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Real-time tracking of nanoparticle self-assembling using GISAXS

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ABSTRACT

The self-assembling of iron oxide nanoparticles deposited on a substrate was studied employing the *in situ* time-resolved grazing incidence small-angle X-ray scattering with a temporal resolution of 28 ms. After the evaporation of the solvent, an ordered monolayer exhibiting a hexagonal close-packed arrangement of nanoparticles was found. The X-ray scattering data from the drop did not show a presence of ordered clusters in the drop volume and/or ordered islands at the drop surface. Three stages of the drop evaporation process were distinguished and analysed.

1. Introduction

The self-assembly of nanoparticle superstructures is one of the most attractive techniques that enable the engineering of nanoscale devices at scales beyond the spatial limit of contemporary lithographic methods. Various techniques making use of nanoparticle self-assembling were developed up to now [1,2]. In the simplest case, an ordered nanoparticle array is formed during the evaporation of a drop of nanoparticle suspension deposited onto a substrate.

Self-assembling is a process where interactions such as van der Waals attraction, hard-core (steric) repulsion as well as drying kinetics and solution/substrate interfacial energy affect the final configuration of the nanoparticle array. The complexity of the process is a serious limitation

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of technological applications of the self-assembly. A deeper understanding of the self-assembling processes is essential to control the assembling process.

Recently a time-resolved study of the self-assembling of iron oxide nanoparticles by the grazing incidence small-angle X-ray scattering (GISAXS) technique was published by us [3]. Our data show that ordered arrays (clusters) of nanoparticles are not formed inside and/or at the drop surface during the drying process. In the final evaporation stage of the drop, a tendency of highly non-linear behaviour was observed. The aim of this work is to analyse the final evaporation stage in more detail using the GISAXS experiments with a time resolution of 28 ms.

2. Experimental

The iron oxide nanoparticles were synthesized by a high-temperature solution phase reaction of metal acetylacetonates ($Fe(acac)_3$) with 1,2-hexadecanediol, oleic acid, and oleylamine in phenyl ether. The details of the preparation procedure are described elsewhere [4]. Toluene is used as a solvent. The Fe_3O_4 nanoparticles are superparamagnetic at the room temperature (the blocking temperature $T_B = 22$ K [5]).

For self-assembling studies, the 5 μL drops of a colloid solution were deposited manually onto Si substrates with a native SiO_2 layer over an area of $\approx$1 cm^2. The drop was dried in air at room temperature.

The small-angle X-ray scattering (SAXS) patterns were taken with a Nanostar device of Bruker AXS using the wavelength of 0.154 nm.

The GISAXS experiments were performed at the beamline BW4 at the Hamburg Synchrotronstrahlungslabor [6]. The focused X-ray beam (65×35 μm^2) with a wavelength of 0.138 nm hit the silicon substrate at 0.2° grazing angle. We used the X-ray camera PILATUS 100 K at a distance of 225 cm from the sample. The camera exposure time was set to 28 ms and the read-out time was 3 ms.

3. Results and discussion

A representative example of the self-assembled monolayer of Fe_3O_4 nanoparticles prepared by drying a drop and taken by scanning electron microscope (FEG Leo 1550) is shown in Fig. 1(a). The monolayer shows a polydomain structure. The typical size of a domain is around 400×200 nm Nanoparticles inside the domains are ordered in the hexagonally close-packed (hcp) array.

The average size and size dispersion of Fe_3O_4 nanoparticles were determined by SAXS (Fig. 1(b)). From the simulation of the experimental data, the average diameter of nanoparticles is 6.2 nm $\pm$ 0.7 nm, i.e. the size dispersion of 11% was determined. The simulation was performed assuming the spherical shape of nanoparticles and a random distribution of nanoparticles in the colloid.

Similar results were found for the GISAXS pattern of the initial stage after the deposition of the drop of colloidal solution on the substrate (not shown). A featureless GISAXS pattern with a monotonous intensity decrease along q_y and q_z axes indicates an absence of ordered arrays and/or islands of nanoparticles in the initial stage after the deposition of the colloid.

A typical GISAXS pattern corresponding to the final stage when the solvent is evaporated and an ordered monolayer is formed and shown in Fig. 2(a). The self-assembled monolayer is manifested by a side maximum at $q_y \sim -0.82$ nm^{-1}. The intense streak at $q_y = 0$ nm parallel with q_z is the radiation scattered by substrate roughness and the nanoparticle layer. As it was shown in Ref. [6], a hexagonal paracrystal model with an average particle diameter of 6.1 ± 0.6 nm, which is in good agreement with the SAXS data, and an average interparticle distance of 7.5 $\pm$ 1 nm resulted from simulations of the pattern.

In order to analyse *in situ* a possible formation of ordered islands or clusters of nanoparticles inside the drop or at the drop surface, we used a standard GISAXS geometry and a modified GISAXS geometry, *a drop mode* [6]. Here, the substrate was vertically translated downwards by 100 μm out of the primary beam after having been aligned and subsequently tilted by 0.1° in order to suppress the X-ray scattering from the substrate. In this way, the X-ray scattering coming from the drop and its surface, as it was crossing the primary beam during evaporation, was measured.