Magnetic Force Microscopy can probe the magnetic properties of individual nanoparticles, and provide precise and localized information of their magnetic structure. Iron NPs with sizes ~50-70 nm were imaged by MFM using magnetic CoCr coated Si probes with a proper tip-sample separation to minimize direct topography effects. The bright and dark contrast observed in the phase images agreed with the single-domain magnetic structure. Indeed, the MFM phase images recorded with opposite tip polarity showed inversed contrasts, confirming the ferromagnetism of the measured Fe NPs. Furthermore, the orientation of the NP magnetization was simulated by modeling the NP and the magnetic CoCr coating as point dipoles. It turned out that as-deposited Fe NPs showed random assemblies with no preferential orientation due to large interparticle distances. The sharp topographical feature of NPs contributed to the additional side contrasts observed in the MFM phase images. At any rate, the detailed determination of the remnant magnetization orientation of the Fe nanostructures, and their domain structure configuration, is beneficial in a multitude of applications where the magnetization of isolated magnetic NPs on surfaces is required.
5.1 Introduction

Magnetic nanoparticles (NPs) have been extensively studied due to their applications in a variety of fields such as data storage \cite{1,2} and biomedicine \cite{3-7} including contrast enhancement in magnetic resonance imaging (MRI), drug delivery, and hyperthermia. The preparation of magnetic NPs can be achieved by various methods, among which inert gas condensation (IGC) provides the technical ability to produce high purity magnetic NPs with nanometric scale precision and diverse motifs. This bottom-up method of material growth and assembly make it possible to control the morphology and size to allow for tailored magnetic properties \cite{8,9}.

In ultrafine magnetic nanostructures, such as Fe NPs in this work, the magnetic properties are dramatically different from the bulk matter. Moreover, the magnitude of ferromagnetic NP moment, particularly of the 3d series, can be influenced by the band structure \cite{10}. In the near surface region the magnetic moment per atom experiences drastic variation with the distance from the surface due to the discreteness, which results from reduced coordination at the surface, leading to an improved moment of NPs such as Fe, Co and Ni compared to their bulk counterparts \cite{11,12}. As the size of the NP is downscaled to a level that is comparable to key magnetic length scale, such as the exchange length (in nm ranges) or the domain wall size (in nm-µm ranges), the magnetization configuration may also be distinctly affected \cite{13,14}. Standard magnetic characterization techniques, as for example the superconducting quantum interference devices (SQUIDs), were used to investigate the magnetic properties of NPs as ensembles of the nanostructures or the macro-performance \cite{15}. Nevertheless, for many applications it is beneficial to probe the isolated magnetic NPs, since under this condition the remnant magnetization of the nanostructure and domain structure configuration can be detected in detail \cite{16}. Imaging and spatially localizing such nanometric scale magnetic structure is of strong interest as a better understanding of the individual NP magnetization configuration, which is advantageous not only for the fundamental physics of nanomagnetism but also for specific technology applications \cite{1-7}.

Magnetic Force Microscopy (MFM) offers significant access to characterize magnetic properties of individual NPs \cite{17-20} instead of the integral properties of ensembles of NPs, which cannot be achieved by standard characterization techniques \cite{21}. In MFM measurements, a cantilever with a micro-fabricated magnetic tip at the end scans across the sample surface with a given tip-sample separation. The tip magnetization (normally in the z-direction, perpendicular to the sample
surface), together with the magnetic field originating from the sample, results in an either attractive or repulsive interaction. The force gradient acting upon the tip is embodied in the variation of the cantilever oscillation behavior (i.e. amplitude and/or phase shift)\textsuperscript{22}, and it can be detected for imaging the magnetic configuration of the sample. This high resolution imaging of nanomagnetism gives a precise local characterization of the magnetic domain structure\textsuperscript{23} to study the finite-size effects of the NPs and the enhanced properties with respect to their bulk counterparts.

In this chapter, high resolution magnetic imaging of the Fe NPs has been carried out by MFM. And analysis of the magnetic properties has shown that the NPs with sizes \(\sim 50-70\) nm are single-domain ferromagnetic crystals. Moreover, the magnetic contrast from MFM images was fitted using magnetic dipole models (Equation (2) and (3)) to obtain the magnetization orientation of the measured NPs.

### 5.2 Experimental Section

Fe NPs were deposited directly onto silicon wafers and carbon-coated transmission electron microscopy (TEM) grids by inert gas condensation using a home modified high pressure magnetron sputtering source\textsuperscript{24,25}. The subsequent exposure to the ambient atmosphere resulted in the initial surface oxidation of the NPs\textsuperscript{8,9}. High resolution TEM imaging (see Figure 5.1) have shown the NPs were consisted of an Fe core surrounded by an iron oxide shell (with thickness \(\sim 3\)nm independent of the particle size)\textsuperscript{8}, yielding an overall average NP size of \(\sim 33.4\) nm with a standard deviation of \(11.0\) nm.

For the MFM study, samples were imaged in air using a Multimode Atomic Force Microscope (AFM) with CoCr coated Si probes (MESP-V2 tips with the CoCr coating thickness of 50 nm). The data were recorded with a scan rate of 0.3 Hz and with 512 lines/pixels per scan direction. The magnetization of the probe was attained by placing a permanent NdFeB block magnet (nickle-plated, size: \(40\times20\times5\) mm) directly underneath the AFM tip holder. The adjacent magnetic poles resulted in a magnetic stray field directing into or out of the sample surface. Furthermore, the MFM approach is essentially a two-pass technique. First the scanning of the sample takes place, where short range interactions (e.g. Van der Waals forces) play dominant role, and topographical information is collected. Subsequently, the phase shift \(\Delta\phi\) of the cantilever oscillation is recorded in lift mode with the cantilever raised up to \(\sim 50-60\) nm above the sample surface, following the topography pattern from the previous scanning, in order to reflect the true magnetic signal due to the stray fields of the sample. The chosen lift height should ensure sufficient separation where the topographic artifacts are eliminated.
and magnetic interactions prevail. All topography AFM and MFM images were flattened to eliminate any virtual sample tilt\textsuperscript{26}, and no further processing took place.

The phase shift variation $\Delta \phi$ along the trace in lift mode is proportional to the magnetic force gradient in z direction. According to Henry’s work on nanowires\textsuperscript{13} and Ramlan’s work on quantum dots\textsuperscript{27}, the z derivative of the magnetic force contrast $\Delta \phi$ given by Equation (4) can be described as a function of the tip position expressed by the y and z coordinates. The magnetization orientation of the NP is described by the angle $\theta$ between the MFM tip magnetic moment and the NP magnetization. Finally, by changing the parameters in the force function, the phase shift at each tip position can be numerically modeled. The simulated phase shift profile can be fitted to the experimental data. The fitting process employed here is the downhill Simplex method due to Nelder and Mead\textsuperscript{28,29}. In the phase shift curve $\Delta \phi = \Delta \phi(y)$ the horizontal axis corresponds to the tip position on the y axis. The $\chi^2$ in the fitting procedure was defined as the variance between the experimental data $\Delta \phi_i$ and the modeled data $\Delta \phi_{i,\text{cal}}$ as $\chi^2 = \Sigma_{i=1}^{k} (\Delta \phi_i - \Delta \phi_{i,\text{cal}})^2$. For the Simplex method reasonable starting estimates for all the fitting parameters have to be provided, and varying the input parameters in Equation (5.4) the fitting was optimized by minimizing $\chi^2$.

5.3 Results and Discussion

A TEM overview image of the Fe NPs deposited on a carbon-coated TEM grid is shown in Figure 5.1(a). A characteristic selected area electron diffraction (SAED) pattern from an area of the sample containing several NPs is shown in Figure 5.1(b) and indicates the presence of bcc Fe and Fe oxide (Fe$_3$O$_4$ and/or $\gamma$-Fe$_2$O$_3$)\textsuperscript{8}. Indeed, in a previous work\textsuperscript{8} it has been demonstrated that the Fe NP constitutes of a bcc-Fe core surrounded by an iron oxide shell. Figure 5.1(c) presents the height topography image collected in tapping mode. The height and size of the NPs was determined by fitting a two-dimensional parabolic function to the height profile extracted from each particle through the center, which is an approximation in good agreement with the TEM analysis\textsuperscript{21}. The contrast observed in the corresponding MFM phase image (Figure 5.1(d)) has indicated that the phase shift of the cantilever oscillation was caused mainly by the magnetic tip-sample interaction. A dark contrast (negative phase shift relative to the background signal) indicates an attractive interaction, while a bright contrast (positive phase shift) indicates a repulsive interaction\textsuperscript{30}. The bright and dark contrast was in agreement with single-domain magnetic NPs, while some of the particles showed a dipole contrast resulting from the interaction of the
in-plane particle magnetization and the external out-of-plane magnetization of the probe.

Figure 5.1 (a) Overview image of the Fe NPs deposited on a carbon-coated TEM grid; (b) selected area diffraction pattern of the deposited NPs that agrees with a structure composed of a bcc Fe core and a magnetite/maghemite shell (the labels indicate the $d_{hk}$ interplanar distances in Å); (c) the height topography image collected in tapping mode; (d) the corresponding MFM phase image was recorded in lift mode with 60 nm lift height (tip-sample separation) where the magnetic forces give the most significant contribution on the phase shift variation $\Delta \varphi$ of the oscillating cantilever. The AFM/MFM scanning area is 5×5 $\mu$m$^2$. 
Prior to scanning Fe NPs, MFM measurements were performed on a standard magnetic sample in order to confirm that the tip was properly magnetized (see Figure 5.5 in Appendix). Moreover, the scan angle was varied to check if the asymmetry of the NP morphology influenced the outcome since the tip radius is non-negligible during scanning nanometer scale structures (see Figure 5.6 in Appendix). To explore the magnetic property of Fe NPs, the MFM tip was magnetized in two opposite directions: pointing into (Figure 5.2(a)), and out of (Figure 5.2(b)) the silicon surface plane. The MFM phase images shown in Figure 5.2(c) and (d) were taken on the same NP with the tip magnetized into and out of the silicon surface plane, representing the magnetic moment projection in x-y plane. The phase shift profiles demonstrated in Figure 5.2(e) were extracted from the phase images along the dash line, whose position and direction were indicated in Figure 5.2(c) and (d), with the substrate background subtracted.

The Fe NPs, besides the ferromagnetism of the bulk counterpart, exhibit distinct magnetic configurations depending on the particle size. The critical size for multi- and single-domain ferromagnetic NPs is given approximately by $\delta \approx 2A^{1/2}/M_s$, where $A$ is the exchange constant and $M_s$ is the saturation magnetization\textsuperscript{31}. Below this critical size, the ferromagnetic NP behaves as a single-domain structure. When the NP is downscaled further approaching the superparamagnetic limit, the total magnetization behaves as a super-spin inside each particle showing no coercivity\textsuperscript{32,33}. As it can be identified from the MFM phase images, the into-plane magnetized tip produced a dark-bright-dark contrast, which indicated an attractive-repulsive-attractive magnetic force configuration, while an inversed contrast was observed when the tip was magnetized out of the substrate surface. This shows a clear indication of the ferromagnetism of the Fe NP, with the corresponding phase shift profiles in Figure 5.2(e) demonstrating a consistent result. The possibility of being paramagnetic can be excluded as the local magnetic moment, in the case of paramagnetism, would align with the magnetic field of the tip without variation using reversed tip magnetizations\textsuperscript{27}.

5.4 Comparison with Theory

The long range magnetic interactions between the tip and the NP result in the variation of the mechanical behavior of the cantilever\textsuperscript{34}. In our experiments, the phase shift $\Delta \phi$ originated from the magnetic field of the NP was used to characterize the magnitude of the magnetic force, which is proportional to the $z$ derivative of the magnetic force and it is given by\textsuperscript{35}
Figure 5.2 Schematic of the MFM measurement geometry is shown with the tip magnetized in two opposite directions: pointing into (a) and out of (b) the sample surface plane. MFM phase images recorded with the tip magnetization pointing into and out of the sample surface show inverted contrasts, indicating the ferromagnetism of the NPs. The phase profile (c) was extracted along the dash line (from left to right) with the asterisk as the origin of the x axis \(x=0\). The variation of the phase shift \(\Delta\phi\) caused by the magnetic field of the NP is shown in (e), which quantitatively shows the inversion of the contrast relative to the substrate. The MFM scanning took place at a lift height of 60 nm. The MFM phase images are 350×180 nm² in size, and the size of the NP is approximately 56 nm according to the topographic information obtained in tapping mode (see Figure 5.7 in Appendix).
\[ \Delta \varphi = \frac{Q}{k} F'_{\text{mag}} \]  

(5.1)

Where \( Q \) is the quality factor of the cantilever, and \( k \) is the spring constant of the cantilever. Various levels of approximations could be applied to theoretically evaluate the magnetic force gradient exerted on the MFM tip, depending on the degree of the complexity of the model employed to describe the magnetization state of both the tip and the NP\(^{13}\). In our approach, the magnetized tip and the NP were modeled as magnetic point dipoles\(^{13,27,36}\) as it is shown in Figure 5.3(a). Although we adopted an earlier model\(^{13,27}\), it was modified for the measurement of isolated magnetic NPs. The position vector of the magnetic tip with respect to the center of the NP (at \( \vec{r} = 0 \)) is denoted by \( \vec{r} = x\vec{x} + y\vec{y} + z\vec{z} \), and the point magnetic moment at the tip position is given by \( \vec{\mu} = m_{NP} (\alpha \vec{x} + \beta \vec{y} + \gamma \vec{z}) \) where \( m_{NP} \) is the magnitude of the NP magnetic dipole moment, as well as \( \alpha \), \( \beta \), and \( \gamma \) are the direction cosines of the magnetic moment. The stray field emanating from the magnetic NP is given by\(^{13,27}\)

\[ \vec{H}_{NP} = \frac{3(\vec{\mu} \cdot \vec{r})\vec{r}}{r^5} - \frac{\vec{\mu}}{r^3} \]  

(5.2)

The magnetic force gradient (i.e. the z derivative of the force), which is detected by the probing tip of the MFM, reflects the interaction between the NP and the magnetized tip and it is given by\(^{13,27}\)

\[ F'_{\text{mag}} = m_{tip} \frac{\partial^2 (\vec{H}_{NP} \cdot \hat{z})}{\partial z^2} \]  

(5.3)

The orientation of the magnetization of the NP is characterized by the angle \( \theta \) between the magnetic moment of the NP and the equivalent magnetic moment of the tip. Figure 5.3(a) shows that \( \beta = \sin \theta \) and \( \gamma = \cos \theta \). Upon substitution the phase shift \( \Delta \varphi \) is given by\(^{13,27}\)

\[ \Delta \varphi \propto F'_{\text{mag}} = C \times \left[ \frac{9 \cos \theta}{(y^2 + z^2)^{5/2}} - \frac{45z(y \sin \theta + 2z \cos \theta)}{(y^2 + z^2)^{7/2}} + \frac{105z^3(y \sin \theta + z \cos \theta)}{(y^2 + z^2)^{9/2}} \right] \]  

(5.4)
where $C = m_{tip} m_{NP}$. The magnetic force gradient $F'_{mag}$ in Equation (5.3) was defined as a function of the tip position (described by $y$ and $z$, extracted and modified from the height information $(y_0, z_0)$ collected in tapping mode) and the orientation of the NP magnetization (as described by the angle $\theta$).

As the center of the dipole-modeled tip should be located at a raised height $h'$ with respect to the surface point of the tip-apex, this additional parameter should be taken into account, besides the lift height $h$, when describing the tip trajectory ($y = y_0, z = z_0 + h + h'$). Equation (5.4) was used to fit the phase shift data in lift mode along the dash line shown in Figure 5.2(c) and (d). The experimental phase shift profile and the fitting are shown in Figure 5.3(b) and (c). A multitude of different values for $\theta$ were used to optimize the fitting. The results show that the NP dipole is along the dash line and at an angle of $177^\circ$ and $-6^\circ$, respectively, with respect to the tip magnetic moment, as shown at the right of Figure 5.3(b) and (c). With the polarity of the MFM probe reversed, the corresponding phase imaging exhibited a consistent orientation of the ferromagnetic NP.

Finally, based on the measurements of a large number of NPs, as-deposited Fe NPs on silicon substrate showed no preferential orientation due to large interparticle distances. Phase images with different magnetization orientation were shown in Figure 5.4, showing the evolution of the phase images with $\theta$ varying from $0^\circ$ to $315^\circ$. Fe NPs with a magnetization oriented parallel or antiparallel ($\theta = 0^\circ$ or $180^\circ$) to the magnetic moment of the tip showed a nearly whole bright (dark) contrast with both sides slightly dark (bright), instead of an entire bright (dark) contrast indicating absolute repulsion (attraction). Li et al.\textsuperscript{15} modulated the phase of the measured in-phase signals by adding an extra phase using the signal processing algorithm. The adjusted phase images for an equivalent vertical (upward and downward) magnetization demonstrated consistent contrasts. The additional side contrasts may be attributed to the strong non-rectilinear trajectory of the magnetic probe, which is the convolution of the NP section shape with the tip-apex shape\textsuperscript{13}. Although it is less pronounced as the NP orientation tends towards the in-plane direction, this effect may indeed occur at whatever orientation angle $\theta$. When the magnetization is oriented in-plane (perpendicular to the tip moment, $\theta = 90^\circ$ or $270^\circ$), the phase image shows a half-dark (bright) and half-bright (dark) contrast without side contrasts. Fe NPs with opposite magnetization were shown inversed phase contrasts.
Figure 5.3 Determination for isolated NP of the magnetization orientation. The schematic of the MFM measurement in (a) shows the trace of the magnetic tip in lift mode, along which the phase shift $\Delta \varphi$ of the cantilever resulting from the magnetic force gradient produced by the NP. The experimental data in (b) and (c) is obtained from Figure 2(c) and (d) along the dash line. The fitting (red diamond) of the one-dimensional MFM phase shift...
profile (black circle) verifies that the NP is described well as a single-domain structure. The value of $\theta$ giving the minimum $\chi^2$ yields the magnetization orientation. Fitting of the phase shift collected on the same NP with opposite tip magnetization (pointing out of (b) and into (c) the substrate surface) gives comparable results as it is shown in the right column of (b) and (c). The small arrow within the circle under the tip represents the alignment of the individual magnetic dipole moment that may act as the field source.

**Figure 5.4** (a) Evolution of the estimated MFM phase images with NP magnetization orientation that is defined by the angle $\theta$. (b) This schematic shows how $\theta$ is defined. All the phase images were collected with a 60 nm lift height. The magnetic moment is along the y axis in the x-y plane.

### 5.5 Conclusions

Fe NPs size ~50-70 nm were produced on silicon substrate by inert gas condensation. MFM measurement based on AFM technique revealed the single-domain ferromagnetism of the deposited Fe NPs, giving a precise and localized characterization of the nano scale magnetic structure. The phase images collected on the same NP with opposite tip magnetization (pointing into and out of the sample surface plane) in lift mode with a 60 nm tip sample separation showed inversed contrast, which indicated the reversion of the magnetic force gradient in z direction and proved the permanent magnetization of the NP. The magnetic moment projection in x-y plane can be derived by symmetry. Subsequently the magnetization orientation is determined by the spatial angle between the tip and the magnetic moment of the NP, which derived by direct fitting of the MFM phase
data using a dipole-dipole interaction model, providing possibilities to study precisely the NP anisotropy. The non-rectilinear trajectory of the scanning tip, resulted possibly from the sharp topographical feature of the NPs combined with the tip-apex shape, contributed to additional side contrasts observed in the phase images. Random magnetic orientations were observed, and our measurements have shown a magnetization orientation variation in the range \(~0-315^\circ\) with respect to the out of plane direction.
Appendix

Figure 5.5 The MFM measurements were performed on a standard magnetic sample to confirm the proper functioning of the magnetic probe with tip magnetized into (a-c) and out of (c-f) the sample surface. The phase profile shown in (c) and (f) were extracted along the solid line marked in (b) and (e), respectively. The corresponding solid line in the topography images (a, d) proved that the extracted profiles reflected exactly the same area. The contrary contrasts in the phase images and the reversal of the profiles manifested that the tip was magnetized properly. The scanning area was 3.5×5 μm².
Figure 5.6 Scan angle was varied to check if the asymmetry of the NP morphology affected the outcome. MFM phase profiles of the same NP while scanning with different angles are shown with the according phase images listed in the right indicating the consistency of scanning along different directions.

Figure 5.7 The topography line scan across the NP was used to determine the particle size by fitting a two-dimensional parabolic function to the peak area. The vertex of the parabola (56.4) was approximated as the NP size.
References


