

## Manipulation of Ag nanoparticles utilizing noncontact atomic force microscopy

M. Martin,<sup>a)</sup> L. Roschier, P. Hakonen, Ü. Parts, and M. Paalanen  
*Helsinki University of Technology, Low Temperature Laboratory, FIN-02015 HUT, Finland*

B. Schleicher and E. I. Kauppinen  
*VTT Chemical Technology, VTT Aerosol Technology Group, P.O. Box 1401, FIN-02044 VTT, Finland*

(Received 8 June 1998; accepted for publication 10 July 1998)

We have developed a scheme to manipulate metallic aerosol particles on silicon dioxide substrates using an atomic force microscope. The method utilizes the noncontact mode both for locating and moving nanoparticles of size 10–100 nm. The main advantage of our technique is the possibility of “seeing” the moving particle in real time. Our method avoids well sticking problems that typically hamper the manipulation in the contact mode. © 1998 American Institute of Physics.  
[S0003-6951(98)00337-4]

It is rather well established by now that scanning probe microscopy (SPM) can be utilized to manufacture nanostructures. Several approaches have been, and continue to be, studied. These methods provide one of the most promising ways to produce room-temperature mesoscopic quantum devices in an efficient fashion. Reliable manufacturing processes are a must before there is any hope for proliferation of such nanoscale devices, e.g., single electron transistors (SET), in the future.

In our laboratory, we concentrate on nanostructures made of nanometer-sized aerosol particles. It was demonstrated recently that an atomic force microscope (AFM) can be used to arrange and manipulate Au clusters<sup>1</sup> and aerosol particles<sup>2</sup> as well as evaporated nanoscale platelets.<sup>3</sup> In these undertakings, the AFM tip was used as a tool to push particles along smooth substrates. Tips as sharp as possible were employed in order to minimize the adhesion force between the particles and the tip. Nevertheless, severe problems with particle sticking were observed. In spite of these shortcomings, good control for positioning of aerosol particles was achieved, and even basic SET operation could be demonstrated.

In this letter, we report a method to position aerosol particles of 10–100 nm in diameter. Our method employs the noncontact (NC) mode both to locate and to move particles on smooth silicon dioxide substrates. Using the NC mode we encounter fewer problems with apex wear and tip degradation due to particle sticking as compared with the work by Junno *et al.*<sup>2</sup> The main advantage of our method, however, is the possibility of knowing the particle position, even when it is moving.

We produce nanometer-sized particles suspended in a carrier gas (aerosol) by a technique called spray pyrolysis.<sup>4</sup> A solution of about 4.5 g of AgNO<sub>3</sub> in 1 l of ultrapure water is sprayed in the form of small droplets into a N<sub>2</sub> carrier gas using a constant output collision atomizer. The mean size of a droplet is about 800 nm. The nitrogen picks up the particles

and transports them in a ceramic tube (inner diameter: 8 cm) through a hot flow reactor (three zone furnace, Lindberg 55666, heated length ~90 cm) heated to about 700° C at a flow rate of about 3 l/min at room temperature and atmospheric pressure. In the reactor water evaporates, AgNO<sub>3</sub> decomposes and an Ag particle is formed from each precursor droplet. The particles leaving the furnace are not uniform in size, but have a lognormal size distribution. These particles are charged in a diffusion charger and subsequently a differential mobility analyzer (DMA) extracts a desired particle size by their electric mobility. The 95% monodisperse, charged aerosol particles leaving the DMA are removed from the gas and precipitated in an electric field on a SiO<sub>2</sub> substrate (100 nm of thermally grown oxide on top of bulk (100) Si) that was swept clean with an AFM in contact mode before the deposition.

Because of nearly spherical shape of the aerosol particles, their adhesion force to the sample surface is much smaller than in the case of evaporated dots of the same dimensions. Imaging of these particles with contact mode AFM is not really possible unless stabilization by sintering is done.<sup>5</sup> The adhesion force fails to keep the particle stationary during contact mode scanning and, as a result, the particle is either moved unintentionally or lifted away from the surface by the tip.<sup>2</sup> Hence, only the noncontact mode imaging can be used to locate particles on the substrate. In the NC mode, the tip is vibrating at a constant frequency, slightly above its resonance frequency. The vibration amplitude diminishes as the distance decreases, so that one can image the topography in a safe way, as the van der Waals force between the tip and the sample is about a few of piconewtons.

We employed our AFM (PSI Autoprobe CP) in NC mode all through this work. This differs from the earlier work<sup>2</sup> where a combination of contact and noncontact modes was used. The AFM was operated in ambient air (relative humidity 50%) using cantilevers (PSI Ultralevers) with resonance frequency of  $f_{\text{res}} = 104$  kHz. The spring constant of these triangular silicon cantilevers is  $k = 2$  N/m and the  $Q$  value is about 100. The cantilever deflection was measured continuously by a laser beam which reflected from the cantilever to a double channel ( $A/B$ ) photodetector. The tip ra-

<sup>a)</sup>Permanent address: CNRS-CRTBT, BP 166X, F-38042 Grenoble Cedex 9, France. Electronic-mail: michmart@boojum.hut.fi

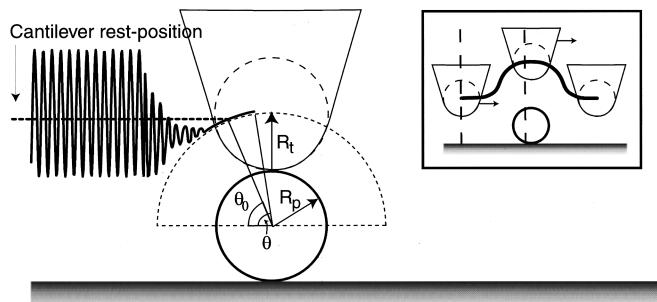


FIG. 1. Schematic view of our scan method to move particles utilizing the noncontact mode. The trace in the inset illustrates an overall scan, made first to locate particles on the substrate; the line scan, selected to move a particle with radius  $R_p$ , is denoted by the dashed vertical lines. The oscillation amplitude on the left depicts the vertical movement of the tip over the scan line when the feedback is switched off. The tip is brought closer to the substrate till the particle starts to move at the right end of the scan. Angles  $\theta_0$  and  $\theta$  parameterize the “zero force” and the scan reversal points on the sphere, respectively.

dius  $R_t$ , nominally 20 nm, was verified afterwards using a scanning electron microscope (SEM); in the worst case it was found to be 50 nm.

The algorithm we developed to move particles is described as follows (see Fig. 1): first, an image of sample topography is taken to check the particle position. The feedback loop is still on and a line, scanned at a rate of 2 Hz, is selected in the desired direction for the chosen particle. The length of the line scan is about two or three times the particle diameter. An offset is made to place the end of the scan above the particle; this guarantees that the movement begins in the desired direction. The feedback loop is then switched off to have direct control of the  $z$  axis. The sample height is increased gradually until there is a clear change in the vibration amplitude of the tip. The point at which the tip touches the particle is easy to find as the vibration amplitude becomes zero. Depending on how the particle reacts, one can choose either to lift or lower the sample in order to achieve a suitably strong tip-particle interaction. As the tip touches the particle, it tries to push it towards the end of the scan. The displacement of the particle may take place in one single push or it may take a few scans. As we monitor the vibration amplitude in real time, it is easy to follow the reaction continuously and, thereby, the position of the particle. After the particle has been moved, a new offset is given to the scan line to continue the movement until the final position is reached. At this point, it is possible to select another particle for movement without taking a topography image as the position of the displaced particle is well known.

The tip-particle interaction during the movement, as seen by the difference  $A-B$  of the photodetector, is illustrated in Fig. 2. Three different regimes can be resolved in the trace of the oscillation amplitude. First, on the left the vibration amplitude is determined almost solely by the drive ( $f_{dr}=f_{res}+0.5$  kHz) and the response of the cantilever, although the presence of the substrate slightly decreases the swing; for free vibration the amplitude was set to  $100 \text{ nm}_{\text{peak-peak}}$ . In the second regime, where the tip starts to feel the van der Waals force more strongly, the resonance frequency shifts and the oscillation amplitude is reduced substantially owing to the reduced coupling of the fixed-frequency drive. As the tip-

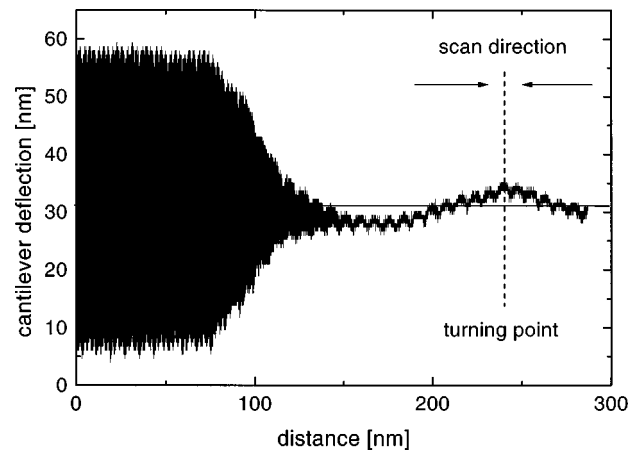


FIG. 2. Trace of the differential photodetector signal  $A-B$  as the tip ( $R_t \sim 50$  nm) approaches a 55 nm particle and moves on top of it. The cantilever is excited at a constant drive frequency  $f_{dr}=f_{res}+0.5$  kHz. The horizontal line indicates the equilibrium height of the cantilever, i.e., the position where the vertical force is zero.

particle separation decreases further, the tip is eventually trapped by the surface (“negative deflection”) and the vibration amplitude becomes zero. The tip then starts to track the particle, but the pushing begins only after the cantilever deflection has become positive. The hysteresis observed in the contact/off-contact points was rather small. This we interpret so that there is not much water adsorbed on the particles at our operating conditions.<sup>6</sup>

The scan illustrated in Fig. 2 was made 5 nm below the top of the sphere. During this scan the particle did not move, although the parameters were rather close to those at which movement starts. The horizontal force  $F_x$  can be estimated in a straightforward way without friction. Using the parameterization given in Fig. 1, the force may be written as

$$F_x = \frac{k(\sin \theta - \sin \theta_0)R_p}{\tan \theta}.$$

According to this formula, the lateral force needed to induce movement is about 2 nN for 55 nm silver particles. The measured threshold force depended on the particle size and varied strongly among different positions of the particles, i.e., it depended on the variation in the roughness of the substrate ( $\sim 0.8 \text{ nm}_{\text{rms}}$ ). Compared with typical atomic friction forces,<sup>7</sup> our values are larger by an order of magnitude.

The accuracy of our displacement method depends on the particle radius. Provided that the particle and tip radii are on the same order, one can rather simply move particles to predefined locations within about 10% of their diameter. However, it is quite difficult to get below this limit. It is not clear at all if the particles can be moved  $\text{\AA}$  by  $\text{\AA}$  as the surface potential may contain a complicated distribution of local minima. The operating range can be easily varied: particles can be pushed over several micrometers or only a few nanometers. Figure 3 illustrates the resolution achieved when writing the letters LTL using 45 nm diameter silver particles. Under optimum operation conditions, the structure shown in Fig. 3 can be constructed in a few hours. Since the particles can be followed well during the movement process, we don’t see any real obstacle in speeding up our manipulation method by automation.

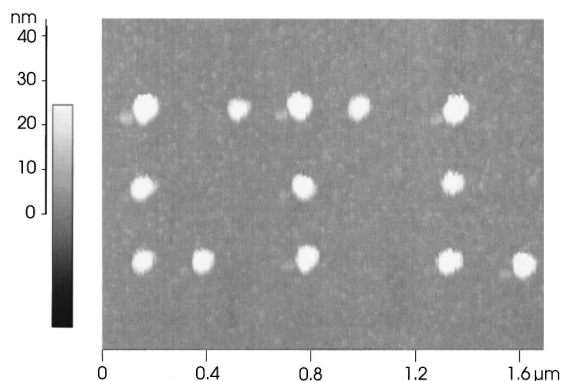


FIG. 3. Low temperature laboratory (LTL) written in block letters with 45 nm silver particles on top of silicon dioxide substrate.

We have also tried the contact mode by Junno *et al.*<sup>2</sup> Using this method we encountered severe sticking problems as was the case in their own work. Clearly, the contact mode requires extremely sharp tips for which the adhesion force towards the apex is smaller than towards the substrate. In our method, on the contrary, we have been able to move 8 nm particles using a tip having  $R_t = 37$  nm almost without any sticking problems. The lateral force with 8 nm particles was clearly less than with 45 nm particles.

It is not clear to us why our method avoids so well the problem of sticking. Inertial forces due to tip vibration might favor sticking to the stationary substrate. Our numerical simulations, however, do not support this view. Any material dependence is excluded by the fact that we have sticking when using the contact mode scheme. This leaves capillary condensation as the only possible source for the difference in the sticking behavior. Hence, we conjecture that sticking is caused mostly by condensed water and, in our case, the con-

tact time of 50-100 ms is not long enough to produce a binding between the adsorbed water layers. This conjecture will be tested in the future in a dry nitrogen atmosphere.

In summary, we have developed a method to manipulate nanometer size aerosol particles using an AFM microscope. Our method is based on continuous scanning of a line and simultaneous acquisition of the vibration amplitude of the cantilever. The main advantage of this technique is the possibility of “seeing” the moving particle in real time, which allows the control of position down to 10% of the particle diameter. Surprisingly, minimal sticking of silver particles on silicon tips was found under our experimental conditions, even when moving particles ten times smaller than the apex of the tip.

The authors want to thank P. Davidson, T. Junno, L. Montelius, U. Tapper, and R. Vuorinen for useful discussions and assistance. This work was supported by the Academy of Finland, by TEKES of Finland via the Nanotechnology program, and by the Human Capital and Mobility Program ULTI of the European Community.

<sup>1</sup>D. M. Schaefer, R. Reifenberger, A. Patil, and R. P. Andres, *Appl. Phys. Lett.* **66**, 1012 (1995).

<sup>2</sup>T. Junno, K. Deppert, L. Montelius, and L. Samuelsson, *Appl. Phys. Lett.* **66**, 3627 (1995).

<sup>3</sup>L. Montelius, T. Junno, S.-B. Carlsson, and L. Samuelsson, *Microelectron. Eng.* **35**, 281 (1997).

<sup>4</sup>A. Gurav, T. T. Kodas, T. Pluym, and Y. Xiong, *J. Aerosol Sci.* **19**, 411 (1993).

<sup>5</sup>T. Junno, S. Anand, K. Deppert, L. Montelius, and L. Samuelsson, *Appl. Phys. Lett.* **66**, 3295 (1995).

<sup>6</sup>With a considerable amount of condensed water, even dragging of particles with a sharp tip is possible.

<sup>7</sup>T. Gyalog and H. Thomas, *Z. Phys. B* **104**, 669 (1997).