Chapter 9

Final Conclusion and Outlook

Iron oxide nanoparticles of mean diameter 20 nm and 18 nm synthesized chemically and dispersed in toluene were self-assembled on silicon substrates. Depending on the concentration of toluene, monolayer and multilayer of nanoparticle films were formed. The nanoparticle films were then annealed at 80°C in air, 170°C in air, 230°C in vacuum and 500°C in vacuum. The annealing assisted in tuning the magnetic properties by tuning the structural properties of the corresponding iron oxide phase without affecting the shape and size of the particles. A series of x-ray diffraction and electron diffraction measurements were performed to reveal the crystal structure of the nanoparticles. The diffraction measurements show that all the samples are in a mixed phase state of wüstite (Fe₉O), maghemite (γFe₂O₃) and magnetite (Fe₃O₄) except the sample annealed at 170°C in air, which corresponds to a single phase magnetite or maghemite. The crystalline structure of individual nanoparticles were revealed by dark field TEM and HRTEM investigations. These studies show that each nanoparticle is in a mixed phase state. Some particles are also single crystalline. The magnetometry measurements corroborate the x-ray and TEM studies. The magnetization versus temperature measurements under zero field cooling and field cooling protocols for the sample annealed at 80°C in air clearly shows the presence of wüstite in the sample. The exchange bias in the film confirms an antiferromagnetic and ferrimagnetic interfacial interaction. The samples annealed at higher temperatures represent superparamagnetic behavior with strong dipolar interactions. The sample annealed at 230°C in vacuum shows the Verwey transition at 111 K, which is a
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Figure 9.1: Schematic structure of individual nanoparticles after different heat treatments.

signature of the magnetite phase. The Verwey transition has rarely been observed in nanocrystalline materials in the literature. The appearance of Verwey temperature in this case indicates at the formation of high purity magnetite with the desired stoichiometry. The schematic of different iron oxide phases after different heat treatments are shown in Figure 9.1. The magnetic measurements further indicate at the presence of magnetic dipolar coupling between the particles. Thermoremnant magnetization (TRM) and isothermoremnant magnetization (IRM) curves were measured as the finger prints of the mixed phase magnetic structure, where one is antiferromagnet and the other is a ferrimagnet. The samples annealed at 170°C in air and 230°C in vacuum show unusual peaks in the TRM and IRM curves, which has not been observed in the literature so far. The peak position (magnetic field where it appears) gradually decreases with temperature, which can be compared to the magnetic phase diagram of the antiferromagnetic wüstite in nanocrystalline state.

The nanoparticles were ordered in hexagonal close packed structures as shown by the SEM image in Figure 9.2a. The long range in-plane and out-of-plane ordering were revealed by XRR and GISAXS measurements. The multilayer Bragg peaks in the reflectivity measurements for samples annealed at different temperatures show that the out-plane ordering remains intact as obtained by a simple spin-coating technique. The Bragg peak corresponds to a five layer system and the position of the Bragg peak corresponds to a layer ordering of 19.5 nm, which matches well with a hexagonal close packed structure. The GISAXS images show satellite peaks, which correspond to the in-plane hexagonal ordering.
of the nanoparticle films as shown in Figure 9.2b. The peak positions match with a two-dimensional hexagonal lattice. The hexagonal ordering remains intact in the multilayer case albeit smaller coherence length compared to the monolayer.

The self-assembly process generally depends on the surface energy of the deposited material and the substrate. In case of spin-coated samples it was observed that the nanoparticles self-assembled on different substrates in different morphology. The resemblance of the morphology of nanoparticle films to three thin film growth modes, Frank van der Merwe growth (layer by layer), Volmer-Weber growth (island) and Stranski-Krastanov growth (layer by layer plus islands) obtained in case of atomic thin films is one of the highlights of the present work. These samples were investigated by SEM and GISAXS measurements, which complement each other by correlating the real space image to the reciprocal space image.

The nanoparticles were also self-assembled on pre-defined templates made by electron beam lithography processes and reveal satellite peaks in the rocking scans corresponding to the separation of the trenches. Further investigation is currently going on to measure the magnetoresistance of these samples in our group. The dependence of resistance on the geometric confinement is highly interesting for spintronics applications.
So far the magnetic behavior from the total volume of the sample was only measured. But polarized neutron reflectivity (PNR) reveals the depth dependence of the magnetization profile. For PNR measurements the samples annealed at 230°C in vacuum was used, which contains the highest amount of magnetite with highest magnetization. The PNR curves correspond to a five layer multilayer similar to the one investigated by XRR. The Bragg peaks shown by arrows in Figure 9.3 a and b corresponds to a multilayer ordering of 19 nm, which matches with the XRR measurements. A simple model system was used to fit the reflectivity and PNR curves as shown in Figure 9.3c. Each layer was subdivided into a tri-layer system consisting of the oleic acid shells and the iron oxide in the middle. The two PNR curves measured for up and down neutrons at an applied field of 5 kOe (Figure 9.3a) show a magnetization state, where the film is 80% magnetized. The PNR curves measured at remanence (Figure 9.3b) show a demagnetized state with zero net magnetization. The depth dependence of nuclear scattering length density profile (Nb) was same for both the samples and shows a gradient (Figure 9.3d).
But the magnetization over individual layers persist as obtained from the fitting, which shows non-zero magnetic scattering length density (Np) at remanence. This behavior was explained by taking the magnetic dipolar coupling amongst the particles into account. The dipolar coupling leads to local magnetic states, where spins are aligned even in the absence of a field similar to a ferromagnet. The domains are bigger than the coherence length of the neutron wave field and hence shows non zero magnetization value per layer. This case resembles to a Superferromagnetic state formed purely by dipolar coupling. These domains are different from the regular ferromagnetic domains and do not have an extended domain walls. These domains are confined to the individual layers, such that magnetic flux lines can not go out of the film plane. Figure 9.4a and b show the magnetic SLD values at 5 kOe and at remanence, respectively. Figure 9.4c and d show the corresponding sketches of the domain states in case of a dipolarly coupled nanoparticles. In case of a monolayer, the situation is identical, which confirms the hypothesis of the formation of Superferromagnetic domains.

In summary, the thesis provides a complete structural and magnetic ordering
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of nanoparticle films formed by self-assembly. The structural ordering spans a length scale from atomic to the microscopic scale. The combined structural and magnetic investigation is necessary to identify different iron oxide phases present in the system. Advanced scattering techniques are used to quantify the in-plane and out-of-plane ordering of nanoparticle films. The PNR measurements along with the fitting is successfully implemented to understand and highlight the influence of magnetic dipolar interaction in formation of Superferromagnetic states both in multilayer and monolayer. As nanoparticles are compared with atoms and many atomic structures are mimicked with nanoparticles, one would expect that the same can be extended to the magnetic systems as well. In case of magnetic systems, the atomic spins are replaced by superspins and different spin structures can be made artificially by tuning the dipolar interaction. The present work takes a small step in realizing that goal by showing the existence of ferromagnetic like domains in the chemically synthesized magnetic nanoparticle systems.