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PROBING ATOMIC LEVEL INTERACTIONS IN NI NANORODS AND AFM CANTILEVER USING ATOMIC FORCE MICROSCOPY BASED *F–D* SPECTROSCOPY

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Abstract: Atomic force microscopy based force-displacement spectroscopy is used to quantify magnetic interaction force between sample and magnetic cantilever. AFM based F–D spectroscopy is used widely to understand various surface-surface interaction at small scale. Here we have studied the interaction between a magnetic nanocomposite and AFM cantilevers. Two different AFM cantilever with same stiffness but with and without magnetic coating is used to obtain F–D spectra in AFM. The composite used has magnetic Ni nanophase distributed uniformly in an Alumina matrix. Retrace curves obtained using both the cantilevers on magnetic composite and sapphire substrate are compared. It is found for magnetic sample cantilever comes out of contact after traveling 100 nm distance from the actual point of contact. We have also used MFM imaging at various lift height and found that beyond 100nm lift height magnetic contrast is lost for our composite sample, which further confirms our F–D observation.

Keywords: AFM, MFM, F–D spectroscopy, Magnetic nanocomposite, Nano-Porous Alumina (NPA), Magnetic interaction.

1. INTRODUCTION

The increasing interest in the study and development of magnetic nanomaterials for different technological applications has encouraged development of modern tools and methodology for the characterization and comprehensive understanding of magnetic properties at the nanometer scale [1]. Among these cutting-edge methodologies, magnetic force microscopy (MFM) is widely used for obtaining surface magnetic domain distribution in magnetic materials. This enables to aquire phase images as a result of the interaction of magnetic forces [2] between sample and magnetic cantilever. Force displacement spectroscopy obtained using atomic force microscope (AFM) gives an understanding of the various interactions between the indenter and sample surface. It has become a widely used tool for understanding surface chemistry and interaction in materials engineering, biochemistry, and biology [3]. Force spectroscopy curves represent the displacement derivative of interatomic potential between the AFM probe mounted on a cantilever and the test surface. With commercially available cantilevers, it is possible to measure forces down to ~10 pN [7]. The force is quantified with the help of change in deflection response of the cantilever due to the interactions and associated change in effective stiffness. Hence, it is possible to investigate complex molecular interactions with wide ranges, the mechanical properties of molecules and the strength of individual bonds [8]. Earlier uses of the AFM was limited towards the surface characterization of various materials [4]. But with the recent interests in the understanding of the surface forces have given rise to technological modification of conventional AFM. Such a recent development is using the magnetic tip in place of regular AFM tips to probe the magnetic fields with sub 100 nm resolution [5]. The understanding of the various parameters for operation of force spectroscopy has been first explored by the earlier work [6]. Nevertheless, despite the wide employment of MFM technique for the qualitative characterization of magnetic materials, there are not substantial studies of the correlation between phase map obtained using MFM and magnetic interaction force variation over the separation.

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In this present work force between AFM cantilever and sample is measured with respect to changing distance. Series of force vs distance curve is obtained on magnetic nanocomposite and a non-magnetic sapphire sample. Two different AFM tips with almost identical stiffness but with and without magnetic coating is used. We have tried to develop an understanding on how the interaction forces modify when the magnetic sample comes in close proximity with cantilever with and without magnetic coating. We have also collected series of MFM image to confirm the range beyond which magnetic interaction becomes weaker.

2. SAMPLE PREPARATION

Two different samples are used for magnetic force micrsocopy and F–D spectrosocpy studies. Sapphire standard sample supplied by Bruker for stiffness calibration and the second sample is magnetic nanocomposite (MNC) synthesized in our laboratory. Synthesis process of the MNC involves two-step anodization of 99.999% pure aluminum substrate using 0.3 M Oxalic acid at room temperature, with an anodization voltage of 40 V. Anodisation results in highly ordered porous structure. The as-grown porous oxides have a barrier oxide layer at the junction of pure aluminium and poros alumina. Thickness of the barrier oxide is ~40–50 nm. The barrier layer at the bottom of pores is thinned down by using step-voltage reduction, and chemical pore widening so as to provide an electrical path for the growth of the Nickel wires using pulse electrodeposition method. The aluminum substrate is used as the working electrode and Platinum as the reference electrode. An electrolyte solution of Nickel Sulphate (30 g), Nickel Chloride (4.5 g), and boric acid (4.5 g) in 300ml of DI water is used and solution temperature is maintained at 40 °C. A pulse voltage with T_{ON} –17 V for 2.5 msec and T_{OFF} 0 V for 50 msec is used. The overgrown Nickel on the top surface of the pores is removed by mechanical polishing. Top and cross-sectional SEM of anodized porous structure (a) and Ni deposited (b) is shown in Figure 1.

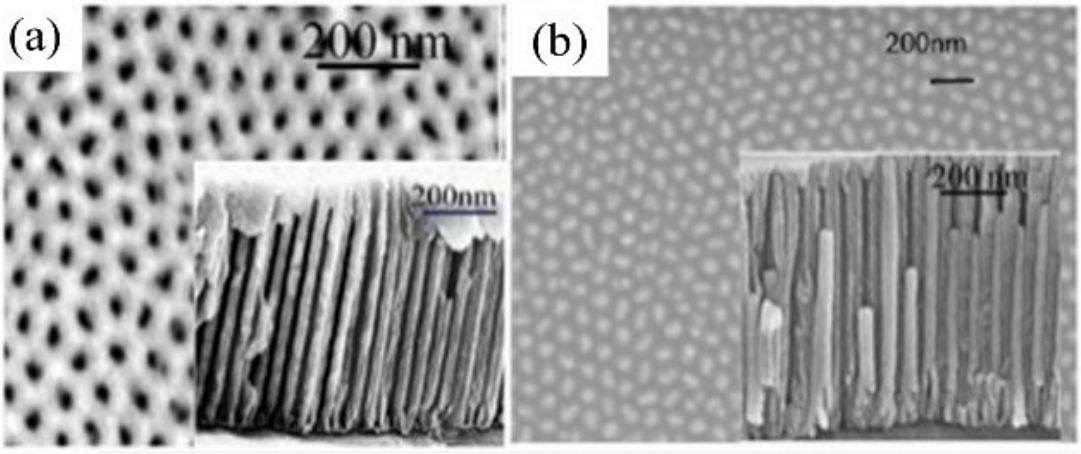

Figure 1. SEM Images of (a) Porous Alumina and (b) MNC (Porous alumina filled with nickel). Inset shows cross-sectional SEM of both porous alumina and MNC.

3. EXPERIMENT DETAILS

Atomic force microscope Bruker Nanoscope Analysis, USA is used for all the imaging and force-distance curve measurements. Two types of cantilevers with almost identical stiffness is used. Normal tapping mode cantilever (Si_3N) and cantilever with a magnetic coating (Monolithic Silicon coated with cobalt alloy with magnetic moment ~10–16 Am^2 and Coercivity ~300 Oe) are used. Stiffness is calibrated prior to measurements and found to vary between 3 to 5 N/m. Due to shape anisotropy; the magnetization of the magnetic cantilever is preferentially oriented in-plane of the magnetic layer. Therefore, at the tip apex, usually, the magnetization is oriented along the tip axis (z-direction). In order to ensure a predominant orientation of the magnetic vector field, the probes are magnetized prior to taking measurements. The tip is magnetized using a permanent magnet provided by the manufacturer. Both the cantilevers are used to obtain series of F–D curves on sapphire and synthesized MNC using peak force QNM mode. In this mode of operation, F–D curve is obtained from each pixel

while the tip scans the surface. We have also collected magnetic phase image and topography of porous alumina and MNC using MFM mode at various lift heights. In MFM probe scans by lightly tapping the surface to produce a topography image of the physical surface. While returning to the same track on the surface, the tool is set to its lift mode operation. The lift mode allows imaging of relatively weak long-range interaction between tip and sample arising due to stray magnetic field. Prior to obtaining FD spectra and images, samples are cleaned thoroughly with acetone, IPA and dried with nitrogen.

4. RESULTS

Figure 2 shows typical force-displacement curves obtained on both the samples. (a) and (b) shows FD curve obtained on sapphire and MNC sample respectively using a normal tapping mode cantilever with spring constant ~3 N/m. (c) and (d) shows F–D curve obtained on sapphire and MNC sample respectively using a cantilever with a magnetic coating but almost identical stiffness.

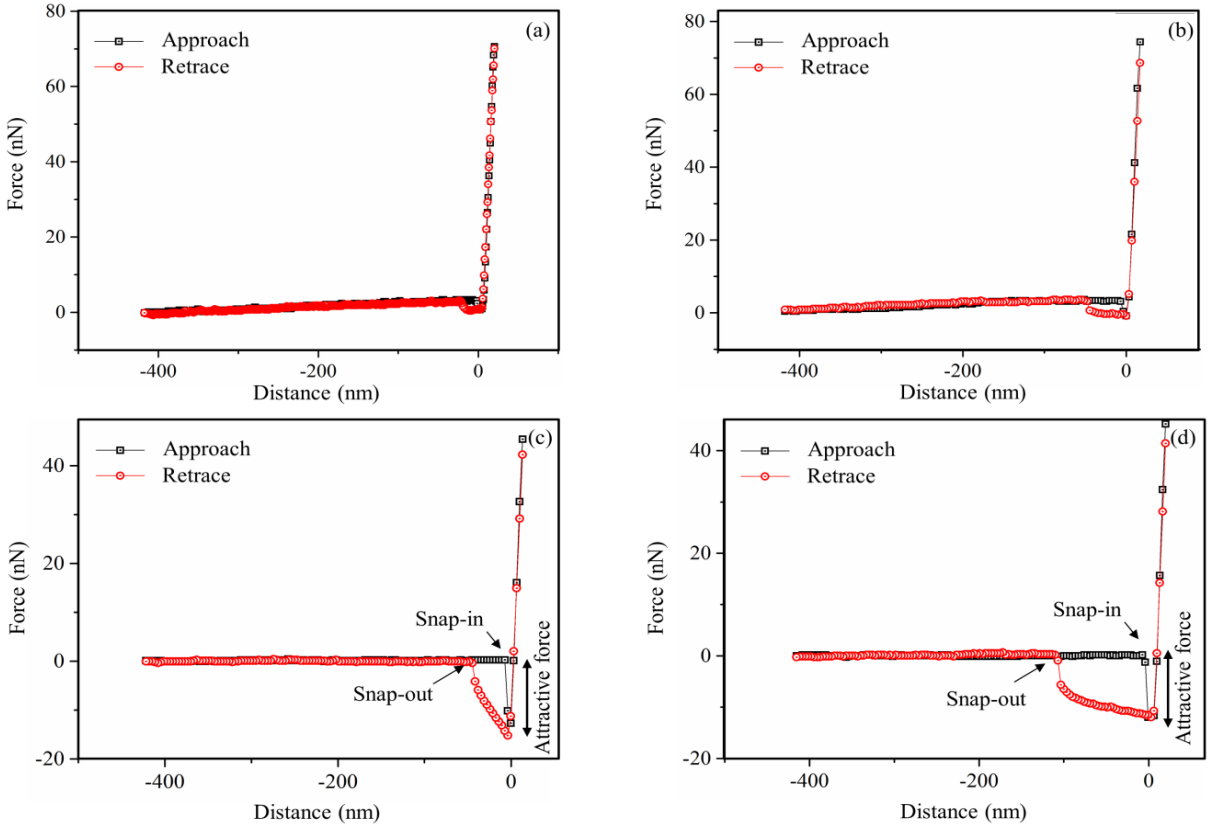

Figure 2. FD curve obtained using uncoated tapping tip on (a) sapphire standard sample (b) Magnetic nanocomposite. FD curve obtained using MFM tip (c) sapphire standard sample (d) Magnetic nanocomposite.

Initially, the tip and the sample are separated by large distance, there is no interaction between them and the cantilever remains in an equilibrium state. As the separation decreases, the tip is brought close to the sample at a constant speed and various attractive forces (van der Waals or Coulomb force) act on the tip. Once the total force acting on the tip exceeds the stiffness of the cantilever, it jumps into contact (snap–in). Beyond snap-in point as the tip moves into the sample, deflection is due to electronic repulsions between overlapping atomic orbital of the tip and sample atoms. The linear region gives information on the elastic properties of the sample provided tip stiffness is higher than sample stiffness. During withdrawal, adhesion or any other bonds formed during contact with the test surface causes the tip to adhere to the sample. Cantilever travels larger distance beyond the initial contact point on the approach curve to pull-off to non-contact position [6, 9].

It is seen that when magnetic cantilever is used, the tip travels a larger distance for coming out of contact with respect to snap-in point. Even attraction force also found to be higher for magnetised tip

compared to non-magnetised tip. From Figure 2 (a) and (b) it is seen that the tip travel ~20 nm and ~25 nm respectively for sapphire and MNC for coming out of contact. The tip has to overcome an attractive force ~5 N/m to come out of contact. Whereas, Figure 2 (c) and (d) shows that the cantilever travels ~50 nm and ~ 100 nm prior to coming out of contact. Attractive force is ~ 15 N/m. Both the samples are cleaned thoroughly, and cantilevers used are of same stiffness but one with magnetic coating. We repeated the experiments multiple times on various days and have seen similar trend at different locations on the samples.

Comparing F–D curves in Figure 2, it is evident that small adhesion force is present when F–D curve is obtained using non-magnetic tip. It is thought that origin of adhesive type force could be due to capillary effect or other surface interactions for the F–D curves as shown in Figure 2 (a) and (b). F–D curves in Figure 2 (c) and (d), adhesive type interaction is much stronger. Experiments are performed on same day (five different days) using two different cantilevers inside clean room environment where temperature and humidity is controlled (Repeated back and forth by changing sample and cantilever). Hence origin of stronger adhesion type force can be due to long range magnetic dipolar interaction between magnetic tip and sample dipoles.

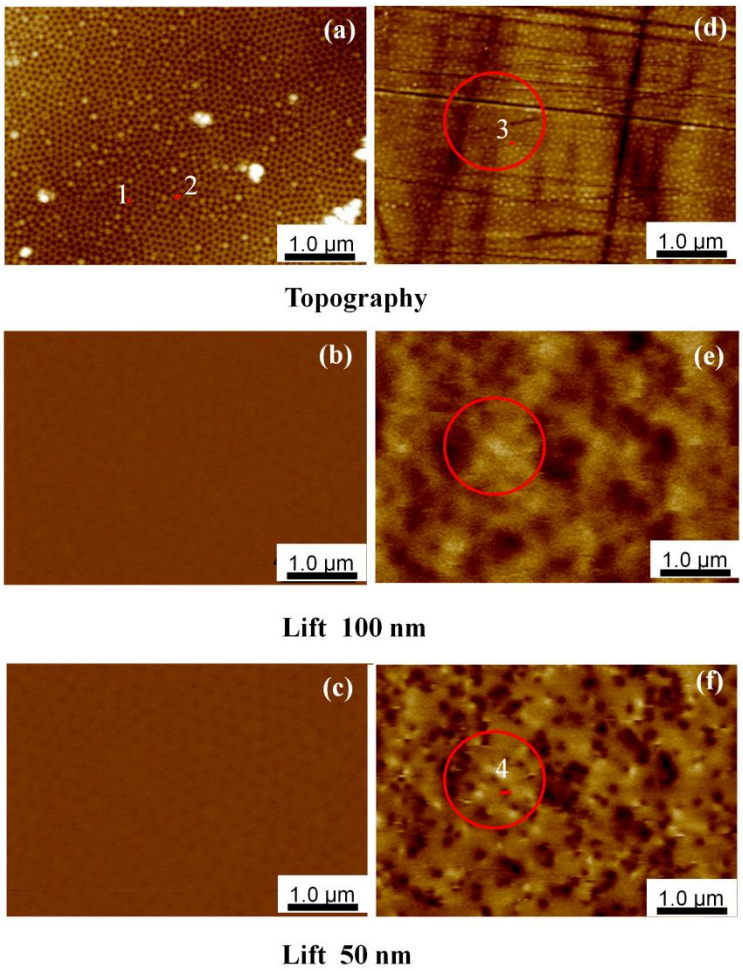

Figure 3. AFM Topography (a) porous alumina (d) porous-alumina based -MNC and MFM phase image of porous alumina and porous-alumina based –MNC.

Figure 3 shows topography and phase image collected on porous alumina and porous alumina based MNC sample. Phase image gives magnetic information of the sample. Stray filed generated from atomic spin moment of the sample interacts with stray field of the tip. Bright and dark regions on the phase image forms due to different spin orientation at different location. (a) and (b) shows topography image of porous alumina and porous alumina filled with nickel respectively. For porous alumina based MNC, topography shows the top view of Ni nanorods impregnated inside the ceramic matrix. Top view of Ni appears as Ni dots. (b) and (c) shows phase image collected on porous alumina at two

different lift heights and no magnetic contrast is observed. (e) and (f) shows phase image collected on porous alumina based MNC at a lift height of 100 nm and 50 nm. Phase image at a lift height of 100 nm lack details and appears blur. For 50 nm lift height magnetic contrast is improved. We see more details on magnetisation state, which is not resolved for 100 nm distance. The red circle is showing topography and corresponding phase change information with lift height on the NPA MNC sample. From AFM, the pore diameter and pitch are found to be ~62 nm and ~82 nm respectively. The diameter of Ni dot is also ~62 nm. Whereas phase image is showing a black contrast of size ~155 nm. It appears that collective stray field is recorded for porous alumina based MNC. Magnetic contrast at various lift height is collected. It is found with reduced lift height as tip and sample interaction gets stronger, phase contrast improves. We could not see any magnetic contrast from the sample when lift height is beyond ~110 nm. From Figure 2 (d), it is seen that tip comes out of contact after travelling ~ 100 nm distance from snap-in point. This observation leads to the understanding that probably the origin of attractive force in F–D curve obtained using magnetic cantilever could be due to magnetic interaction as beyond 100 nm lift height MFM phase image does not form any magnetic contrast.

CONCLUSION

In the present work, we used magnetic force microscopy and force distance spectroscopy as a tool to understand interdependence of magnetic field interactions as a function of the separation of two magnetic dipoles. The Terrain Correction is used to interpret and separate the magnetic interactions (long-range) from the topographic (short-range) interactions qualitatively. MFM imaging at various lift height shows that beyond 100 nm lift height, magnetic contrast is lost for the composite sample, which is further confirmed from the F–D observation. More than hundreds of F–D curves on various days are collected and it is found that the lift height at which MFM signal gets weaker resembles with F–D curve distance at which tip comes out of contact. Although shape of the F–D curve collected using magnetic cantilever resembles as adhesion force, but origin of force here could be due to magnetic dipolar integration as the behaviour is much weaker for non-magnetic cantilever. Hence, it could be possible to use AFM based F–D spectroscopy quantifying very small magnetic dipolar interactions between small volume of magnetic materials.

REFERENCES

[1] L. Angeloni, D. Passeri, M. Reggente, D. Mantovani and M. Rossi. Removal of electrostatic artefacts in magnetic force microscopy by controlled magnetization of the tip: application to superparamagnetic nanoparticles, Scientific Reports, 2016, vol. 6.
[2] U. Hartmann, Magnetic Force Microscopy, Ann. Rev. Mater. Sci. 1999, 29, 53–87.
[3] B. Cappella, G. Dietler, Force-distance curves by atomic force microscopy; Surface Science Reports, 1999, 34, 1–104.
[4] B. Bhushan, GS. Blackman, Atomic Force Microscopy of Magnetic Rigid Disks and Sliders and Its Applications to Tribology, ASME. J. Tribol., 1991, 113(3): 452–457.
[5] Y. Martin and H.K. Wickramasinghe, Magnetic imaging by "force microscopy" with 1000 Å resolution, Appl. Phys. Lett, 1987, 50, 1455–1457.
[6] F. L. Leite, L. H. C. Mattoso, O. N. Oliveira Jr, P. S. P. Herrmann Jr, The Atomic Force Spectroscopy as a Tool to Investigate Surface Forces: Basic Principles and Applications. Modern Research and Educational Topics in Microscopy (ed. A. Méndez-Vilas and J. Díaz), FORMATEX, 2007, 747-757.
[7] M. B. Viani, T. S. Schäffer, A. Chand, M. Rief, H. E. Gaub and P. K. Hansma, J. Appl. Phys., 1999, 86, 2258.
[8] J. H. Hoh, J. P. Cleveland, C. B. Prater, J. P. Revel and P. K. Hansma, (1999). J. Am. Chem. Soc. 114, 4917 (1992). & W. F. Heinz and J. H. Hoh, Trends Biotechnol. 17, 143.
[9] A.L. Lavanya Devi, Upendra Nongthomba, M.S.Bobji, Quantitative characterization of adhesion and stiffness of corneal lens of Drosophila melanogaster using atomic force microscopy, Journal of the mechanical behavior of biomedical materials, 2015, 53, 161–173.