Structural properties in monolayers and multilayers of magnetic self-assembled nanoparticles.

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Cluster-assembled systems or so-called nanocrystal superlattices are currently investigated extensively due to the potential to fabricate novel materials with tunable structural, optical, electronic or magnetic properties\cite{1}. Nowadays, by chemical synthesis one can achieve perfectly homogeneous particles with a very narrow size distribution of less than 5\%, leading to an improved self-assembly of NPs, a process driven by various interaction energies (inter-particle and particle-to-substrate) and the entropy \cite{2}. The process of self-assembly of NPs strongly resembles the pseudomorphic growth process of thin epitaxial films. For thin films there exist three basic growth modes, i.e. Volmer-Weber (island) growth, Stranski-Krastanov (combination of layer and island) growth and Frank-van-der-Merwe (layer-by-layer) growth. In the Institut für Experimentalphysik IV of the Ruhr-Universität Bochum, it was possible to reproduce all three growth modes also in NP superlattices after spin-coating NP-solutions onto various substrates \cite{3}. In order to investigate the different NP assembly modes and to determine the short-range and long-range structural correlations, GISAXS experiments were performed at Hasylab, BW4. The results provided an insight on the NP-superlattice orderings as function of different substrates and spin-coating conditions and allow to trace an analogy with colloidal epitaxial growth.

Commercially available NPs from Ocean Tech LLC, prepared by thermolysis of iron oleate complexes in presence of oleic acid at elevated temperatures were used for the purpose of this study. The NPs have a mean diameter of 18 nm with a size distribution of 5\% and are dispersed in toluene as solvent. The substrates used were silicon (Si) and PMMA (with different molecular weights) coated silicon (PMMA 4P, PMMA 33P). The PMMA 4P and PMMA 33P substrates were prepared by spin-coating PMMA on Si. In another experiment self-assembly was achieved by sedimentation on PMMA 4P with excess of toluene.

SEM was used for real space characterization, while grazing incidence small angle x-ray scattering (GISAXS) was used for the reciprocal space mapping. The GISAXS patterns were measured at Hasylab beam line BW4 at a photon energy of 8.978 keV. The GISAXS images were captured by a MAR CCD camera with 2048×2048 pixels and a pixel size of 79.1μm. The sample to detector distance was 210.44 cm, which gives an angular resolution of 0.00215. The angle of incidence was 0.5. Figure 1a shows an SEM image of the NPs spin-coated on Si substrate, a monolayer of NPs in hexagonal close packed (HCP) order. Figure 1b shows the SEM image on PMMA 4P. The NPs form 3D islands of 1μm in size, separated by few hundred nms from each other. The NPs inside each island (inset of the figure), lack long-range order. The NPs on PMMA 33P (Figure 1c) form a network of islands. The inset shows that the NPs are arranged in HCP structure. The GISAXS pattern for the NPs on Si (Figure 1d) has two key features, the ring like intensity distribution, representing the form factor of the NPs and the Bragg peaks, representing the structure factor of the lateral pair-correlation function\cite{4}. The Bragg peak positions could be assigned to a 2D HCP lattice with lattice constant 20.38 nm. The GISAXS pattern on PMMA 4P (Figure 1e) shows only broad rings without any in-plane Bragg peaks, due to the absence of any long range ordering inside the islands. The position of the ring matches with the intra particle distance. The GISAXS pattern on PMMA 33P (Figure 1f) shows again a 2D HCP lattice reflecting the polycrystalline like order inside the islands. The NP film formation reveals a striking similarity to the atomic thin film growth process. The three thin film growth modes are (a) Layer by layer growth (Frank-van-der-Merwe/FM growth), (b) Island growth (Volmer-Weber/VW growth) and (c) Layer plus Island growth (Stranski-Krastanov/SK growth). In the atomic growth process the different modes are basically driven by two parameters, namely lattice mismatch and surface interaction energy.
between the deposited material and the substrate. In the current scenario for NPs the first parameter could be neglected because the NP diameter is much bigger than the atomic lattice. So the deciding factor is the NP solution and film interaction energy, which shapes the film morphology. The two surface energies involved in the process are substrate-NP (SN) and NP-NP (NN) interactions. In a simple model, NN < SN implies FM growth, NN > SN implies VW growth and NN = NN implies SK growth mode. The NP growth on Si resembles FM growth, while that on PMMA 4P resembles VW growth.

![Figure 1: SEM (a, b, c) and GISAXS (d, e, f) images on Si, PMMA 4P and PMM 33P substrates respectively.](image)

References