

Manipulation and writing with Ag nanocrystals on Si(111)-7×7

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Manipulation of Ag nanocrystals derived from up to 200 000 atoms was performed using the tip of a scanning tunneling microscope. By varying the scanning conditions, it was possible to move them laterally on contamination-free Si(111)-7×7 surfaces or to remove them. In both cases, thin Ag tracks were left behind. This demonstrates the concepts of nano patterning and nano painting with metals on clean semiconductor surfaces. © 1998 American Institute of Physics.

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The modification and manipulation of nanometer-scale structures on surfaces has attracted considerable interest.¹ Manipulation of single atoms and small clusters with a scanning tunneling microscope (STM)²⁻⁵ has been demonstrated, and atomic scale lithography has been accomplished by selective-area desorption of hydrogen with the STM tip.⁶ Manipulation or positioning has been reported for α -MoO₃ on 2H-MoS₂,⁷ C₆₀ on NaCl, graphite, and Si(111),⁸ and Cu-TBP-porphyrin on Cu(100).⁹ Clusters and liquid droplets have also been manipulated with scanning probe tips in air or rough vacuum.¹⁰

To date, the manipulation of metallic nanostructures on clean reactive silicon surfaces has been considered unfeasible because production of such nanostructures by conventional atom deposition results in surface wetting and strong interface bonding. However, by using our buffer-layer-assisted growth and delivery technique,¹¹ we have been able to produce Ag nanocrystals with up to 200 000 atoms that can be moved laterally in a controllable fashion on clean Si(111)-7×7. This manipulation leaves tracks due to adhesive wear as Ag atoms are transferred in a way that reflects the local chemical activity of the 7×7 surface. The flexibility of the growth technique allows us to control the size of nanocrystals and to explore other metal-semiconductor systems as well.

The experiments were performed in a system equipped with a STM and a cold finger stage (base pressure $<5 \times 10^{-11}$ Torr). Clean Si(111)-7×7 surfaces were prepared and characterized before being transferred to a cold finger and cooled to 50 K. Buffer layers of Xe were then formed by exposing to 600–3000 L of Xe where 1 L = 10^{-6} Torr s, giving 60–300 ML thick layers.¹² The buffer layers served to isolate the Si surfaces from processes associated with subsequent Ag adatom deposition. Those adatoms were supplied by physical vapor deposition at ~ 0.6 Å/min. After Ag clusters were grown, the buffer layer was desorbed and the sample was transferred to the STM stage for imaging at room temperature. The tungsten STM tips used in these studies were electrochemically etched and then annealed *in situ* by electron bombardment.

Figure 1(a) shows a STM image of Ag nanocrystals on Si(111)-7×7. In this case, we deposited 0.2 Å of Ag on a 60 ML thick Xe layer. The white features are Ag nanocrystals (average height 30 Å, average size 3300 atoms, density 2.6

$\times 10^{10}$ cm⁻²). The number of atoms on a given nanocrystal was estimated by measuring the height and assuming a hemispherical shape.¹² Imaging was done with +2 V sample bias and 0.2 nA tunneling current. Under these conditions, the

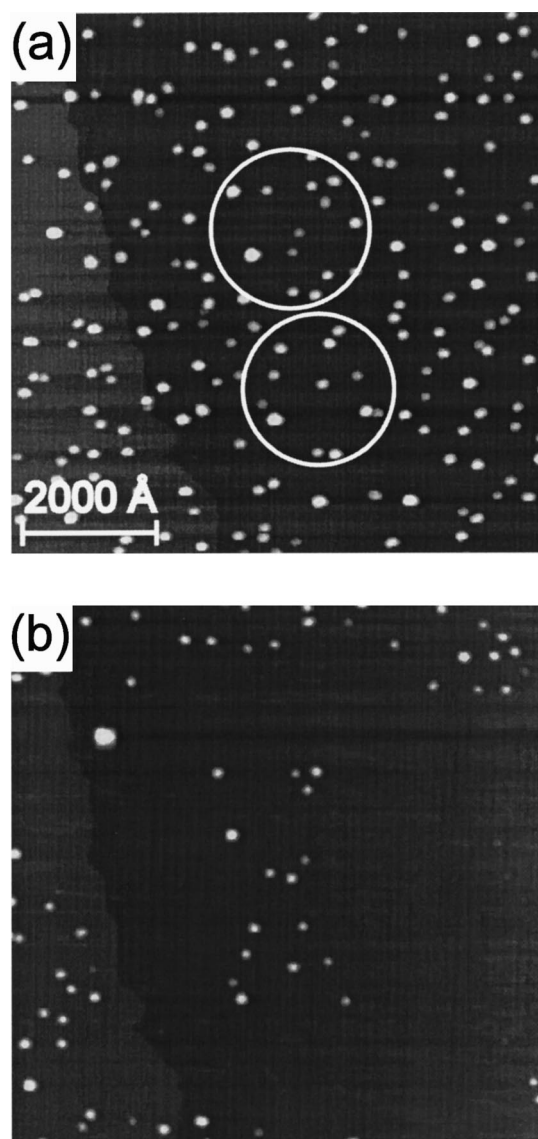


FIG. 1. (a) Distributed Ag nanocrystals on Si(111)-7×7 (average size 3300 atoms) prepared by buffer-layer-assisted growth. (b) Same area after tip manipulation to leave only those that formed the letters U and M.

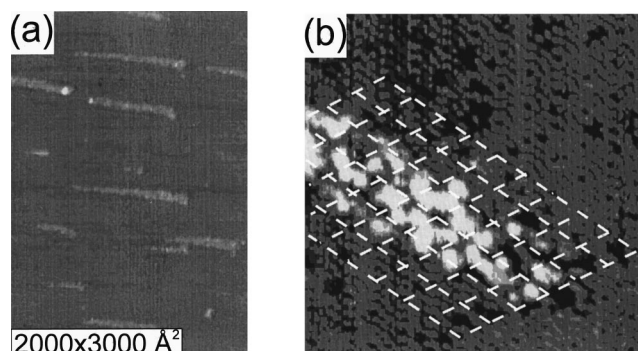


FIG. 2. (a) Close-up of Fig. 1(b) showing Ag tracks produced by translation of the Ag particles. The tapering track indicates a size reduction as the nanocrystal was abrasively worn by contact with the Si(111) 7×7 surface. The “push” direction was from right to left. (b) Details of a 70 Å wide Ag track. The grid shows the 7×7 unit cell to emphasize that the corner holes remain visible because of the site selectivity for Ag transfer. Sample bias = +1.7 V, $I_t = 1.0$ nA.

nanocrystals remained stable. A monolayer height step is visible on the left side of the image. The surface is clean, and higher resolution images show the 7×7 reconstruction.

Figure 1(b) shows the same area as Fig. 1(a) after a “UM” pattern was created by removal of unwanted Ag nanostructures. Removal was done in either of two manipulation modes by laterally pushing the nanocrystals with the STM tip. In one procedure, we scanned a large area in the imaging mode and then placed the path of a line scan over the feature to be changed. A single line scan was then made with a scan speed that was fast enough that the feedback could not respond (>10 $\mu\text{m/s}$). Hence, contact was established and the nanocrystal moved with the tip. The second approach involved a line scan at a slower scan speed (~ 1000 Å/s) with the feedback disabled. Similar results were obtained with both modes, and the results were reproducible with different tips, different Si samples, and nanocrystals of different sizes.

Nanocrystal removal produced an elongated track that originated from the initial position of that nanocrystal. Figure 2(a), which is a close-up view of Fig. 1(b), shows streaks with the sharp end pointing in the direction of the line scan. This shape indicates that the nanocrystal size decreased as the Ag track was created. The initial track width as observed by STM is approximately twice the height of the original nanocrystal. (The track provides a better estimate of the crystal footprint than does direct imaging because the latter represents a convolution with the tip.) A high resolution empty-state image of one track, Fig. 2(b), shows its maximum height to be 1.6 Å above the adatoms of the 7×7 unit cell, considerably higher than the 0.5–1.0 Å observed after Ag atom deposition onto Si(111)- 7×7 at 400 K.¹³ Similar features were seen in filled-state images. Although we could not observe atomic features within the tracks, site selectivity was apparent since the corner holes of the 7×7 unit cell remained free of Ag atoms. We attribute the unique structures in Fig. 2 to the fact that atoms were transferred through atomic-scale adhesive wear as the particles were moved across the clean surface. The contact area for such adhesive wear would involve the Si adatoms of the unit cell, and both geometric and kinetic constraints prevent the transferred Ag atoms from finding lowest-energy bonding configurations.

There is a definite correlation between the total area of the track and the size of the original nanocrystal. The latter can be estimated by assuming a hemispherical shape where the base of the nanocrystal is twice the height.¹² The density of the track was estimated from the total number of atoms of a nanocrystal before and after a short-distance “nudge” where we can measure the height change and the area of the Ag track. This gives a planar density of $\sim 1.0\times 10^{15}$ atoms cm^{-2} , somewhat larger than half the density of Ag(111), namely 1.4×10^{15} atoms cm^{-2} . Hence, the Ag tracks of Fig. 2 account for $\sim 1/3$ of the atoms from the 3000–4000 atoms of these nanocrystals. We were able to vary the Ag track length by changing the position of the end of the line scan. When the end point was close to the starting point, a larger fraction of the nanocrystal adhered to the tip. Transfer of the nanocrystal to the tip occurred as it slipped across the surface.

Removal of the nanocrystal occurs when the tip moves away from the surface to reestablish a tunneling gap at the end of a line scan. Removal indicates that the bond between the particle and the tip exceeds that between the particle and the surface. Tip-particle adhesion will depend on the tip configuration and the Ag atom dynamics associated with the contact area.¹⁴ After several manipulation events, the tungsten tip would be coated with Ag, and the high mobility of Ag on Ag suggests that additional material associated with subsequent transfer will wet the tip.¹⁵ However, redeposition of the Ag from the tip onto the surface was not feasible under our experimental conditions. It is intriguing to image the dynamics associated with this pushing and transfer from surface to tip.

The fact that a Ag track is left on the Si surface shows a new aspect of nanocrystal interaction with regard to tip and substrate. The Ag track indicates adhesive wear that is now resolved on the atomic scale for clean reactive surfaces under ultrahigh vacuum (UHV). Such wear takes place when adhesion between the sliding bodies is larger than the cohesive energy of the plastically deformed material. Here, the two surfaces are derived from Ag atoms and the 7×7 structure of Si.¹⁶ For the latter, the adatom density is 9.6×10^{13} cm^{-2} , and it is the adatoms that can come in contact with the Ag surface, forming the bonds that ultimately facilitate material transfer. The contact surface of the nanocrystal probably has steps and multiple defects, and material is likely to detach from the steps in the form of atoms or small clusters depending on the force experienced at the interface. Indeed, the Ag particle will change its contact on a local scale as it is pushed across the surface and atoms are transferred from it. We emphasize that our results differ from previous results¹⁰ because of the strength of the interface bonds. Previous studies of manipulation of large clusters focused on systems with van der Waals bonding, and they could not detect the transfer of material associated with adhesive wear.¹⁰ Here, there are both chemical bonds and van der Waals bonds.

To investigate manipulation of larger nanocrystals, we deposited 1.3 Å of Ag on a 300 ML thick Xe multilayer. Subsequent delivery to the surface produced nanocrystals with a wide distribution of crystal height, from 14 to 120 Å (density 1.1×10^{10} cm^{-2}). After imaging to obtain Fig. 3(a), we nudged the structure labeled I, moving it a distance of ~ 1000 Å to a position below structure A. Nudging was done

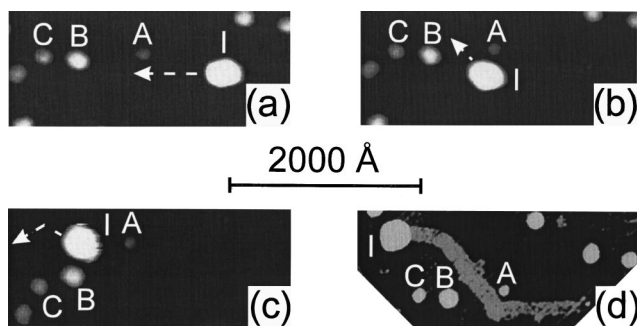


FIG. 3. STM images demonstrating manipulation of a nanocrystal derived from 100 000 atoms. (a) Shows the starting surface with nanostructures prepared by depositing 1.3 Å Ag onto 300 ML Xe and then desorbing the Xe. Arrows indicate the directions and lengths of line scans used to manipulate structure I. (b) Shows that nanocrystal I has been nudged ~ 1000 Å and is next to feature A. (c) Shows the position of I after another nudging action, demonstrating that the nanocrystal could be moved between obstacles A and B. The frame is rotated by 25° due to change of scanning configuration. (d) Demonstrates further nudging, with different contrast to show the Ag track formed by adhesive wear. The total number of Ag atoms in the track is ~ 40 000. During imaging, the parameters were sample bias +2 V, current 0.2 nA. During nudging, the scan speed was $20 \mu\text{m/s}$.

by using the same technique as for nanocrystal removal except that the length of the line scan was short to reduce the Ag track length. This prevented the nanocrystal from falling below ~ 80 Å in height (experience has indicated that structures of < 80 Å in height were removed, as above). Note that feature I had a height of 92 Å, as measured with the STM, which corresponds to approximately 100 000 atoms. The line scan for nudging was performed along the dashed line shown on Figs. 3(a), 3(b), and 3(c). In Fig. 3(d), the contrast of the scanned area was adjusted to show the Ag track, and we estimate that the total number of Ag atoms in the track is ~ 40 000. Note that the line scans for nudging events were done in the manipulation mode, and the direction of movement could be controlled via the scan direction.

While nano-painting and nanocrystal removal could be done with features having heights below ~ 80 Å, nudging was generally restricted to those having heights of 80–120 Å. For nanocrystals taller than ~ 120 Å, neither painting nor nudging was possible. Instead, an apparent tip crash was observed after a line scan, and the location of the nanocrystal did not change in those cases where we were able to find the original imaging location. Structure with this large interfacial area were bonded to the surface too well to undergo shearing.

We demonstrated that Ag nanocrystals can be removed or nudged on a Si(111)- 7×7 surface by the STM and that tracks are created due to adhesive wear. This concept could be used to nano-paint metal lines and to fabricate monolayer thick metal quantum lines or quantum dots for nanoscale devices. Manipulation of these novel structures should give new insights into nanotribology where the surface quality can be controlled. For example, studies of more reactive materials deposited onto Si(111)- 7×7 will show differences related to their interface bonding while those deposited onto passivated or coated surfaces will show different behaviors.

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