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Fabrication of Nanoparticle Pattern Through Atomic Force Microscopy Tip-Induced Deposition on Modified Silicon Surfaces *

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With an atomic force microscopy (AFM) tip used as a "nib" and gold colloidal particles as "ink", patterns of gold colloidal particles have been deposited successfully from the AFM tip onto specific regions of silicon surfaces modified by bifunctional mercaptosilane, i.e. (3-mercaptopropyl)-triethoxysilane. This was used as an adhesion agent and can immobilize nanoparticles delivered from the AFM tip onto the substrate surface.

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Scanning probe microscopy (SPM), including scanning tunnelling microscopy (STM) and atomic force microscopy (AFM), has been used to modify surfaces on a nanometre-scale through various interactions between the tip and the substrate, besides obtaining the sample topographical image of surfaces.[1−4] Researchers have performed the applications of the high resolution and alignment accuracy,[5,6] thus making it possible to fabricate reliable nanometre-scale electronic devices which cannot be achieved by conventional lithography techniques.[7] The most popular lithography techniques to fabricate nanostructures are SPM, resist film lithography[8] and lithography by oxidation[9], and a less popular way is direct scratching of the sample surface by the probe.[10] Based on SPM nanooxidation using its ultra high-resolution,[11,12] research works have been put forward on position-controllable assembling of colloidal nanoparticles on solid substrates. This has received a great deal of attention over the last few years for its potential applications in catalysis, nonlinear optics, sensors, magnetics and nanoelectronics.[13−15] Recently, a direct-write "dip pen" nanolithography (DPN) has been developed to deliver collections of molecules in a positive printing mode and writing alkanethiols with 30 nm linewidth resolution on a gold thin film achieved in a manner analogue to that of a dip pen.[16−18] Although using the DPN technique can "write" a perfect organic molecular pattern, it is necessary to find out whether metal nanoparticles can also be deposited from the AFM tip to solid surfaces with this method.

In this letter, we demonstrate the fabrication of the nanoparticle pattern employing the DPN principle with an AFM tip used as a "nib" and gold colloidal particles used as "ink". The substrates were modified by bifunctional mercaptosilane, i.e. (3-mercaptopropyl)-triethoxysilane (MPTS), which can immobilize the nanoparticles delivered from an AFM tip onto the substrate surface.

The employed substrates were silicon (100) wafers with a ∼2 nm thick SiO_2 cover formed by exposure to the atmosphere. In order to make the transported gold nanoparticles anchor to the substrates through chemisorption, the substrates used were modified by bifunctional MPTS. Figure 1 shows the experimental procedures for fabricating patterns of gold colloidal nanoparticles delivered from the AFM tip onto chemical modified silicon substrates. The polished silicon (100) substrate was firstly immersed in potassium dichromate-vitriol (20 g potassium dichromate dissolved in 20 ml water and added to 400 ml dense vitriol) for 5 h, thoroughly rinsed in two distilled water baths and dried with nitrogen. Then it was baked at 100°C for 30 min to remove the water adsorbed on the substrate surface. SiO_2 is liable to be terminated by hydroxyl groups in the atmosphere, as shown in Fig. 1(a). Afterwards, the sample was immediately immersed in a 1 mM distilled toluene solution of a bifunctional MPTS for 5 h. Then the sample was successively rinsed in toluene and acetone to remove the residuals. The MPTS treatment replaces the hydroxyl groups (OH) adsorbed on the SiO_2 substrate with MPTS molecules forming a siloxane bond between the SiO_2 on one end of the MPTS molecules and an oxygen atom on the SiO_2 surface. As a consequence, the thiol group attached on the other end of the MPTS molecule is oriented away from the substrate which can immobilize the gold colloidal particles on the substrate surface because of the strong affinity of sulphur to gold (Fig. 2(b)). The gold colloidal particles with 10 nm in diameter on average (confirmed by transmission electron microscopy (TEM)) in this letter were synthesized using a reduction of chloroauric acid ($HAuCl_4$) with trisodium citrate.

In our experiments, a silicon nitride tip was coated with gold colloidal particles by dipping the cantilever

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into the aqueous gold colloid for about 2 min. Then it was blown dry with nitrogen gas and was scanned across three areas, 160 nm in width and 5 μm in length, to demonstrate that the gold nanoparticles can transport from the AFM tip to the modified silicon surface. The contact mode is used with the "set point" set at 0 V, and the force between the tip and the substrate surface is about 5 nN. The substrate is kept in a clear place for about 5 h. A new silicon nitride tip is used to image the pattern formed by the deposited gold nanoparticles (Fig. 2) in tapping mode. A letter has been drawn in the same way (Fig. 3). All our experiments were performed with a Nanoscope Ⅲa AFM (Digital Instruments, Santa Barbara, CA).

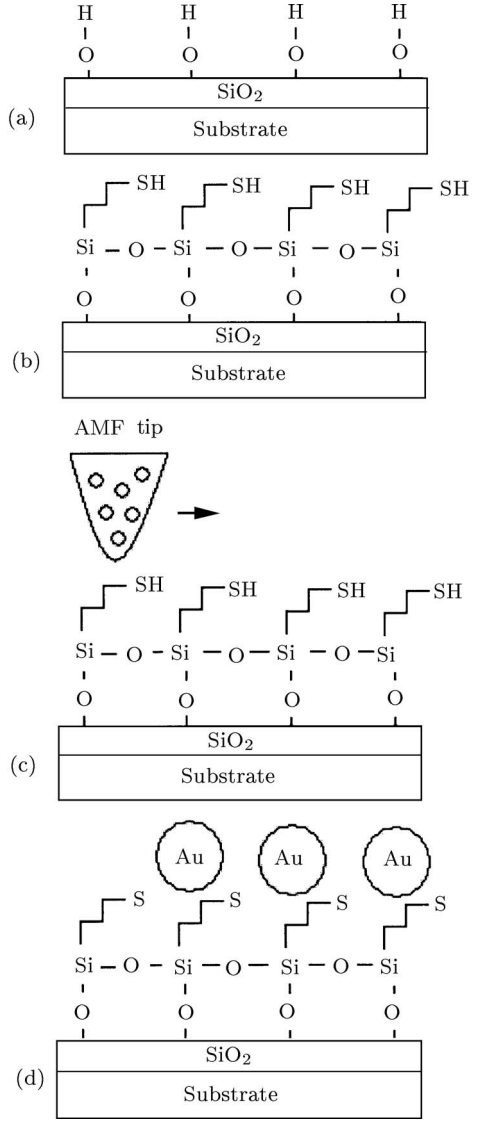


Fig. 1. Experimental procedures for fabricating patterns of gold colloidal nanoparticles selectively delivered from the AFM tip onto chemical modified silicon substrates: (a) hydroxyl group terminated SiO_2 surface; (b) mercapto functional silane deposition; (c) delivering of gold colloidal particles from AFM tip; (d) immobilization of gold colloidal particles.

Figure 2 shows an AFM image of three lines, 160nm in width and 5 μm in length. Before deposition, the modified silicon surface was scanned for regular patterns and none was found, so the pattern in Fig. 2 is faithfully formed by the gold nanoparticles delivered from the AFM tip to the modified silicon surface. The linewidth we obtained equals the width we scanned, which indicates that when the gold nanoparticles transport to modified silicon surface, they immediately anchor to the substrate through chemisorption. From Fig. 2 we can also see a heap of gold nanoparticles at the right end of the lowest line and for this we suggest that when AFM tip engage the surface, there are more gold nanoparticles on the tip than those later to be delivered onto the surface. With no similar cases afterward it is demonstrated indirectly. Figure 2 implies that gold nanoparticles can be transported from the AFM tip to the solid surface. The mechanism of the transportation is speculated to be similar to the DPN technique.[16] In brief, the narrow gap capillary formed between the AFM tip and the sample when an experiment is conducted in air condenses water from the ambient and the water will either be transported from the substrate to the tip or vice versa. In our experiments, the former case is predominant.

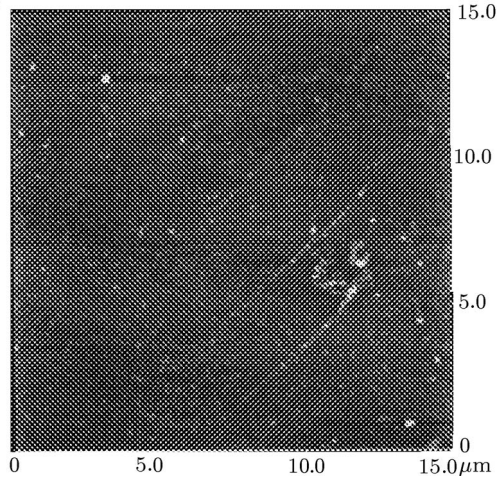


Fig. 2. AFM image of three parallel lines arranged by gold colloidal particles.

To demonstrate the ability to deposit gold nanoparticles to a specific region, a letter "L" is fabricated. Figure 3(a) shows the AFM image of the letter "L". At the two ends of the line, bends appear because when the tip began to engage or leave the surface, the piezotube would result in a slight quiver. In Fig. 3(b), where an individual gold nanoparticle can clearly be seen, the AFM image of the part is shown within the black line frame in Fig. 3(a). The larger particles in Fig. 3(b) are suggested to be the congregations of the single gold nanoparticles. The lateral size of the particles obtained from the AFM image ranges from 30 nm

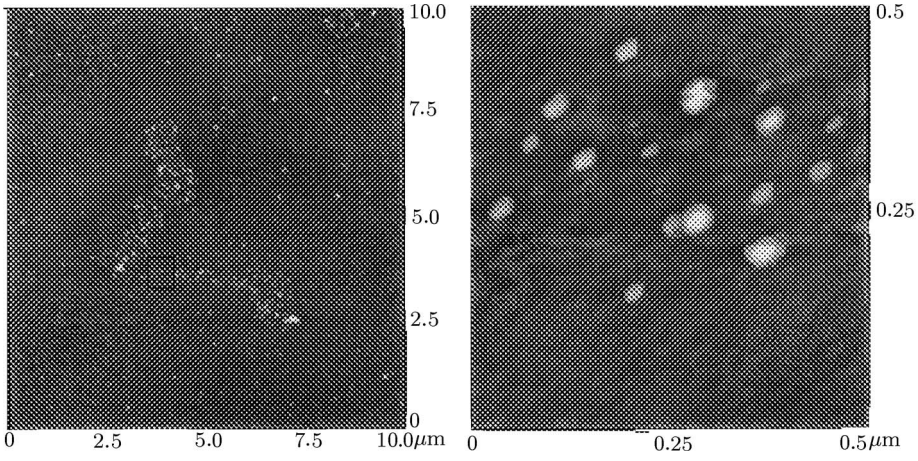


Fig. 3. (a) AFM image of the letter "L" formed by deposited gold nanoparticles, and (b) the magnified image within the frames of (a).

to 40 nm, remarkably larger than the value measured with TEM, which can be attributed to the magnification effect of the AFM tip. The gold nanoparticles deposited from the AFM tip to the modified surface are discrete, making it possible to deposit single gold nanoparticles at a specific region which is useful to fabricate nanodevices. The related studies are being performed in our laboratory.

In conclusion, a simple and convenient method has been presented to form the nanoparticle patterns using the AFM tip-induced deposition on a modified silicon surface. Patterns of gold colloidal particles have been obtained by arranging the particles using commercial AFM tips. This process is a reliable means of fabricating patterns which can be done in air without great care. Also, because deposited gold nanoparticles are discrete, this method is promising to be used to fabricate nanodevices such as quantum dots through which electron transport can be investigated.

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