Fabrication of two-dimensional arrays of nanometer-size clusters with the atomic force microscope

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An atomic force microscope tip is used as a vector positioner to manipulate nanometer-size preformed Au clusters deposited on atomically smooth substrates. Using this technique, two-dimensional cluster nanostructures can be assembled at room temperature. © *1995 American Institute of Physics.*

The weak binding of preformed metallic clusters to atomically smooth substrates has presented an impediment to the study of supported nanometer-size clusters using scanning probe techniques. The sweeping of supported clusters on flat substrates by a scanning probe tip has been identified as a problem.[1] Unless special precautions are taken, only those clusters pinned at defect sites are routinely observed in scanning probe studies of nanometer-size clusters.

Recently, Schaefer *et al.* have shown that by using an atomic force microscope in the noncontact mode, clusters deposited on flat substrates from a cluster beam can be imaged in their as-deposited positions.[2,3] Utilizing this breakthrough, Mahoney *et al.* have recently reported a systematic study of cluster–substrate interactions using a wide variety of atomically flat substrates and have provided a rank ordering of substrates based on their ability to immobilize Au clusters.[4]

In what follows we take advantage of these developments and show how the weak binding of clusters to substrates allows the assembly of nanometer-size clusters at room temperature in a predetermined pattern utilizing the vector control of the atomic force tip.

Gold clusters used in this study were produced in the gas phase using a multiple expansion cluster source (MECS). As described elsewhere,[5,6] the MECS is a gas aggregation cluster source in which both controlled cluster growth via accretion of single atoms or via cluster–cluster aggregation can be promoted. The Au clusters used here were annealed at 1400 K and are expected to be single fcc crystals having roughly the shape of a truncated octahedron.[7]

The atomic force microscope (AFM) used here is a custom-built instrument capable of operating in the constant force (contact), constant height, and noncontact (attractive) modes, and has been described elsewhere.[3] Detection of the cantilever displacement was done using a laser deflection method.[8–10] The output of a bicell position sensitive detector was digitized by a 68030 CPU based computer system similar to that described previously.[11] The computer was used to handle all data acquisition and system control.

For the purposes of this study, there are two important features of the AFM apparatus. First, the AFM was mounted inside a small stainless-steel chamber which could be evacuated to forepump pressures (~500 mTorr) and backfilled with dry nitrogen gas. This feature minimized contamination due to water vapor or hydrocarbon adsorption on the substrate surface. Second, drift due to piezo hysteresis was minimized by independently tracking the position of the sample with a separate diode laser and bicell position sensitive detector. This feature prevented catastrophic tip crashes while the tip was used as a repositioning tool.

The weak binding of a cluster to a substrate discussed in Ref. 3 can prove advantageous for the assembly of nanometer-size structures from these clusters. By proper computer control of the the AFM tip, it is possible to move individual clusters to preselected positions on the sample with the AFM tip. This capability is demonstrated in Fig. 1, where a Au cluster is intentionally moved across a highly oriented pyrolytic graphite (HOPG) substrate to a preselected site.

Figure 1(a) shows the initial noncontact AFM image of the sample. The clusters range in size from 9 to 20 nm in height. A cluster was identified for relocation and two points on the surface were selected, defining a path for the AFM tip [see Fig. 1(b)]. After removing the tip oscillation voltage, the AFM tip was lowered into contact with the HOPG substrate at the position marked by an ‘‘x’’ beside the cluster labeled 1. With the feedback disabled, the tip was then moved across the substrate to a selected final position as shown by the dotted line. Another noncontact scan was taken of the same region and revealed that the preselected cluster had been successfully moved [see Fig. 1(c)].

To further demonstrate the capabilities of the AFM to form nanoscale structures from nanometer-size clusters, Au clusters were randomly deposited on a WSe_2 substrate and were subsequently arranged using the AFM tip, as demonstrated in Fig. 2. WSe_2 is a chemically inert transition metal dichalcogenide.[12] There is a reasonably strong surface force interaction between the Au clusters and the WSe_2 substrate.[4] For this reason, a WSe_2 substrate provides a good test for the demonstration of advanced cluster positioning capabilities.

Figure 2(a) shows the initial AFM image taken in the noncontact mode. The cluster labeled 1 was initially selected for movement in a horizontal direction to lineup with clusters

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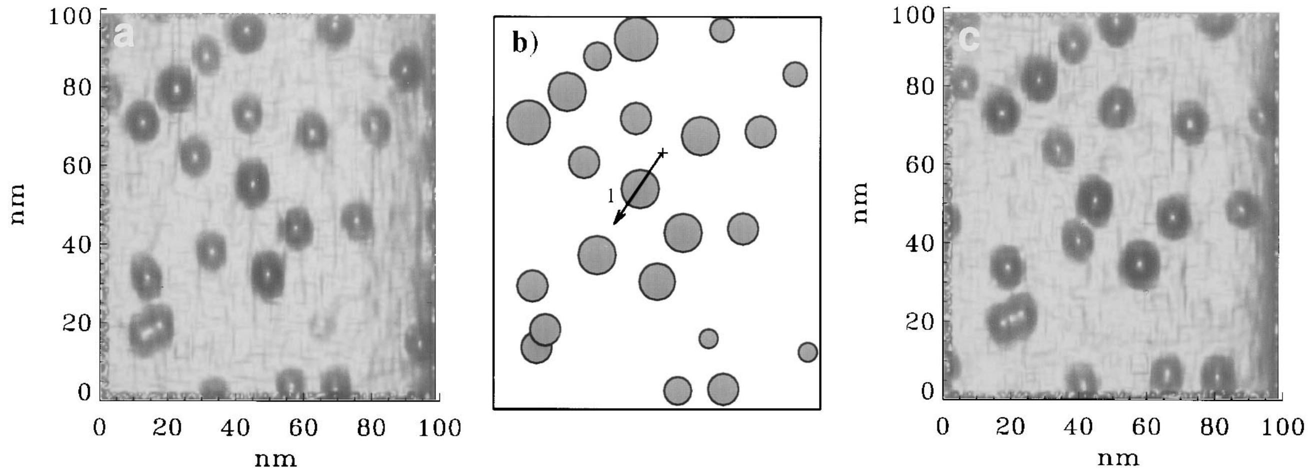

FIG. 1. (a) Initial noncontact image of Au clusters on a HOPG substrate. (b)A schematic showing where the tip is initially brought into contact with the surface, where the tip is dragged, and how the cluster is moved by the AFM tip. (c)The noncontact AFM image immediately after moving the cluster with the AFM tip. The grayscale used in this figure was generated by an algorithm using an artificial light source designed to highlight the cluster location. For this reason, no height information is contained in the grayscale as usually is the case.

4 and 5. The cluster was moved in the same manner as described earlier, and a second noncontact mode AFM image was immediately taken. From this image, it is clear that only cluster 1 has been moved to line up with clusters 4 and 5. The tip oscillation was again stopped, and cluster 2 was moved to the vacant area between clusters 1 and 5. Figure 2(c) shows the line clusters produced, demonstrating the ability of the AFM to form linear arrays of nanometer-size clusters.

As a final demonstration, the AFM was used to perform multiple tasks between scans. After obtaining the image shown in Fig. 2(c) and before obtaining the image shown in Fig. 2(d), the AFM tip was used to (i) move cluster 3 next to cluster 2, (ii) move cluster 6 to a position immediately to the

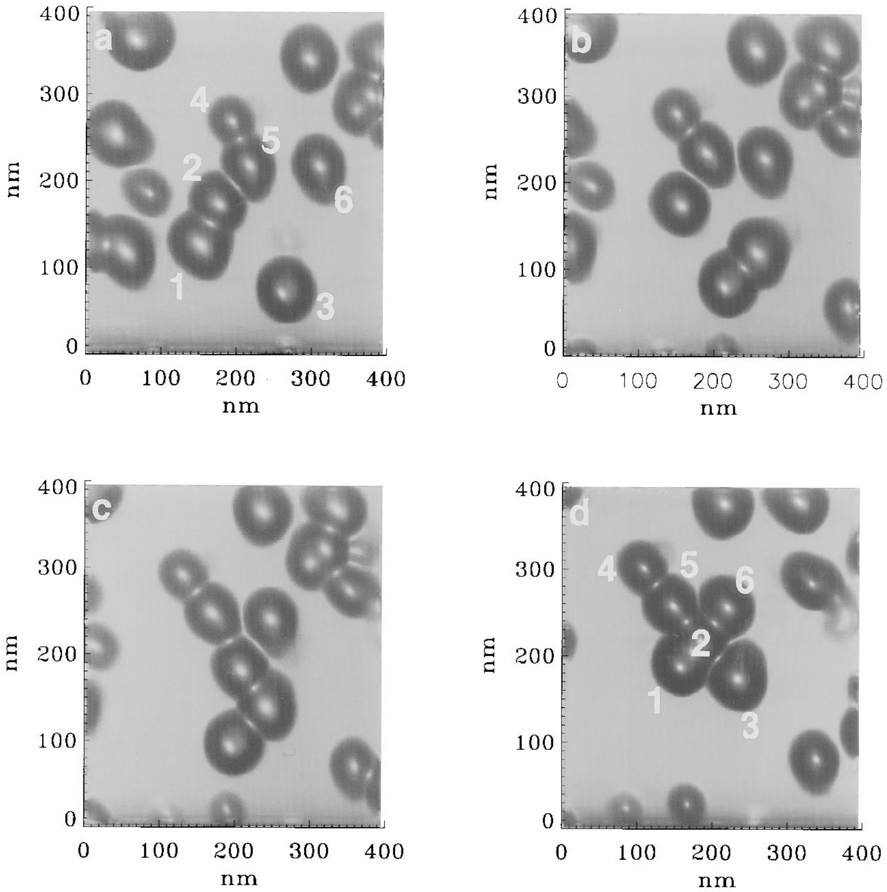

FIG. 2. (a) Initial noncontact image of Au clusters on a WSe_2 substrate. In (b)–(d), sequential noncontact images are shown after the AFM tip was used to reposition a number of different clusters on the substrate. The grayscale used in this figure was generated by an algorithm using an artificial light source designed to highlight the cluster location. For this reason, no height information is contained in the grayscale as is the usual case.

right of cluster 2, and (iii) sweep aside several clusters in the upper right-hand corner of the image, thus isolating several other clusters for later movement. Figure 2(d) shows the final results, with a dagger shaped object being formed. The process can be continued to produce two-dimensional arrays of clusters.

In summary, the ability to arrange supported preformed Au clusters into complex two-dimensional (2D) patterns has been demonstrated. The supported clusters remain intact during the editing process and no cluster debris are found to litter the surface. Furthermore, the assembled cluster array remains stable at room temperature. This capability suggests that prototype 2D devices fabricated from an assembled array of nanometer-size clusters of controlled size and composition can now be attempted. Novel 2D magnetic and electronic effects can be studied by combining a proper choice of cluster arrangement, cluster composition, and substrate properties. Prototype devices utilizing quantum coupled architectures[13,14] can also be assembled and studied using these techniques.

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