Understanding electrostatic and magnetic forces in magnetic force microscopy: towards single superparamagnetic nanoparticle resolution

Alexander Krivcov¹, Tanja Junkers²,³ and Hildegard Möbius¹

¹ Department of Computer Sciences/Micro Systems Technology, University of Applied Sciences Kaiserslautern, Amerikastr. 1, 66482 Zweibrücken, Germany
² Polymer Reaction Design Group, School of Chemistry, Monash University, Clayton VIC 3800, Australia
³ Institute for Materials Research, Hasselt University, Martelarenlaan 42, 3500 Hasselt, Belgium

E-mail: Hildegard.moebius@hs-kl.de

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Abstract

The detection of superparamagnetic nanoparticles by magnetic force microscopy (MFM) at the single particle level faces difficulties such as superposition of nonmagnetic signals caused by electrostatic interactions as well as reaching the resolution limits due to small magnetic interactions. In MFM the magnetic force is measured at a certain distance to the substrate following the topography measured in a first scan to avoid an influence of short range forces (lift mode). In this work we showed that performing MFM on superparamagnetic nanoparticles the increase of the tip-substrate distance above the nanoparticle in lift mode scans leads to a reduction of the electrostatic forces resulting in a positive phase shift in contrast to the negative phase shift of the attractive magnetic force. Identifying the electrostatic force in MFM on nanoparticles as a capacitive coupling effect between tip and substrate the origin of often seen topography mirroring in phase images of nanoparticles in general is theoretically explained and experimentally proved. Minimization of the capacitive coupling by adjusting the work function difference between tip and substrate as well as using an optimized tip allows the magnetic visualization of single 10 nm superparamagnetic iron oxide nanoparticles (SPIONs) at ambient conditions with and without an external magnetic field.

1. Introduction

The unique magnetic properties of superparamagnetic iron oxide nanoparticles (SPIONs) are of high interest in many medical and biological applications such as magnetic resonance imaging (MRI), contrast enhancement, hyperthermia, drug delivery etc [1–3]. Intensive research activities are going on to characterize superparamagnetic iron oxide nanoparticles at the single particle level [4–6]. However, characterization of different properties, such as spatial distribution, size and magnetic behavior of single superparamagnetic nanoparticles is difficult to perform at ambient conditions and mostly a combination of different measurement techniques is needed. Magnetic force microscopy (MFM) proved to be a promising technique to successfully image clusters of small superparamagnetic nanoparticles without labelling and provides all the information described above in a single pass [7–11]. Recent investigations demonstrate the capability of MFM for biological systems e. g. to evaluate the iron distribution in biological tissues [12] and to study the cellular uptake of magnetic nanoparticles [13]. Nevertheless the interaction of the probe with nanoparticles is not yet fully understood. The literature to date lacks evidence for MFM signals from single SPION without applying an external magnetic field. So far, there still is the need for suppression of electrostatic forces which are overlapping and concealing the magnetic signals as well as a need for higher sensitivity due to the comparatively small magnetic interaction [14–19]. The atomic force microscopy (AFM) tip is a very sensitive antenna and therefore
gives a response to every signal and interaction from inside and outside the system [20]. Typically, a total force is measured with unknown contribution of different single forces, therefore it is difficult to obtain quantitative information on magnetic forces. The additional forces can often lead to a misleading interpretation of measured MFM data [21]. The aim of this work is to theoretically and experimentally prove that the mirroring of the topography often seen in MFM phase shift while imaging nanoparticles [5, 15, 19, 22] is due to capacitive coupling between tip and substrate. Understanding this effect this work aims at decreasing the capacitive coupling in order to magnetically visualize single SPIONs. Angeloni et al [15] discussed the mirroring of the nanoparticles in the phase shift as a topographically induced effect due to the capacitive tip-sample coupling. The increase of the average tip-substrate distance above the nanoparticle leads to a reduction of the attractive electrostatic forces which results in a positive phase shift. Different approaches exist to reduce the capacitive coupling. It is possible to change the electrostatic interaction by applying a constant voltage to the tip or sample [23]. Neves et al [5] describe the possibility to decrease the phase shift from nonmagnetic nanoparticles by applying a bias to the tip and therefore distinguish between nonmagnetic and magnetic particles due to an attractive signal from magnetic nanoparticles with diameter around 40-60 nm. Variable voltage in every measurement point can effectively reduce the capacitive coupling and therefore the electrostatic force for heterogeneous samples which is shown by Jaafar et al for magnets of micro scale [14]. Angeloni et al [16] describe an option to distinguish electrostatic and magnetic forces by changing the tip magnetization. In our work we compare different scan modes verifying the theory of the electrostatic forces behavior made by Angeloni et al [15]. Furthermore, we provide simulations which support the practical work. We show that the origin of the additional electrostatic force is indeed due to the average distance changes of the oscillating tip to the substrate since the influence of the nanoparticles itself is negligibly small due to the size ratio of the tip and single nanoparticle. The magnitude of the electrostatic forces and magnetic forces of single SPION is in the same order but due to the capacitive coupling the forces point in opposite direction. In case of high electrostatic interaction and low magnetic interaction magnetic forces are hidden by electric forces.

We show the possibility to reduce the capacitive coupling by choosing a substrate with a work function that is adapted to the work function of the tip. This reduces the need of additional parameters for minimization of electrostatic forces and therefore minimizes the risk of possible disturbances in the tip sample system during the measurement. By applying an external magnetic field during the MFM measurement, the strength and direction of tip magnetization can be changed unintentionally and therefore may falsify the results or rather makes the evaluation of results more difficult [24].

We present theoretical simulations including both magnetic forces between the tip and the superparamagnetic nanoparticle and the capacitive coupling effect predicting a minimum in the phase signal as a function of the lift height. Thus, the calculations reveal an optimum lift height for MFM measurements on single superparamagnetic nanoparticles. Using an optimized substrate material to minimize the work function difference between tip and substrate and an optimized tip we demonstrate that MFM measurements allow the imaging of SPIONs at a single particle level with and without applying an external magnetic field.

2. Experimental details

The kelvin probe force microscopy (KPFM) and MFM measurements described in this work were performed under ambient conditions using a Bruker’s Dimension Icon Atomic Force Microscope. The universality of this device can provide additional information to the surface topography during the second scan in certain distance to the surface (lift). The KPFM allows measuring the contact potential difference in each point of the sample and the applied bias voltage can be adjusted during the scan. Using a magnetic and conductive tip with CoCr coating it is possible to combine MFM with electric force microscopy (EFM) and KPFM.

The measurements in this work were done with MF MV (Bruker AFM Probes), ASYMFM (Asylum Research), SSS-MFMM (Nanosensors) and ASYMFMM–HM (Asylum Research) tips. The tips and most important parameters are represented in table 1.

The morphology of the samples is analyzed via tapping mode and additional magnetic and electrostatic behavior of the samples in dynamical interleave mode by specified distances between 5 and 100 nm. The two scan pass allows distinguishing short (e. g. van der Waals) and long range (e. g. magnetic) forces. The tip oscillates near its resonance frequency for both scans. The varying amplitude during the first pass is a signal for topography changes and the phase shift during the second pass in certain distance shows changes in force gradient. The signals of long range force during the second scan are often indicated by phase because of it local linearity and high signal to noise ratio compared to frequency or amplitude mode [25].

The following substrates are used in this work: Polished silicon (100) wafer (Siegert Wafer) is used as received. Copper substrate (Cu-ETP, 99.9% purity) is polished to remove native oxide layer.
Magnetic nanoparticles for MFM measurements were synthesized by co-precipitation described by Ramirez et al. In order to verify the resulting product Raman spectroscopy, powder x-ray diffraction and vibrating-sample magnetometer (VSM) measurement were performed. The results of these measurements prove that the synthesized particles are magnetite nanoparticles, showing superparamagnetic behaviour at room temperature. The size of the particles was determined to be 9 \pm 1 nm in diameter (figure S1 is available online at stacks.iop.org/JPCO/2/075019/mmedia).

A permanent magnetic field was applied using neodymium magnet N 35 with \( B_r \) in the range of 1.17-1.20 T. MFM measurements were processed using Nanoscope software.

### 3. Theory

#### 3.1. Capacitive coupling effects in MFM on nanoparticles

In order to understand why magnetic signals of magnetic nanoparticles are often hidden because of electrostatic forces we first discuss the origin of the electrostatic forces by MFM measurements of nanoparticles. Performing the interleave mode measurement (second step of a MFM measurement) the distance between tip and surface structure of the substrate, the lift height \( z \), is constant at every point. Therefore, nanoparticles on the surface of the substrate lead to a distance change between measuring tip and substrate surface from \( z \) to \( z + d \) where \( d \) corresponds to the diameter of the nanoparticle as shown in figure 1. That distance change leads to capacitive coupling effects described below.

The electrostatic force between a conductive tip and the substrate is calculated using a tip-surface model assuming two parallel plane surfaces, the distance of which corresponds to the lift height \( z \). The electrostatic energy of this system is given by:

\[
U = \frac{1}{2} C (V_{tot})^2
\]

(1)

where \( C \) is the capacitance and \( V_{tot} \) the voltage between tip and sample accounting for the contact potential difference \( V_{CPD} \) due to the difference in the workfunctions of tip and substrate, the DC-voltage applied between substrate and tip \( V_{tip} \) and the effective surface potential \( V_Q \) proportional to trapped charges on the sample surface according to equation (2) [23].

\[
V_{tot} = V_{tip} + V_{CPD} + V_Q
\]

(2)

An increase of \( V_{tot} \) will lead to an increase of the capacitive coupling. The contact potential difference is typically in the order of a few hundred millivolts [27]. In the following we assume the absence of electrostatic charges \( V_Q = 0 \).
The attractive force applied on the tip is calculated as the derivative of $U$ with respect to $z$:

$$ F = \frac{1}{2} \frac{\partial C}{\partial z} \frac{V_{\text{tot}}^2}{2} $$

where $V_{\text{tot}}$ and $V_{\text{CPD}}$ do not depend on $z$.

Therefore, the force gradient $F'$ acting on the tip during MFM measurements can be calculated as:

$$ F' = \frac{\partial F}{\partial z} = \frac{1}{2} C''(V_{\text{tot}})^2 $$

where $C''$ is second derivative of the capacitance. The MFM phase shift is given by:

$$ \Delta \phi_{\text{el}} = -\frac{Q}{k} \frac{\partial F}{\partial z} = -\frac{Q}{k} F'(z) $$

where $Q$ is the cantilever quality factor and $k$ the spring constant.

In absence of electrostatic charges on the surface the tip is attracted by the sample leading to a negative phase shift as shown in equation (6).

$$ \Delta \phi_{\text{el}} = -\frac{1}{2} \frac{Q}{k} C''(V_{\text{tip}} + V_{\text{CPD}})^2 $$

Assuming two parallel plane surfaces the capacitance with an effective area $A$ is given by $C = \epsilon_0 \frac{A}{z}$. Without applying a DC-voltage ($V_{\text{tip}} = 0$) the MFM phase shift is given by:

$$ \Delta \phi_{\text{el}} = -\frac{Q}{k} \epsilon_0 \left( \frac{A}{(z)^3} (V_{\text{CPD}})^2 \right) $$

Using the lift-mode in MFM measurements the distance from the substrate relevant for the capacitive coupling increases when the tip is above a nanoparticle $(z + d)$, where $d$ is the particle diameter. The negative phase shift because of the capacitive coupling at $z$ is larger than the negative phase shift at $(z + d)$ leading to a positive phase contrast:

$$ \Delta \phi_{\text{el}} = -\frac{Q}{k} (F'(z + d) - F'(z)) > 0 $$

$$ \rightarrow \Delta \phi_{\text{el}} = -\frac{Q}{k} \epsilon_0 \left( \frac{A}{(z + d)^3} (V_{\text{CPD}})^2 - \frac{A}{(z)^3} (V_{\text{CPD}})^2 \right) > 0 $$

Although the electrostatic forces are attractive forces measuring above nanoparticles the phase signal is positive explaining the mirroring of the topography often observed in MFM phase images [5, 15, 21, 28]. The increasing distance between tip and substrate leads to changes in capacitive coupling.

The effective area between substrate and tip contributing to the capacitive coupling is not constant for different lift heights due to the form of the tip apex. The influence of the tip apex is considered until when $F'(z + d) \sim 0.1\%$ of $F'(z)$. Increasing the lift height leads to an increasing effective area (figure S2). Calculating $\Delta \phi_{\text{el}}$ as a function of lift height (figure 2) the phase shift decreases with increasing lift height as observed by Angeloni et al [15] in accordance with theory, however this effect does not depend strongly on the size of the particles and is almost the same for 10 nm and 50 nm nanoparticles. Thus, the capacitive coupling leads to a positive phase shift almost independent of the nanoparticle diameter, but strongly dependent on the lift height.

In summary the positive phase shift in MFM measurements above nanoparticles theoretically derives from capacitive coupling between tip and substrate. This effect occurs for structures with a relief and lateral
dimensions equal to or smaller than the tip radius. The effect significantly contributes to the phase shift for small lift heights.

3.2. Magnetic forces
The magnetic force gradient acting on a model tip due to a single domain superparamagnetic particle is calculated using a point dipole-dipole approximation between the tip and a spherical particle [19, 29]. The tip is approximated by a uniform magnetized sphere. The magnetic moment of the particle is obtained by

\[ m_p = M_p V_p \] (figure S1(d)) and \( V_p \) is the particle volume. Magnetic force gradient and phase shift can be calculated using the following equation:

\[ F' = \frac{6 \mu_0 m_p m_{tip}}{\pi (z + s)^5} = \frac{\mu_0 d^3 M_p m_{tip}}{(z + s)^5} \] (9)

where \( z \) is the lift height, \( d \) is the diameter of nanoparticle and \( m_{tip} \) is the magnetic moment of the tip. The additional distance \( s \) is calculated as following

\[ s = \frac{r_{tip,mag}}{2} + \frac{d}{2} \] (10)

where \( r_{tip,mag} \) is the magnetic dipole radius of the tip.

The magnetic moments of the superparamagnetic nanoparticles orient in the magnetic field of the tip leading to an attractive force resulting in a negative phase shift in the MFM image:

\[ \Delta \phi_{mag} = -\frac{Q}{k} \frac{\partial F}{\partial z} = -\frac{Q \mu_0 d^3 M_p m_{tip}}{k (z + s)^5} \] (11)

As the phase shifts of the capacitive coupling effect above nanoparticles and the phase shift due to magnetic interaction of tip and superparamagnetic nanoparticle have different signs the distinguishing of magnetic and nonmagnetic signal is possible.

Theoretical calculations based on vibrating-sample magnetometer (VSM) measurements of the nanoparticles and the model of dipole-dipole interaction reveal that the magnetic field of the probe is sufficient to induce a magnetic moment at lift heights up to 30 nm.

By calculating the magnetic force for 10 and 25 nm nanoparticles, we observe that the phase shift for 10 nm nanoparticles due to the magnetic interaction is in the same order as the phase shift due to the capacitive coupling (figures 2, 3) but contrariwise. Those signals often overlap and hide each other. In case of 25 nm particle the phase shift caused by magnetic force is stronger than that of capacitive coupling. Therefore this effect was not observed in case of bigger nanoparticle with greater magnetic interaction with the tip. However, has to be taken into consideration for measurements of superparamagnetic nanoparticles with low magnetic moment.

3.3. Theoretical MFM phase of superparamagnetic nanoparticles taking into account the capacitive coupling effect and the magnetic interaction
As can be seen in figure 3 taking into account both electric and magnetic forces the curve of phase shift versus lift height significantly depends on the substrate material. For materials with a work function close to that of the tip material theory predicts a minimum and therefore an optimum distance between tip and substrate (lift height) for measurements of single superparamagnetic nanoparticles.

Since a contribution of all the forces is measured during the interleave scan (MFM measurement), both electric and magnetic forces affect the tip oscillation and change the phase. Therefore, both forces has to be taken in consideration for measurements evaluation. In case of silicon substrate and magnetic tip the contact potential difference was measured to be 0.4 V, therefore the electric force dominates the magnetic force of single superparamagnetic nanoparticle and completely hides the magnetic signal as can be seen in figure 3(a) for 10 nm particle. In case of 25 nm particle (figure 3(b)) an attractive signal is present on silicon substrate. By adopting the work function of the substrate material to the work function of the measuring tip the electric force can be minimized. In case of copper substrate the contact potential difference was measured to be 0.125 V. The magnetic force for 10 nm particle dominates in the range between 5–15 nm lift height as can be observed in figure 3(c). Thus, theoretical considerations show the existence of an optimal lift height for MFM measurements of superparamagnetic nanoparticles depending on the size of the nanoparticle.

4. Results and discussion

4.1. Capacitive coupling effects: proof of origin
In order to prove the theory of capacitive coupling a measurement of the same area with two different interleave modes is performed. Lift mode and linear mode are used for those measurements. The difference between those
two modes is that the lift mode follows the topography as described in 3.1 (figure 4(c)) and the linear mode has the same distance to the substrate at every point ignoring the topography (figure 4(f)). Figure 4(a) shows topography measurements of a single nonmagnetic nanoparticle. The associated phase image is shown in figure 4(b) for lift mode and 4(e) for linear mode. Figures 4(b) and (c) show a standard interleave lift measurement, the topographically induced signal in the MFM phase image, described and theoretically explained in 3.1, can be observed in figure 4(b). Using linear interleave mode, which is shown in figures 4(e) and (f), no phase changes are observed above the particles, which confirms the theory of capacitive coupling effects above structures with dimensions similar or smaller than the tip radius. Figure 4(d) shows a cross section of the nanoparticle topography and phase shift in figures 4(a), (b) and (e) with associated phase shifts. As soon as the structure is big compared to the tip size these effects will diminish as the capacitive coupling will occur between

Figure 3. Calculation of electric and magnetic phase shifts for 10 nm and 25 nm magnetic iron oxide nanoparticles; (a) 10 nm magnetic nanoparticle and (b) 25 nm magnetic nanoparticle on silicon substrate $V_{CPD} = 0.4$ V; (c) 10 nm magnetic nanoparticle and (d) 25 nm magnetic nanoparticle on copper substrate $V_{CPD} = 0.125$ V.

Figure 4. (a) Topography measurement of a single nonmagnetic nanoparticle; (b) phase image taken in interleave lift mode; (c) sketch of the interleave mode; (d) cross section of the nanoparticle with associated phase taken in lift and linear mode (e) phase image taken in interleave linear mode; (f) sketch for interleave linear mode (SSS-MFM tip, silicon substrate, lift height: 15 nm).
tip and the structure and no longer between tip and substrate. If the electrostatic force is constant during the whole measurement, it will not affect the phase image. Qualitatively a repulsive force is applied to the tip above a small structure due to the diminution of the capacitive coupling between tip and substrate. The contribution of the nanoparticle itself is negligible small. The effective interaction area of the tip (47 ± 7 nm radius, ASYMFM) and a single separated nanoparticle (5 ± 1 nm radius) is less than 2% of the total interaction area of the tip. The change in distance, however, is more than 50% in case of 20 nm lift height and 10 nm nanoparticle diameter and even more for smaller lift heights. Therefore, the distance change between tip and substrate is the main reason for the changes in phase image and cause the mirroring of the topography [5, 7, 15]. Schreiber et al [7] observed that the interaction of the MFM phase of superparamagnetic particles is similar to that of a nonmagnetic probe indicating that non-magnetic interactions are responsible for the phase contrast measured. Comparing magnetic and non-magnetic nanoparticles Neves et al [5] found as well significant electrostatic interactions between atomic force microscopy probes and nanoparticles which could be reduced by applying a DC voltage between tip and sample. These nonmagnetic interactions gave positive phase shifts indicative for repulsive interactions with MFM probe. Angeloni et al [15] discussed the mirroring of the topography as a topographic induced effect due to the capacitive tip-sample coupling. The results of Schreiber [7], Neves [5] and Angeloni [15] can now be explained using the model proposed in this paper.

4.2. Minimization of capacitive coupling effects

In the following different approaches to reduce the capacitive coupling are discussed. In order to detect an attractive magnetic signal of a single superparamagnetic nanoparticle the capacitive coupling has to be reduced. Equation (12) describes the phase shift caused by electric forces because of capacitive coupling. It is possible to reduce the coupling by reducing the effective capacitor area A e. g. the radius of the tip (i). By applying a tip bias \( V_{tip} \) the potential between tip and substrate can be varied and therefore minimized (ii). Another possibility is to perform the measurement on a substrate with almost the same work function as that of the tip to reduce the potential difference \( V_{CPD} \) (iii). It is possible to eliminate the distance changes \( d \) and therefore changes of electric force between substrate and the magnetic tip above the nanoparticle by performing linear scan or embedding the nanoparticles into substrate (iv).

\[
\Delta \phi_{el} = -\frac{Q}{k} \epsilon_0 \left( \frac{A}{(z + d)^2} (V_{CPD} - V_{tip})^2 - \frac{A}{(z)^3} (V_{CPD} - V_{tip})^2 \right)
\]  

Possibilities to minimize \( \Delta \phi_{el} \)

| Possibility | Description |
|-------------|-------------|
| (i) Effective area A | Decreasing the area of the capacitor by choosing magnetic tip with smaller diameter |
| (ii) Tip bias \( V_{tip} \) | Applying appropriate tip bias to decrease the potential difference between tip and substrate |
| (iii) \( V_{CPD} \) | Choosing a substrate with comparable work function to the tip to decrease the contact potential difference |
| (iv) Distance changes \( d \) | Eliminate distance changes during the measurement above nanoparticle |

The effect of capacitive coupling can be reduced by using tips with smaller radius (i) as \( \Delta \phi_{el} \) is directly proportional to the effective area \( A \) of the tip according to equation (12). Figures 5(b) and (c) show topography mirroring of particles with approximately the same diameter of 8 ± 1 nm on silicon substrate taken with two different tips. The effective area of the SSS-MFMR tip is a factor of 7 smaller than that of the MFMV tip. Figure 5(a) compares the capacitive coupling influence for those tips by simulating the phase as a function of lift height for both tips. Figures 5(b) and (c) show topography measurements of single nonmagnetic nanoparticles with associated phase shifts obtained by MFM interleave scan measured with the MFMV tip with a tip radius of 40 nm (b) and the SSS-MFMR-tip with a tip radius of 15 nm (c) indicating the reduction of the capacitive coupling effect using a tip with smaller tip radius.

Another possibility (ii) to reduce the capacitive coupling is by applying a voltage \( V_{tip} \) compensating the tip-sample contact potential \( V_{tip} = V_{CPD} \) according to equation (12).

For homogeneous samples the electrostatic contribution can be eliminated by applying an appropriate tip bias [17]. EFM is the method used for these measurements.

For heterogeneous samples such as nanoparticles on a flat substrate Jaafar et al [14] proposed combining KPFM and MFM techniques. Measuring on different materials, e. g. as shown for cobalt wires with structures larger than the tip size on a silicon substrate by Jaafar et al [14], the combination of KPFM and MFM can eliminate the electrostatic contribution. Measuring instead nanoparticles with dimensions similar or smaller than the tip size, KPFM measurements are expected to show no difference between measurements above the particle and measurements above the substrate as \( V_{CPD} \) remains constant. In KPFM data of a single nanoparticle
on silicon substrate no potential changes are observed above the single nanoparticle using a magnetic MFMV tip by 20 nm lift height confirming the statement above (figure 6). Therefore in this case combining KPFM with MFM does not reduce the capacitive coupling effect.

The capacitive coupling will be quenched if $V_{\text{tot}}$ in equation (2) is reduced to zero. Figure 7 shows the phase shift for magnetic and nonmagnetic nanoparticles taken with the magnetic SSS-MFMR tip as a function of applied tip bias on silicon substrate in 11 nm lift height.

Dotted and dashed lines represent the calculations for the nonmagnetic and magnetic nanoparticles with 10 nm diameter, respectively. The dashed line represents the capacitive coupling calculated for different applied tip biases without taking magnetic interaction into account (nonmagnetic nanoparticles). Adding the magnetic interaction between superparamagnetic nanoparticles and the tip leads to the dotted line. The calculated lines perfectly fit the measurements on magnetic and nonmagnetic particles. For tip bias smaller than approximately 1.7 to 2 V the magnetic attraction of the superparamagnetic nanoparticle leads to negative phase shift and a black

Figure 5. (a) Calculated phase shift as a function of lift height for SSS-MFMR and MFMV tips above a single nonmagnetic nanoparticle with 10 nm diameter; (b) Topography and phase shift for MFMV tip ($r_{\text{tip}} = 40$ nm; $V_{\text{CVD}} = 0.4$ V); (c) topography and phase shift for SSS-MFMR tip ($r_{\text{tip}} = 15$ nm; $V_{\text{CVD}} = 0.4$ V); (b) and (c): lift height: 10 nm.

Figure 6. KPFM measurement on silicon substrate with single SPION; 20 nm lift height, MFMV tip.
spot in the MFM phase image. Figures 7(b) and (c) show topography and phase images respectively of magnetic and nonmagnetic nanoparticle in a single measurement.

In order to reduce the amount of measurement parameters and decrease the capacitive coupling, $V_{CPD}$ can be reduced by choosing an appropriate substrate material (ii).

By reducing the CPD between tip and substrate, the electrostatic force decreases and therefore the change of electrostatic force above the nanoparticle is smaller. Our approach in this paper is to reduce the disturbing capacitive coupling during the second scan by reducing CPD through substrate change. A clear difference is observed in phase shifts for silicon and copper substrates at different tip bias using MFMV tip (figure 8). The phase shift as a function of the tip bias is a parabola with shifted minimum according to the equation (12). The silicon substrate shows a minimum at $-300$ mV. Using fresh polished copper substrate the minimum is found to be $-125$ mV, however after a few months the substrate changes and the minimum shifts to $-400$ mV due to oxidation. The shift of the parabola minimum is due to the CPD between tip and substrate. A clear difference in CPD between used MFM tip and silicon and MFM tip and copper substrate of a ratio of 3.2 leads to a factor of 10.24 in the phase shift signal according to equation (12).

Figure 9 shows phase image shifts for silicon and copper substrates at different lift heights. The measurements in figure 9 are done on nonmagnetic nanoparticles to avoid additional magnetic interaction. So we simply detect nonmagnetic interactions e.g. electrostatic behavior. The measurements are done with a MFMV tip. Due to the conductivitiy of the tip, the electrostatic response and capacitive coupling of the tip with different substrates could be measured. We observe a clear difference between silicon and copper substrates. The phase shift for the copper substrate does perfectly fit our theory and calculation. However, the phase shifts for the silicon substrate are larger than the calculated values since we do not take trapped charges into consideration. The electrostatic interaction with semiconductor substrates is more complex as described and summarized by Sorokina et al [30]. The charge-density and the potential inside the semiconductor have to be taken into account [31].

Another possibility to completely eliminate the capacitive coupling is by eliminating the distance changes $d$ (iv in equation (12). If $d$ is reduced to 0 nm both terms for $z$ and $(z + d)$ will be equal and $\Delta \Phi_{z}$ will be eliminated allowing the measurements of only magnetic forces. This can be achieved by applying a linear mode measurement above the substrate (figure 4) or by embedding the nanoparticles in the substrate.

4.3. MFM on superparamagnetic nanoparticle: towards single particle resolution

In 4.2 different approaches to decrease the capacitive coupling and therefore the phase shift caused by electric force are discussed. In the following those approaches are applied solely or in combination to achieve single nanoparticle resolution. Figure 10 shows an aggregate of superparamagnetic nanoparticles on copper substrate. A high magnetic moment tip (ASYMFM-HM) is used for the measurements. A permanent magnetic field was applied parallel to the substrate as shown in figure 10 using neodymium magnet N 35 with $B_t = 1.17-1.20$ T. The aggregate has a height of 26 nm and 31 nm width (after deconvolution). The phase image was taken in 35 nm lift height. Obviously the magnetic force is dominant in the picture. A transition of positive phase into negative phase can be observed in figure 10(b). The particles are magnetized parallel to the substrate due to the external magnetic field. Figure 10(c) show a cross section of the particles along the $y$-axis and corresponding phase shifts.
Using high moment ASYMF-M-HM tip for standard lift height measurements of single superparamagnetic nanoparticles, however were not successful due to the strong capacitive coupling of the tip with the substrate. The effective area is large and therefore the single nanoparticles appear as mirrored topography in phase image. By using linear mode (figure 4(f)) and therefore eliminating the changes of the electric force due to the capacitive coupling completely it was possible to observe a positive and negative phase contrast applying an external magnetic field parallel to the substrate, shown in figure 11. The magnetic vector of the nanoparticle is aligned
parallel to the substrate. The transition of phase shift in figure 11(b) clearly reveals a magnetic behavior of the single nanoparticle.

Using linear mode for imaging superparamagnetic nanoparticles in general is difficult since the tip end can be easily destroyed due to crash of the tip with the substrate since the topography is ignored. Therefore, only small areas of the substrate can be measured.
In order to further decrease the capacitive coupling of the tip with substrate while measuring in lift mode and to avoid an external magnetic field we used a super sharp magnetic tip (SSS-MFMR) and did the measurements on copper substrate. Combining two approaches to minimize the capacitive coupling an attractive signal above a single magnetite nanoparticle with 10 nm diameter could be observed due to the magnetic interaction. A cross section of a measurement with SSS-MFMR tip on copper substrate is shown in figure 12(c). The interleave measurements were performed in 11 nm lift. Measurements with lower lift height increase the risk of van der Waals interactions. We demonstrate that minimization of disturbing electrostatic forces during MFM measurements allow the magnetic visualization of single 10 nm SPIONS at ambient conditions. Even if the magnetization of the SSS-MFMR tip is a fourth of the MFMV tip magnetization, the super sharp tip fits better for imaging single superparamagnetic nanoparticles due to the lower capacitive coupling.

5. Conclusion

In summary we could image single 10 nm superparamagnetic nanoparticles with and without applying an external magnetic field in the AFM topography as well as in the MFM measurements by suppression of electrostatic effects. The origin of the mirroring of the topography in MFM lift mode measurements reported by many authors was experimentally investigated and theoretically explained by capacitive coupling effects. Lift mode measurements on structures smaller than or comparable with the size of the tip radius lead to a positive phase shift due to electric interaction overlaps the negative phase shift due the magnetic interaction of the tip with the superparamagnetic nanoparticle and can completely change the phase image observed. The comparison of lift mode and linear mode measurements on nonmagnetic nanoparticles confirms that capacitive coupling is primarily responsible for the positive phase shift seen in MFM phase images of nanoparticles. We showed that this effect can significantly be reduced by choosing a substrate with a minimized work function difference between tip and substrate as well as by using a sharper tip to reduce the effective area. We magnetically could detect superparamagnetic nanoparticles at the single particle level on copper substrate with a super sharp tip without using additional parameters as e.g. tip bias or external magnetic field.

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ORCID iDs

Alexander Krivcov @ https://orcid.org/0000-0001-7741-6571
Tanja Junkers @ https://orcid.org/0000-0002-6825-5777
Hildegard Möbius @ https://orcid.org/0000-0003-2725-9752

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