

Fabrication of Nanostructures by Hydroxylamine Seeding of Gold Nanoparticle Templates

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Received August 14, 2000. In Final Form: December 18, 2000

Hydroxylamine-seeding of colloidal gold particles has been used to fabricate gold nanostructures on a SiO₂ substrate. Gold nanoparticles (15 nm diameter) were randomly deposited on a SiO₂ surface that had been modified with aminopropyltrimethoxysilane (APTS). The nanoparticles were then manipulated using a scanning force microscope (SFM) tip to produce 1-D templates for gold deposition. We demonstrate the utility of this approach by fabricating a gold nanowire by using 13 nanoparticles as a template. The junction between joined (coated) particles was examined by mechanical manipulation, and homogeneous deposition was shown to form stable structures. This approach was also used to fabricate nanostructures in a small gap between two gold electrodes. Particles were pushed into the gap, and then gold deposition was used to "connect" the particles and electrodes. Although the particular structure tested was not electrically connected to the electrode, we suggest that this approach will be useful in tackling the difficult problems associated with electrically connecting nano- to microscale structures.

Introduction

The fabrication of nanostructures is being pursued with increasing interest and activity in chemistry, physics, material science,¹ and even biology.² Increased ability to fabricate nanostructures is essential to the further development of nanoscale devices. Nanowires (one-dimensional, 1-D, nanostructures) are of major interest for the development of very small structures that can be used for efficient electron transport. Several approaches have been used for nanowire fabrication. One approach is based on direct deposition. Fang et al.³ demonstrated a large-scale synthesis of Si nanowires by sublimation of silicon powder. The resulting Si wires were uniform in diameter but arranged in complex, random shapes. Over the past several years, nanowires from other semiconductors⁴ and metals have been prepared. However, the electrical conductivity of such nanowires is still an open question. Recently, Heath et al.⁵ demonstrated the fabrication of a three-terminal Si-nanowire device, which they used to investigate the electrical properties of Si nanowires. The unique electrical characteristics of carbon nanotubes have been exploited and such wires investigated.⁶ Direct surface modification by electrochemical deposition⁷ and etching⁸ has also been used to form metallic nanowires.

Another approach for nanostructuring is the use of well-defined structures as templates. It is possible to use inherent surface structures, e.g., atomic steps, reconstruction sites, and grain boundaries, as templates. Ogino et al.⁹ have grown Ge nanostructures on Si substrates based on such surface structures. Other methods have utilized different techniques to create templates for nanostructures. Jorritsma et al.¹⁰ fabricated a large array of gold nanowires by using a V-grooved InP substrate made by holographic laser interference lithography. Au was evaporated on this substrate to form a Au-nanowire matrix. Braun et al.¹¹ used DNA as a template for the fabrication of 100 nm wide silver wires. Membranes and microtubules have also been used as templates for the synthesis of metal nanowires¹² and polymer nanostructures;¹³ in these approaches, the wires must be subsequently released from the matrix and deposited on a substrate.

Carbon nanotubes and metal nanoparticles can also be useful as templates. Both can be synthesized in a variety of sizes, and exhibit diverse chemistry that can be used for further modification of the nanotemplate. Single-wall and multiwall carbon nanotubes have been used as building blocks for nanostructures and nanotemplates.^{6,14}

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Use of particles and clusters as templates is limited by the ability to deposit the particles in a controllable way and by the ability to manipulate these building blocks. Early in the seventies, Ashkin and co-workers¹⁵ demonstrated the manipulation of micron size particles by optical tweezers. Since then, this technique has been used for manipulation of different particles and biological cells.¹⁶ The first report by Alivisatos¹⁷ showing the adsorption of semiconductor nanoparticles on a metal surface by using self-assembled organic molecules catalyzed subsequent efforts to controllably deposit colloidal nanoparticles. Kim et al.¹⁸ also demonstrated the manipulation of 500 nm polystyrene beads by using carbon-nanotube tweezers.

Scanning probe microscopy (SPM) techniques provide powerful tools for building nanostructures. For example, Nagakiri et al.¹⁹ formed latex-nanoparticle structures by using a STM probe to electrochemically and locally degrade organosilane layers. A similar approach was used by Zheng et al.²⁰ to fabricate a quasi-1-D array of gold nanoparticles by using a SFM (scanning force microscope) to define amino-terminated regions. Previously, we showed that 15 and 30 nm gold particles could be manipulated with an SFM to form 2- and 3-D structures.²¹ This ability can be used to fabricate a gold template for further chemical modification, for example, by subsequent deposition of metals.

Natan et al.²² have shown that hydroxylamine seeding can be used to produce monodisperse colloidal gold particles by "growing" the smaller particles. The seeding process is based on the use of the Au-particle surface as a catalyst for the reduction of Au³⁺ cations by hydroxylamine.²³ It has also been shown that the same process can be used to form thin films of Au on glass substrates,²⁴ with characteristics similar to those of evaporated Au films.

In this paper, we investigate the use of hydroxylamine seeding to form a gold nanowire by using a gold nanoparticle structure as a template. We find that this is a promising approach for fabricating nanostructures and electrically connecting them to larger scale structures.

Experimental Methods

Chemicals. All aqueous solutions were prepared from Millipore water (resistivity, 18 M Ω ; Millipore Systems). All solvents (analytical grade), HAuCl₄ (99.999%), and NH₂OH (99.99%) were obtained from Aldrich or VWR, and were used without further purification. 3-Aminopropyltrimethoxysilane (APTS) was purchased from Gelest Inc. and was used without further purification.

Sample Preparation. Electron-beam lithography was used to fabricate a pattern of gold grids on a SiO₂ substrate. The

patterned sample was necessary to ensure that we could return to a previously built nanostructure (template) after dipping the sample into the seeding solution. The patterned samples were sonicated for 10 min in each of the following solvents: acetone, isopropyl alcohol, and methanol. Then, the samples were treated in an UV/ozone chamber for 10 min in order to oxidize organic residues. For APTS deposition, the samples were immersed for 2 h in a 1 mM APTS solution in methanol that contained 2% added water. After deposition of the APTS monolayer, the samples were rinsed thoroughly with methanol and "blow-dried" with nitrogen. Subsequently, the samples were annealed in air for 30 min at 120 °C. Colloidal (15 nm) Au particles (EM.GC15; Ted Pella Inc.) were deposited from aqueous solution by placing a 10 μ L drop on the modified substrate for 5 min. The short deposition time of the colloidal particle solution yielded a low coverage of particles. The samples were then rinsed and "blow dried" by nitrogen. Prior to the manipulation step, the samples were treated for 3 min in an UV/ozone chamber to oxidize the APTS layer.

Imaging and Manipulation. Experiments were carried out using an Autoprobe CP AFM (Park Scientific Instruments) operated in dynamic mode in air. Triangularly shaped silicon cantilevers (Park Scientific Instruments, 13.0 Nm⁻¹ spring constant, and 340 kHz resonance frequency) were used. Probe Control Software (PCS) that was developed in our group and previously described²⁵ was used for direct manipulation of the Au nanoparticles.

Hydroxylamine Seeding of Colloidal Gold Nanoparticles. After nanoparticle manipulation, the sample was immersed for 5 min in a Teflon beaker containing an aqueous solution of 0.01% HAuCl₄ and 0.4 mM NH₂OH. The deposition was stopped by removing the sample and rinsing it with water.

Results and Discussion

We used patterned substrates in this study so that we could compare the images obtained from a particular area before and after the gold deposition process, and thus be able to measure gold deposition on particular nanoparticles. Figure 1 shows scanning force microscopy (SFM) images of 15 nm colloidal particles deposited on an APTS-modified SiO₂ substrate (a) as prepared and (b) after a 5 min treatment in the seeding solution. The images shown are of the same area on the sample. After gold deposition, the particles were coated by a 20 \pm 3 nm thick gold layer. Similar values were obtained in other experiments. The distribution of particle heights is in agreement with the results obtained by Natan and co-workers.²⁴ Although SFM tip convolution affects quantitative analysis in the *x*-*y* plane, particle height measurements are accurate.²⁶ Qualitative analysis in the *x*-*y* plane also shows that the particles are wider, and the space between neighboring particles is smaller as a result of deposition. In addition, particles which were close together (marked with an arrow) seemed to be joined as a result of the deposition. Separate enlarged particles were almost spherical in shape, but particles that were close to each other formed more complex shapes. This indicates that closely arranged particles can serve as a template for more complex structures.

Controlling the nature and strength of the junction between particles is crucial for nanostructure fabrication. The convolution effect in the *x*-*y* plane on the SFM images, raises questions about whether "close particles" after deposition actually form stable structures in which the particles are solidly connected to one another.

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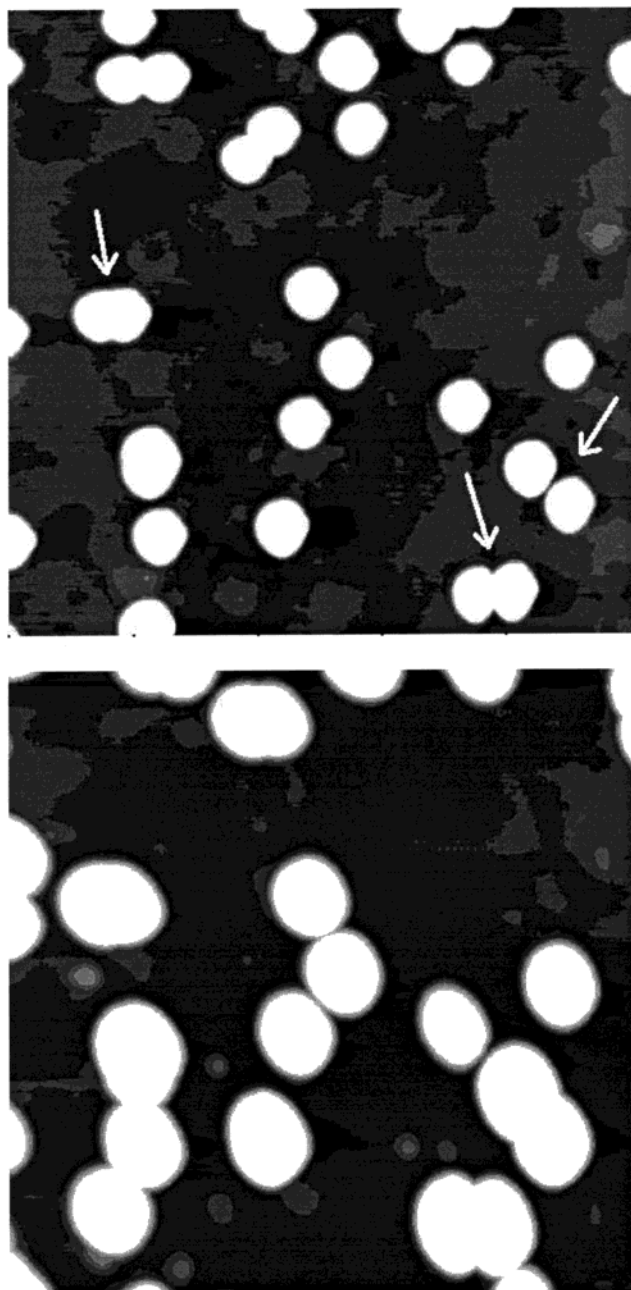


Figure 1. SFM images ($1 \mu\text{m} \times 1 \mu\text{m}$ scan size) displaying 15 nm gold colloidal particles on an APTS-modified SiO_2 substrate (a) as randomly deposited and (b) after 5 min in the seeding solution. The arrows mark close particles that formed dimer units after further deposition. The images are shown with a 5 nm height threshold in part a and a 15 nm threshold in part b to increase the particle to background contrast.

We examined the junction formed by deposition between particles by using our manipulation software to push the formed structures with a SFM tip in dynamic mode. Particles that are strongly bonded to one another by the deposition process should be manipulated as a unit by the tip, whereas particles which are not strongly connected should be separated during the movement of the tip. Figure 2 shows a sequence of SFM images of the manipulation of two dimer units. The arrows indicate the manipulation operation which produced the arrangement shown in the following image. Figure 2a shows randomly deposited particles after 5 min in the seeding solution. In this image,

a few dimers can be seen. The two dimers that were manipulated are marked as “A” and “B”. These dimers formed as a result of deposition on adjacent particles (A formed from the particles marked in Figure 2b as 1 and 2, and B formed from the particles marked in Figure 2b as 3 and 4). Figure 2b shows the translational motion of dimer A, and Figure 2c shows the effect of the same manipulation operation on dimer B. While dimer A was successfully moved intact by manipulation, the dimer marked B broke apart. We further examined the durability of dimer A by a number of subsequent pushing operations. Prior to further manipulation of dimer A, the particles that were at the lower right corner (marked as x) were pushed aside to provide additional space for the manipulation of dimer A. Parts d and f of Figure 2 show the rotation of dimer A, with 2d illustrating rotation around particle 1 and 2f illustrating rotation around particle 2. The two particles stayed connected even when the translational manipulation operation was centered “in-between” particles 1 and 2 (Figure 2e). This should stress the weakest connection in the dimer.

The image in Figure 2a shows that deposition on dimer B was slightly different than that on dimer A, with deposition on dimer A being more homogeneous. The particle marked as 4 is smaller than the particle marked as 3. Indeed, there is a height and shape difference between the two particles after they were pushed apart (Figure 2c). The particle marked as 3 is 28 nm high, while the particle marked as 4 is 25 nm high (heights were determined by single-line scans, not shown). The height of both particles marked as “1” and “2” was 29 nm. These results indicate that only close particles which are covered by a homogeneous gold layer are solidly joined together to form a dimer structure. Manipulation of formed nanostructures, together with embedding²⁷ which is used to fix formed structures to their final positions, provides a versatile approach for nanowire fabrication.

Although we have previously demonstrated the manipulation of gold particles on APTS-modified SiO_2 substrates,^{21a} we found that it was easier to determine the appropriate manipulation parameters after oxidizing the APTS film by treatment in an UV/ozone chamber for 3 min. After oxidation of the APTS layer, the particles remained adsorbed on the surface after the sample was dipped into the seeding solution and rinsed with water. Furthermore, even after manipulation of the particles to different positions, particles were rarely missing as a result of dipping in the seeding solution. These observations can be explained if the particles mask the underlying APTS layer during oxidation, which continues to bond the gold particles to the surface after the oxidation. During manipulation, the particle is moved together with part of the underlying APTS layer, while the remaining part of the APTS layer is left on the substrate. In some cases we saw “bumps” at places from where a particle was pushed. These bumps can be attributed to APTS residues that were masked by the particles from the oxidation process. This interpretation is consistent with our previous^{21a} observations that (i) manipulation takes place by sliding rather than rolling of the particles, and (ii) linked particle structures can be formed by the interaction of the APTS residues with manipulated particles.

After it was clear that the seeding process could be used to form stable nanostructures, we used this procedure to fabricate a nanowire as shown in Figure 3. We manipulated gold particles with measured heights

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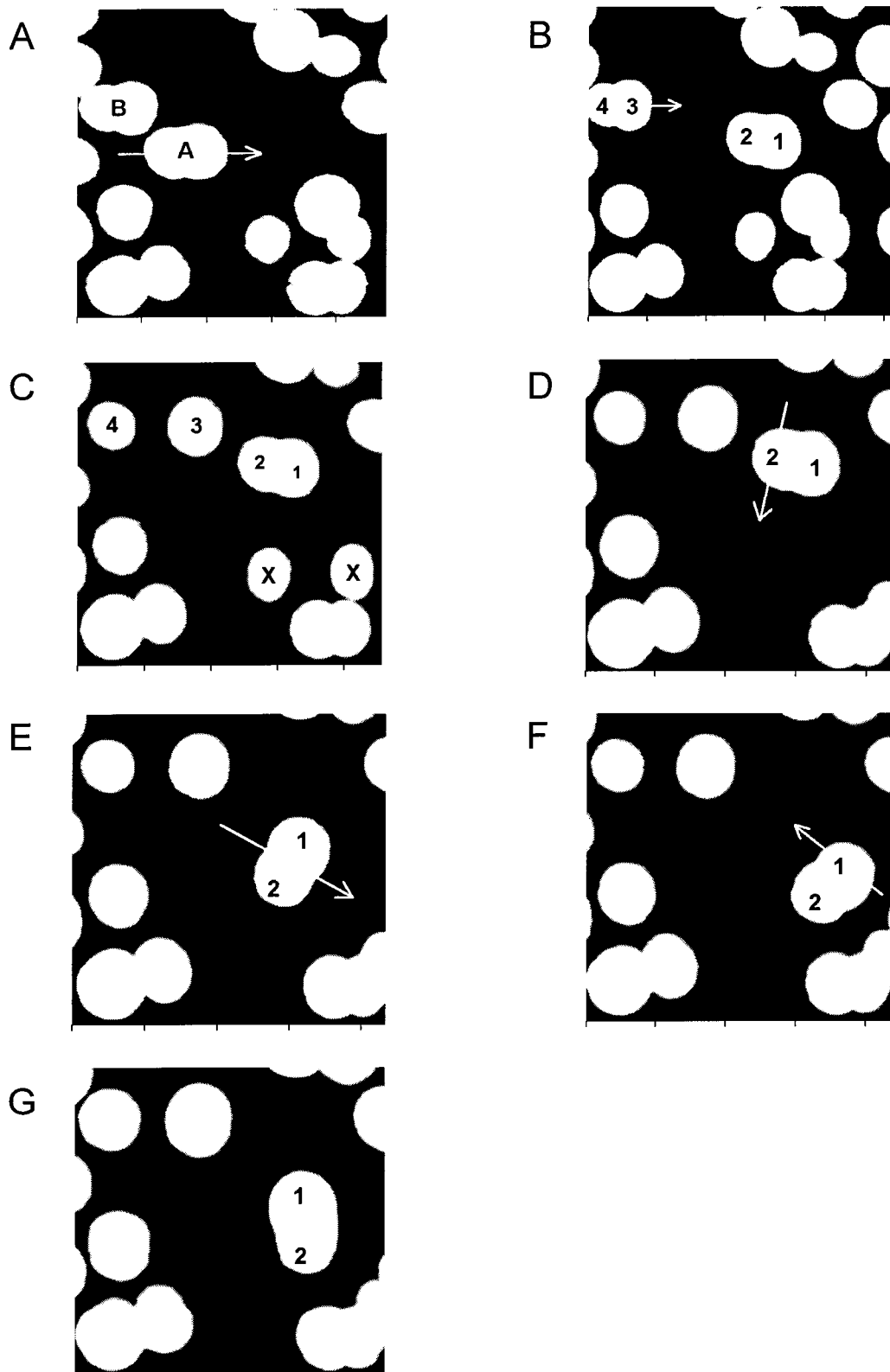


Figure 2. Sequence of SFM images ($450 \text{ nm} \times 450 \text{ nm}$ scan size) displaying the manipulation of two dimers, *A* and *B*, made up of particles 1–2 and 3–4, respectively. The arrows indicate the manipulation direction that produced the arrangement shown in the following image. (a) Particles with an original diameter of 15 nm after 5 min in seeding solution, before manipulation; (b) result of translational manipulation of *A*; (c) result of translational manipulation of *B*; (d) result of moving two particles marked as *X* out of the way; (e) result of the rotation of *A* around particle 1; (f) result of manipulation of *A* in the center of the dimer; (g) result of the rotation of *A* around particle 2. The height scale is 20 nm from black to white (above the height threshold).

of $8 \pm 1 \text{ nm}$ (Figure 3a) to form a “line template” (Figure 3b). After 5 min in the seeding solution, the structure was coated by a layer of gold to form a nanowire (Figure

3d). All three images were taken by using the same tip, and the tip was checked by using a standard sample to verify that the quality of the tip remained the same after

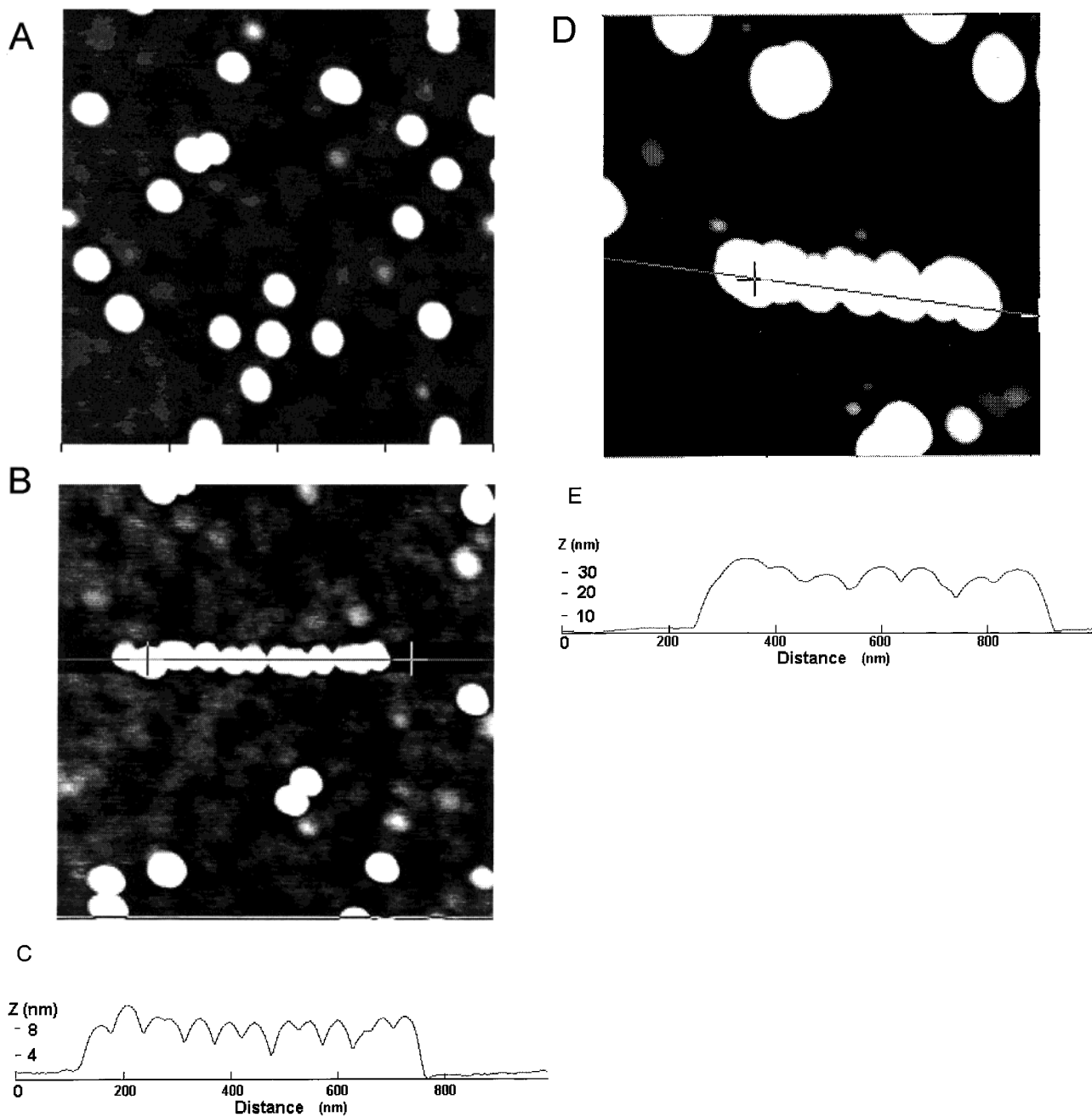


Figure 3. SFM images ($1 \mu\text{m} \times 1 \mu\text{m}$ scan size) displaying 8 nm gold colloidal particles on SiO₂ (a) as randomly deposited, (b) after manipulation of 13 particles to form a wire nanotemplate, and (d) after 5 min in the seeding solution. Parts c and e are linescans that correspond to parts b and d, respectively. The height scale from black to white (above the height threshold) is 5 nm for parts a and b and 20 nm for part d.

Figure 3d was taken. Parts c and e of Figure 3 show the linescans of the template and the nanowire, respectively. The template linescan shows that the particles were pushed sufficiently close to one another for the SFM tip to be unable to resolve any gap between them because of the tip convolution effect. The radius of the tip can be roughly estimated to be ~ 40 nm from the observed width of the first and last particles in linescan C. Analysis of the linescan in Figure 3c reveals that the average distance between particle peaks is ~ 50 nm. Therefore, the aligned particles are not touching each other as a result of the manipulation but, rather, are ~ 40 nm apart. By subtracting the heights in linescans before and after deposition, we can calculate a thickness of the deposited layer of 19 ± 2 nm.

The accuracy of the manipulation depends on the tip apex. A very sharp tip can decrease the effects of tip convolution on the images and help to resolve the actual gap between particles. The particles forming the template shown in Figure 3b were manipulated with an accuracy of ~ 10 nm. There is only one particle in this template, that is "out of line" by 15 nm. An advantage of the seeding process is that the template can be formed by particles that are not in pairwise contact and need not be positioned very accurately. The gaps between the particles will be closed by deposition on the particles on both sides of the gaps. When comparing the two linescans, it can be seen that the height uniformity of the template is better than that of the initially formed structure. This led us to

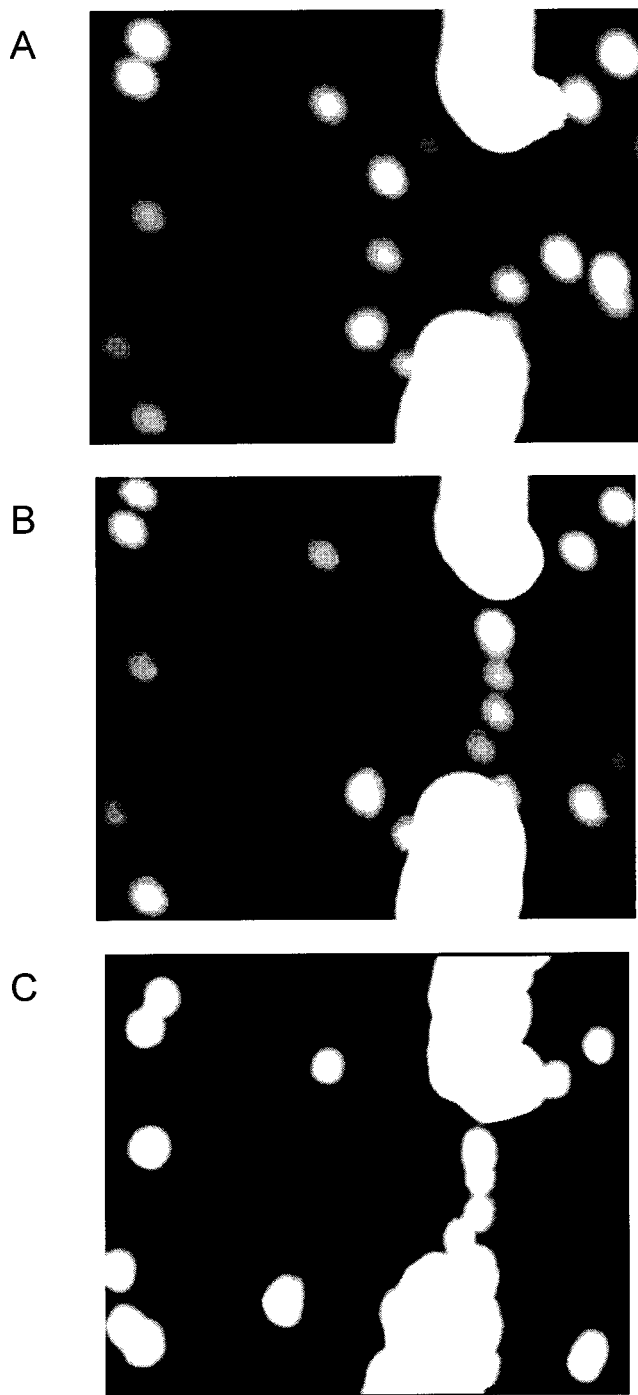


Figure 4. Sequence of SFM images ($750 \text{ nm} \times 600 \text{ nm}$) showing two gold electrodes with a 220 nm gap between them and 10 nm gold particles (a) as randomly deposited, (b) after the manipulation of four particles into the electrode gap, and (c) after a 5 min dip in the seeding solution. The height scale from black to white (above the height threshold) is 5 nm for parts a and b and 15 nm for part c.

conclude that the deposition uniformity here was on the order of 1 nm .

This chemical system can also be used to electrically connect Au nanowires to gold electrodes. As a demonstration, we carried out the following process. Gold colloidal particles were pushed into a gap between two Au electrodes, and a subsequent deposition step was used to fill the gap. Since the electrodes were made of gold, the seeding process should cover both the particles and the electrodes to form a nanowire connected to the two electrodes. Figure 4 illustrates the process of fabricating a nanostructure inside a 220 nm gap between two gold electrodes. Figure 4a shows the randomly deposited particles around the gap area. Four gold particles were pushed into the gap as shown in Figure 4b, and were subsequently covered by a 16 nm thick gold layer after 5 min in the seeding solution, as shown in Figure 4c. As a result of the deposition, the gold electrodes were coated by a 30 nm thick layer, almost twice as thick as the particle coating. The distance between particles in the gap is about 30 nm and the distance between the template and the electrodes is estimated at $40\text{--}50 \text{ nm}$. Because the deposition thickness is $\sim 16 \text{ nm}$ on the particles and $\sim 30 \text{ nm}$ on the electrodes, the nanowire and the electrodes might have been connected. Unfortunately, this did not happen in this particular experiment. Resistivity measurements showed an open circuit, and subsequent SEM images indeed showed a gap in the nanowire. However, we feel that the promise of this technique has been demonstrated. Studies using longer nanowire templates and longer deposition times are in progress. We also plan to use gold nanoparticle templates assembled by SFM manipulation for the deposition of other metals.

Conclusions

Hydroxylamine seeding of colloidal gold particles can be utilized to fabricate gold nanostructures on SiO_2 substrates. The approach presented in this paper involves using SFM nanomanipulation of gold nanoparticles on a modified SiO_2 substrate to produce a template for nanofabrication of Au nanowires. Mechanical nanomanipulation experiments showed that a dimer structure formed by homogeneous deposition is mechanically stable. Another nanostructure was built: a nanowire inside a 220 nm gap between two gold electrodes. This approach should be useful for electrically connecting nanostructures to microscale structures and to repair nanoscale open circuits of gold nanowires.

Acknowledgment. This research was supported in part by the National Science Foundation under Grant EIA-98-71775. We thank Dr. Pierre Echternach from the Jet Propulsion Laboratory in Pasadena for preparing the samples patterned by electron-beam lithography, and Dr. Yoram Seltzer from the Weizmann Institute in Israel for very useful discussions.