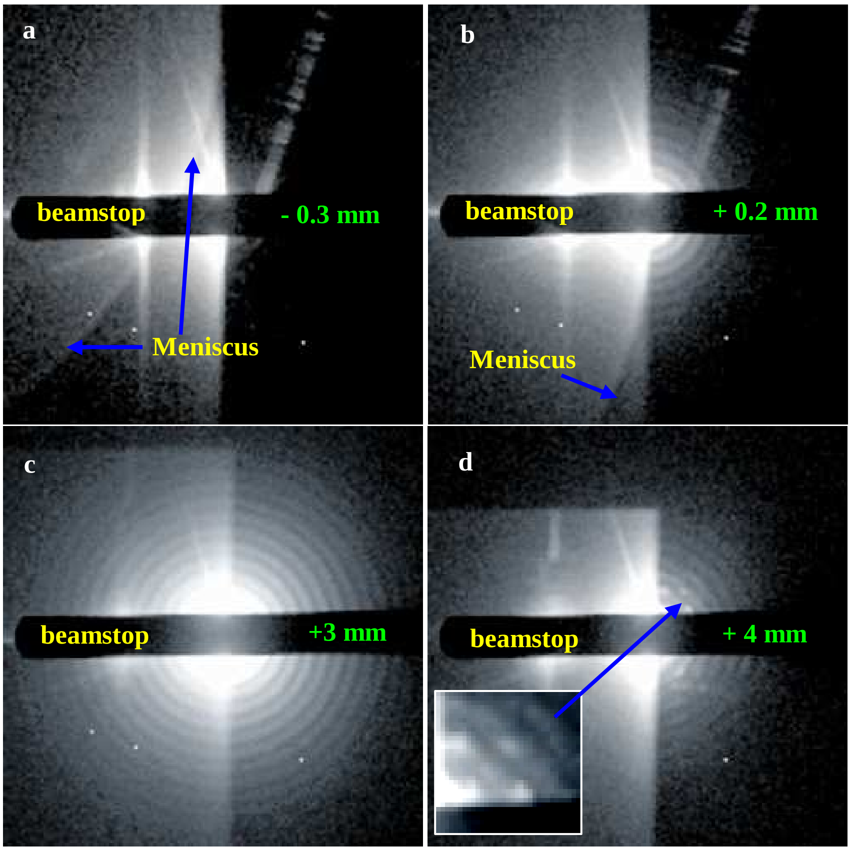


Fig. 2. Grazing incident X-ray images taken during the y-scan measurement in synthesis of AO structure on the Si substrate by vertical deposition technique. The silica single crystal substrate is dipped in 19% water solution of PMMA microspheres with a diameter of 180 ± 9 nm. The numbers show the position of the irradiated spot with respect to the triple gas-liquid-solid interface (below and above the menuscus).

conditions for growing crystal were not fulfilled. Particularly air-conditioning of the hutch significantly changes the temperature regime of the experiment. The results for measurements for the second experimental procedure are presented at Fig. 2. The positions of the irradiated spot with respect to the triple gas-liquid-solid interface (below and above the menuscus) are shown in Fig.2 (a-d). It is seen that when the beam passes through suspension under meniscus, neither concentric rings which corresponds to the scattering by spheres (form-factor of spheres) nor diffraction reflections appear (Fig.2 a). It may mean either that there is low concentration of particles near the substrate, or, more probable, that the contrast between the particles and the solution is very low. In the region of triple gas-liquid-solid interface concentric rings arise, which were identified as the form factor of the spherical particles with the diameter of 190 nm. One concludes that particles accumulate on the substrate straight under the meniscus (Fig.2 b) and become visible as soon as the contrast has changed from particle-suspension to particle-air. The y-scan further up had demonstrated the regions where the scattering intensity and number of rings increases as shown in Fig.2 c or disappear again. There were some regions as well, where one observes the spots coming from the crystal structure (Fig.2 d). These preliminary results should be additionally testified.

The general conclusions, however, are that the spheres form the desirable AO structure during the “drying” process but not in the suspension or under meniscus and that the grazing incidence x-ray diffraction method and x-ray reflectometry are the best to study ordering of the charged spheres at the solid-liquid interface.

**References**


[1] M.G. Nikolaides et al., Nature, 420, 299 (2002)