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# Pushing nanoparticles of La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>

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#### Abstract

Pushing nanoparticles of  $La_{0.7}Sr_{0.3}MnO_3$  (LSMO) on a native SiO<sub>2</sub> surface using atomic force microscopy (AFM) in the tapping mode is presented. The pushing is accompanied by a repulsive tip–sample interaction between the AFM tip and the LSMO nanoparticles and the physisorption of the LSMO on the SiO<sub>2</sub> surface. The AFM images show scratch artifacts on the surface, indicating that artificial scratches are strongly related to the pushing of the LSMO nanoparticles. A possible approach to pushing nanoparticles is proposed. © 2004 Elsevier B.V. All rights reserved.

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#### 1. Introduction

Since its invention, scanning tunnelling microscopy (STM) [1] has been applied to elucidate the important and interesting push at atoms and molecules. Some fascinating studies have shown that atoms [2–4] or molecules [5–9] adsorbed on surfaces were pushed, moved, displaced, or rearranged into special patterns by means of STM tips. However, the pushes were performed in extreme and costly environments, characterized by, for example, low temperature (~4K) or ultrahigh vacuum (~1 × 10<sup>-10</sup> Torr). Nevertheless, pushing atoms and molecules has opened up possibilities for assembling small structures and fabricating surface functional devices on atomic and nanometer scales. Recently, atomic force microscopy (AFM) has been used to push nanoparticles [10,11] at room temperature in an ambient way or in a liquid environment. In addition, AFM can be used as insulators and to measure the forces between tip and substrate. Therefore, not only atoms [12] and large molecules [13–15] but also biomaterials [16–20] can be pushed using AFM.

In this work, we present the pushing nanoparticles of  $La_{0.7}Sr_{0.3}MnO_3$  (LSMO) using an ambient AFM. The LSMO nanoparticles deposited on a native SiO<sub>2</sub> layer of Si(111) are a perovskite-type manganese, and their magnetic properties vary with temperature [21,22]. During the pushing of

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the LSMO nanoparticles, surface scratches are observed on the native  $SiO_2$  surface. The surface scratches are image artifacts because the surface is found to be intact. Therefore, pushing LSMO nanoparticles is strongly related to the surface scratch. A possible approach to pushing nanoparticles is presented.

# 2. Experiments

The pushing of the LSMO nanoparticles was conducted at room temperature using an ambient AFM (NT-MDT, Moscow, Russia). A  $7 \times 7 \text{ mm}^2$ Si(111) wafer cut from a commercial wafer was capped with a 2 nm-thick native SiO<sub>2</sub> layer. Nanoparticles of LSMO were deposited on the native SiO<sub>2</sub> layer from a LSMO target, by off-axis DC magnetron sputtering system. AFM images were acquired using gold-coated Si cantilevers also from NT-MDT. These cantilevers had an average length, width and force constant of  $\sim 0.1 \,\mathrm{mm}$ , 0.35 mm and 11.5 N/m, respectively. Fig. 1 schematically depicts the tapping-mode operation of AFM. A piezoelectric plate vertically oscillated a cantilever (along the z-axis). The oscillation was maintained at a characteristic resonant frequency of  $f = \sim 258 \, \text{kHz}$ , with an amplitude of  $A_0 = \sim 192.3$  nm. When the tip of the cantilever was tapping the sample surface, the oscillating amplitude was set to  $A = \sim 96.2 \,\mathrm{nm}$ , which was approximately  $\frac{1}{2}A_0$ . During scanning, the tip swept right to left (along the x-axis) and forward and backward (along the y-axis). The scanning speed was ~ 25,227 nm/s.

# 3. Results and discussion

Fig. 2 shows three AFM images obtained in three sequential scans, where LSMO nanoparticles were adsorbed and pushed on the native SiO<sub>2</sub> layer in an ambient environment. The AFM image in Fig. 2(a) was obtained during the first scan. Bright circles and a black row were observed on the SiO<sub>2</sub> surface. These bright circles, labelled by letters from A to F, have a mean diameter of  $\sim 130 \text{ nm}$ and height of  $\sim 3 \text{ nm}$ ; they represent LSMO nanoparticles adsorbed on the surface. The black row has a length of  $\sim 3100$  nm, a width of  $\sim$ 115 nm, and a depth of  $\sim$ 1.9 nm; it is a long scratch that runs in the forward scan direction (y-axis) from a position labelled, G, to the top edge of the AFM image. Notably, each result was an average of five measurements taken using the AFM profile function. The strikes across the image may have been due to interference of the AFM tip as it acted on the LSMO nanoparticles.

The second scan, as shown in Fig. 2(b), was performed immediately after the first scan on the same area, using the same scanning parameters. Fig. 2(b) shows that the long scratch and the B nanoparticle disappeared, but the other LSMO nanoparticles did not move, implying that no scratch really occurred on the surface. Restated, the SiO<sub>2</sub> surface from G to B in Fig. 2(a) was not damaged. However, a new short scratch of ~190 nm was observed in Fig. 2(b). It also ran in the forward scan direction (y-axis) from B to the top edge of the image. Then, obtained during the third scan over the same area using the same scan



Fig. 1. 3D schematic of tapping-mode AFM operation.



Fig. 2. Three sequential AFM images (a, b, c) showing that scratches disappear and LSMO nanoparticles are pushed on the native  $SiO_2$  layer in an ambient environment.

parameters, the AFM image in Fig. 2(c) shows that the short scratch also disappeared; neither vanishing of the surface particle nor any new scratch was observed. Consequently, the short scratch is strongly related to vanishing of the B nanoparticle, implying that the long scratch may occur because of a vanishing nanoparticle adsorbed at the G position.

Fig. 3 illustrates the pushing of a nanoparticle using the tapping-mode operation of AFM. Fig. 3(a) schematically shows that a nanoparticle physically adsorbs a surface, and a photodiode receives and registers the reflected laser beam from an oscillating cantilever to trace the surface contour. The nanoparticle is pushed by a lateral



Fig. 3. Sequence of schematic diagrams (a, b, c, d), depicting processes of pushing a nanoparticle in the tapping mode.

interaction with the tip of the cantilever, as shown in Fig. 3(b). After the nanoparticle is moved away, the cantilever is immediately lowered onto the surface in a rather short response time, and the tip of the cantilever is dropped into the native  $SiO_2$ layer, causing damage, as schematically illustrated in Fig. 3(c). Repeating the processes of Fig. 3(b) and (c) causes a scratch on the surface. A line with an arrow represents a scanning trace that is a surface contour.

However, no scratch exists on the surface, so the scanning trace shall not be observed. Fig. 3(d) depicts a simple bending cantilever to elucidate the formation of the scratch and the vanishing of the nanoparticle. After the nanoparticle is pushed away, the cantilever is lowered quite quickly. Therefore, the tip heavily contacts the native  $SiO_2$  surface, and the strong force between the tip and the surface bends the cantilever. The laser beam is reflected into the photodiode at the same position as in Fig. 3(c). Hence, repeating the processes shown in Fig. 3(b) and (d) induces the scratch artifact and the pushing of the nanoparticle.

In this experiment the tip-sample interaction between the AFM tip and the LSMO nanoparticles is a repulsive force. The AFM cantilever is vibrated in a simple harmonic oscillation whose amplitude  $A_0 = \sim 192.3$  nm, but at the tapping surface, the amplitude is reduced to about  $\frac{1}{2}A_0$ . According to Hook's law,  $|F| = k\Delta A = \frac{1}{2}kA_0 =$  $\sim 1.11 \times 10^{-6}$  N, where k = 11.5 N/m is a force constant. A frictional force  $(f_s)$  between the nanoparticle and the surface prevents the nanoparticle from being pushed by the force applied by the tip. If the given force (|F|) is exerted on the nanoparticle along the z-axis, then the maximum frictional force  $f_{\text{max}} = \mu_s F$ , where  $\mu_s$  is a coefficient of static friction that depends on the nature of the surface in contact. If the tip acts on the edge of a nanoparticle, the given force has lateral  $(F_{\nu})$  and vertical  $(F_z)$  components. Hence, the frictional force  $f_s = \mu_s F_z$ . When  $F_v > f_s$ , the LSMO nanoparticles can be pushed away, indicating that the LSMO nanoparticles are physically adsorbed on the surface. Statistically, the occurrence rate of pushing LSMO nanoparticles is  $\sim 15\%$  only in this experiment.

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# 4. Conclusion

Pushing LSMO nanoparticles is presented using the tapping-mode operation of AFM. Because scratch artifacts of the AFM image are observed on the native SiO<sub>2</sub> surface, the pushing of the LSMO nanoparticles is strongly related to scratch artifacts. The tip–sample interaction between the AFM tip and the LSMO nanoparticle is a repulsive force, and the adsorption of the LSMO nanoparticle on the SiO<sub>2</sub> surface is a physisorption. At a lateral force that exceeds the frictional force, the LSMO nanoparticles can be pushed away, but the occurrence rate is ~15% only. Therefore, the pushing of the LSMO nanoparticles in the tapping-mode operation of AFM is still difficult.

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