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Scanning tunneling lithography of silicon nanoparticle films

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Abstract. Monolayer and bi-layer silicon nanoparticle (SiNP) films with wide band gaps (up to 4 eV) have been produced in UHV with narrow size distributions of particles with 2–4 nm diameters and were studied using scanning tunneling microscopy (STM) and spectroscopy (STS). The films then were manipulated by applying different values for the tunneling resistance. Nanoparticle fusion and fission processes allow to shape the particles in the films in various ways and to write in white and black on the film template.

PACS. 81.16.Nd Nanolithography – 36.40.-c Atomic and molecular clusters – 81.16.Ta Atom manipulation – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

Methods for fabricating nanoscale structures have received considerable attention over the last decade. Nanoscale patterning may be used in future technologies such as nanoelectronics, sensors, quantum wire lasers and single-electron transistors. Currently, optical lithography is the standard method used by semiconductor industries to manufacture integrated circuits. The size of structures that can be created is determined by the wavelength of the photons and by the quality of the processing equipment.

X-ray proximity printing and electron beam writing are currently the best lithographic techniques to write structures below 100 nm, and linewidths down to 20 nm have been achieved [1]. In recent years, scanning probe microscopy (SPM) has become a new tool for lithography processing with structures on the nanoscale down to the atomic level [2]. Nanofabrication with SPM is relatively inexpensive and can be used for producing masks [3] or direct patterning [4].

Silicon is of particular interest for nano-imprinting. Nanoscale structures have been written into 20 nm thick light-emitting porous silicon films using an STM [5]. Atomic manipulation has been applied to write nanoscale trenches in Si(001) surfaces with an STM [6]. Another technique is the oxidation of a hydrogen terminated silicon surface, induced by an STM [7]. Nanofabrication on silicon oxide has been achieved by an electron-beam stimulated reaction in the STM tunneling gap [8]. In this paper STM studies are reported which show structural modifications by fission and fusion of silicon nanoparticle films.

The particles were grown on highly oriented pyrolytic graphite (HOPG) upon deposition of several monolayers of silicon. Starting from a base pressure of 3×10^{-7} Pa, the deposition was done by dc magnetron sputtering of silicon at an argon pressure of 500 to 1100 Pa. The silicon target was of 99.999% purity. The amount of deposited material was measured with a thickness rate monitor. Once the Si atoms arrive on the HOPG substrate, they are quickly thermalized and nanoparticles form after surface diffusion by quasi-free growth.

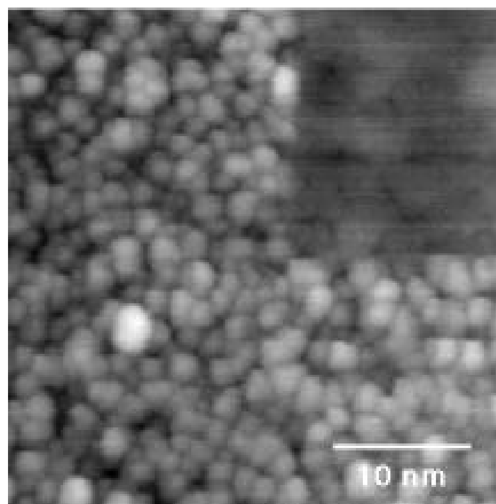

Fig. 1. 35 nm × 35 nm STM image of a silicon nanoparticle film (3.55 V bias voltage, 0.16 nA setpoint current). The dark, flat region on the upper right side is produced by scanning this area of the film with 4.0 V bias and 4.0 nA setpoint current.

After the deposition the samples were transferred to the STM chamber (10^{-8} Pa). The samples were analyzed by STM at room temperature. Stable STM topographs could be achieved applying high bias voltages (3 to 10 eV) and low tunneling currents (< 0.3 nA).

Figure 1 shows the STM image of a compact thin film of silicon nanoparticles. A bias voltage of 3.55 V and

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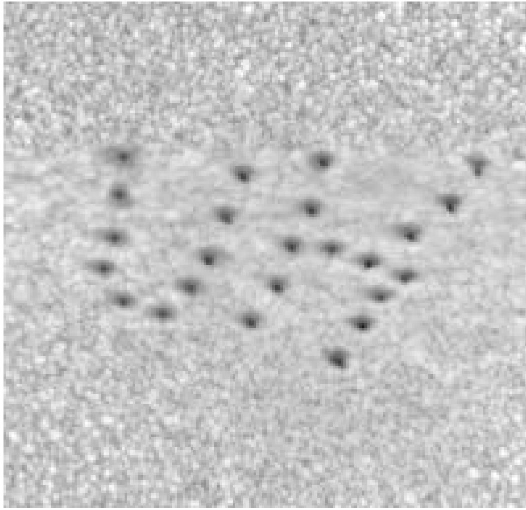

Fig. 2. STM image of a SiNP film with black dots forming the letters U and H. Such a dot was produced by scanning over a ~ 4 nm $\times$ 4 nm area with much lower setpoint current compared to scanning for taking the image.

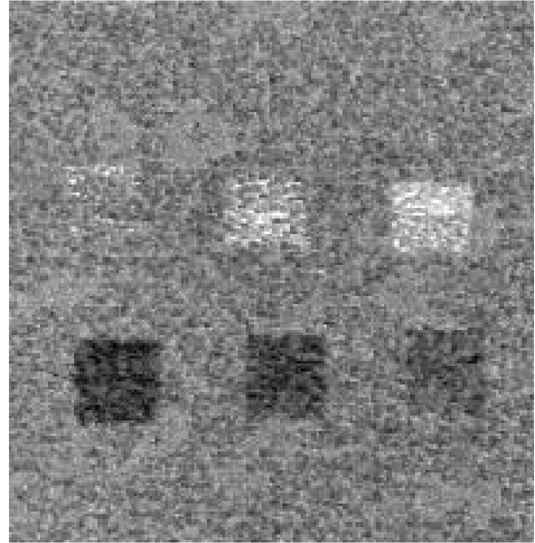

Fig. 3. 700 nm $\times$ 700 nm STM image of a SiNP film taken at 3.85 V and 0.11 nA. The film had been manipulated leaving black and white squares. The black squares are produced with lower tunneling resistance compared to taking an undisturbed image and are scanned one, two and three times from right to left, respectively. For the white squares 100 nm $\times$ 100 nm areas are scanned with very high tunneling resistance (> 100 GΩ), one, two, and three times, from left to right, respectively.

a setpoint current of 0.16 nA were applied. The particles are mostly spherical and have a narrow size distribution. The average particle size is about 3 nm. Images taken with frame sizes up to 1.7 microns and in different regions of the sample show that the films are flat over large dimensions. By variation of the source parameters we found that one particle layer was first forming and completely covering the substrate before the second layer started to form. The layer-by-layer growth makes nanolithographic treatment of the particle films possible.

On the upper right side of Figure 1 we scanned a 15 nm $\times$ 15 nm region of the sample with different bias voltage and setpoint current, 4 V and 4 nA, respectively. This leads to a significant modification of the particle film in this region. Silicon is removed in this area leaving a flat plane with reduced height above the substrate surface. The particles have been flattened at the top by atomic and/or ionic evaporation. We believe that this occurs due to electrons trapped in the particle surface and the high electric field between tip and nanoparticle. We found that more atomic layers are removed when we scan several times over the same region.

Figure 1 also displays very sharp edges on the side of the indentation area. This shows that the electron beam was very sharp. Individual silicon particles are cut on the side. The method allows us to shape individual particles in form of little cubes, since flat facets can be generated both on the top and on the sides.

With the same conditions as just described, black dots can be written into the SiNP film. This is demonstrated in Figure 2, where the letters UH (for University of Hawaii) have been written. For writing one black dot we scanned over a ~ 4 nm wide area inducing fission of particles. Then we moved the tip to another region creating the next dot. A clear pattern of regular dots can be written this way. In the same way we have produced a number of different pattern. We found that these patterns were unchanged over several days while we checked their stability.

We found that with every further scan over a particular area the flat plane became deeper which means darker on the grey particle template. This is illustrated in the bottom half of Figure 3. Three 10 nm $\times$ 10 nm squares are shown becoming darker from left to right because they were scanned one, two, and three times, respectively. Every additional scan makes the plane deeper. In this way we could dig deep down to the graphite substrate and determine the thickness of a SiNP film.

On the upper half of Figure 3, three 10 nm $\times$ 10 nm squares are shown becoming increasingly brighter from left to right, on the grey SiNP template. Producing white regions requires high bias voltages (~ 10 V) and very low setpoint currents (< 0.1 nA).

Using these settings, the three squares, from left to write, where produced by scanning one, two, and three times over this area, respectively. The square on the left is just starting to become white. Inspection of the area shows, that some of the silicon particles have increased their size. It makes them brighter in the STM image and they appear white on the grey SiNP film template. By scanning more often over the same area, more of the silicon particles become enlarged. We analyzed the "white" particle sizes and found that they were generated by fusion of 2–3 particles from the film template. The fusion process occurs at very high voltage-current ratio with a tunneling resistance of ~ 100 GΩ between tip and sample.

The fusion of SiNPs can be used to write dots and letters in white on the grey background of the template.

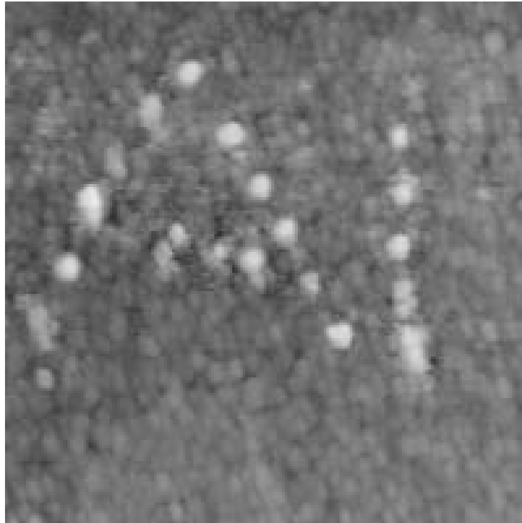

Fig. 4. STM image of a SiNP film where white dots were written for the letters A and I. For a write dot, a 4 nm area was scanned using tunnelling resistance > 100 GΩ. Fusion of two to three particles of the film lead to the formation of the larger particle that appears white on the grey scale of the nanoparticle template.

This is demonstrated in Figure 4 with letters A and I. For forming a white dot we scanned a small area (typically 4 nm × 4 nm) on the SiNP film. This leads to fusion of the nanoparticles in this area. The fused particles become spherical and appear as circular dots on the grey template. Moving to select areas and repeating the fusion process allows us to write specific pattern and letters. These structures were stable over several day periods of monitoring.

Summary

STM studies of structural modifications by fission and fusion of silicon nanoparticle films are reported. The films consist of self-assembled densely packed nanoparticles, with narrow size distribution. For nanofabrication the settings of tunneling current and bias voltage are changed to values where atoms from the nanoparticles are removed. Fusion of particles is observed in areas scanned with very high tunneling resistance. The fission and fusion processes allow us to produce shapes and to write in black and white on the grey SiNP template, respectively.

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