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Manipulation of passivated gold clusters on graphite with the scanning tunneling microscope

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Chemically passivated gold nanoclusters deposited on the surface of graphite have been manipulated with the scanning tunneling microscope (STM) in ultrahigh vacuum. The controlled clearing of a definite shape in a cluster layer is demonstrated. Clusters embedded in a close-packed array could not be removed from the surface, apparently because of the attractive interaction between neighboring ligand chains. A minority channel of cluster fragmentation has been identified and leads to the creation of platelets which can be further manipulated by the STM tip. © *1998 American Institute of Physics.* [S0003-6951(98)01502-2]

Small metal clusters display a multitude of novel characteristics.[1] Recently there has been much interest in surfactant-stabilized metal clusters, as they can be produced in macroscopic quantities and purified to a single size.[2] Ordered layers of such clusters can be produced on surfaces and have been studied with the transmission electron microscope (TEM)[3] and scanning tunneling microscope (STM).[4] The ligand layer is found to isolate the metal core allowing single electron charging effects to dominate the cluster's electron transport properties even at room temperature.[5] These phenomena are of interest for future electronic devices and may form the basis of room temperature single electron transistors.[6] However, to use coated clusters in future devices it will be necessary to pattern a surface such that only selective areas are covered in clusters.

The tip of an STM can be used to modify surfaces or adsorbed species in a spatially selective fashion with nanometer resolution. In this letter we demonstrate that coated clusters can be manipulated with the STM tip. First, selected areas of a cluster-covered surface are cleared by sweeping the tip close to the surface. During such manipulation clusters move onto the tip. Second, we explore the fragmentation of the clusters during high current imaging together with manipulation of the cluster fragments so formed.

The gold clusters were prepared by the inverse micelle method.[7] $NaAuCl_4$ was added to a nonionic surfactant $CH_3(CH_2)_{12}-1(CH_2CH_2O)_5OH$ solution and reduced (by $LiAlH_4$). Addition of dodecanethiol, $C_{12}H_{25}S$, coated the clusters with a passivating layer.[8] Transmission electron microscope measurements on amorphous carbon showed a mean cluster core size of ~30 Å. No further size selection was performed before dilution in toluene and drop deposition onto freshly cleaved highly oriented pyrolytic graphite. Once the solvent drop had evaporated, samples were transferred into an ultrahigh vacuum chamber (at 2×10^{-9} mbar) equipped with an STM (Oxford Instruments).

An example of the controlled manipulation of a cluster film is shown in Fig. 1. Figure 1(a) shows a region of a cluster monolayer on the graphite surface which includes a variety of different cluster diameters (48 ± 11 Å) and heights (45 ± 5 Å). The image was obtained with a tunnel current of 30 pA and sample voltage of -1.5 V in constant current mode. The mean cluster diameter is larger than the known core size by ~20 Å; this would correspond to a dodecanethiol layer of ~10 Å thickness, in the approximation where tip broadening effects are neglected. The central (420 Å × 420 Å) area was then scanned with a much increased current of 30 nA, bringing the tip closer to the surface. A subsequent 1200 Å × 1200 Å image (at 30 pA) showed that the central region had been partly cleared—although around 25% of the clusters remained. A further scan of the (420 Å × 420 Å) area at 30 nA was required to remove the remaining clusters, clearing the area as shown in Fig. 1(b).

This approach removes clusters in a selective manner from a layer, leaving behind a stable cluster-free area. In contrast to a number of previous studies of surface clearing, in which small (bare) particles were displaced laterally by the tip,[9] we do not find a pile-up of new material at the edges of the cleared area.[10] Instead we find that clusters are transferred onto the tip. After high-current tunneling we often observe that a group of clusters has bonded to the tip apex, as evidenced by the convolution with all the surface features in subsequent images. The apparent change in tip shape between the images shown in Figs. 1(a) and 1(b) further demonstrate this. Accounting for the change in tip shape, there is a one-to-one correspondence of the cluster positions between Figs. 1(a) and 1(b) outside of the cleared area (with one obvious exception marked by an arrow).

Regions of the cluster film with a high local packing density are resistant to clearing. The same series of scans performed to turn Fig. 1(a) into Fig. 1(b) produced no change for the region shown in Fig. 1(c). Thus the clearing mechanism depends on the local environment of the clusters in the layer.[11] An isolated cluster on a surface is perturbed more strongly by the tip than a cluster embedded in a dense layer,[4] presumably reflecting a restoring force on one cluster

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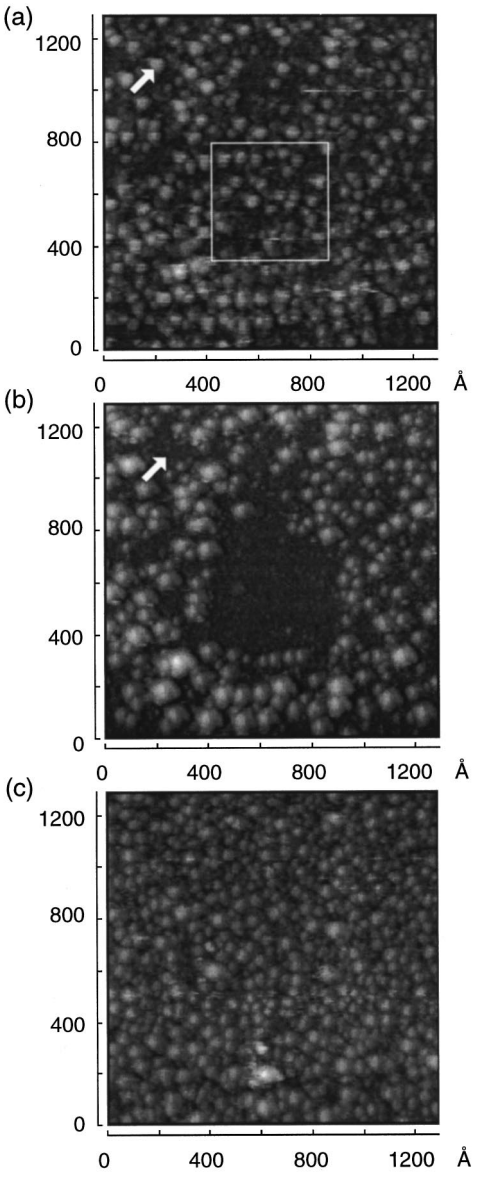

FIG. 1. (a) A region of passivated gold nanocrystals on graphite imaged at 30 pA and −1.5 V sample bias. (b) The same region imaged at 30 pA (−1.5 V) after twice scanning over the central region (indicated by white square) at 30 nA (−15 V). This area has been cleared by the tip. (c) A densely packed cluster layer which was unchanged after the same scanning sequence as that used between (a) and (b).

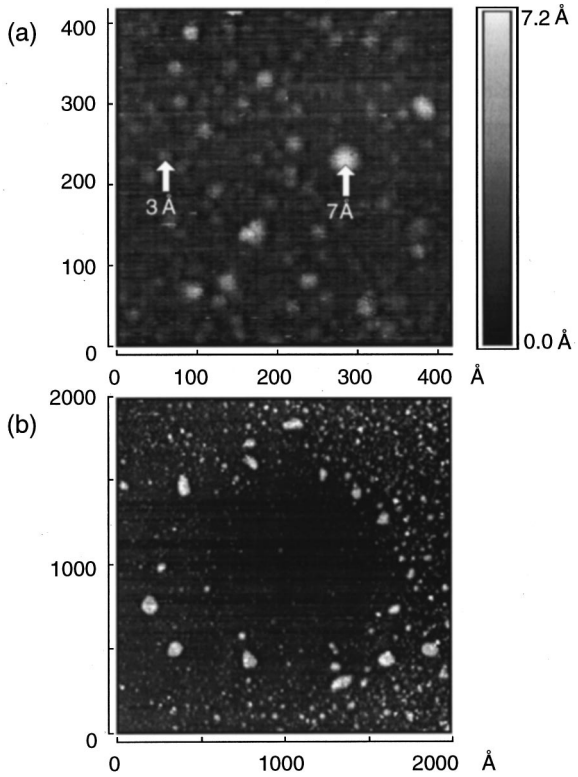

FIG. 2. (a) A region of cleared surface showing in cluster fragments: larger ~7 Å high and smaller ~3 Å high fragments are indicated. This image was acquired with tunneling current 5.8 nA and 1.5 V sample bias. (b) Repeated high current imaging causes displacement of the fragments. A circle of large faceted islands is shown. A sample bias of 1.5 V and tunneling current of 30 pA were used for this image.

due to its neighbors within a packed layer. Molecular dynamics simulations of cluster assemblies indicate that the ligands from adjacent clusters interact so that, for example, the distance between the gold cores of two neighboring passivated nanocrystals is less than twice the ligand length.[12] We believe that the ligand–ligand interaction between clusters in a densely packed region opposes the removal of clusters onto the STM tip, consistent with the behavior observed experimentally. The detailed nature of the attractive force between tip and cluster is not evident from the present experiments. Electrostatic polarization of the cluster core (and ligand layer) is one possibility; attachment of some of the ligands to the tip, or even their detachment from the gold core, cannot be ruled out.

Closer examination of cleared areas reveals that some features are still present. Such features are shown in Fig. 2(a) and are also visible in the interior of the cleared hole in Fig. 1(b). The features divide into two sorts with different lateral sizes and heights: small features of diameter 19±3 Å and height ~3 Å and larger features with diameter 27±5 Å and height ~7 Å. Both are much smaller than the clusters present before clearing, which leads to the conclusion that a minority of the coated clusters have been fragmented.

The ~3 Å high fragments are more strongly bound to the surface than the ~7 Å high features, which are observed to move during scanning at moderate currents (~1 nA). Figure 2(b) shows a region which has first been swept clear of coated clusters and then further cleared of the remaining fragments by repeatedly scanning the central region. The scanned area is now framed with a circle of larger (50–200 Å) diameter islands some of which show obvious facets. These islands are still shallow, again with a height of ~7 Å, so we conclude that they consist of fragments which have become mobile under the influence of the tip, moved out of the scan area and coalesced. Thus the fragments initially produced by dissociation of the three-dimensional coated cluster have been assembled into flat platelets.

In previous STM imaging of small metal clusters on graphite it has been found that smaller clusters are more strongly bound to the surface than larger ones and so are less easily disturbed by STM tip interactions.[13] This suggests that the ~3 Å high features observed here may be gold islands one atomic layer high, while the ~7 Å features may be gold bilayers. The formation of bare gold platelets would require

the removal of the nanocrystal ligands by the STM tip. The removal of similar thiol-terminated alkyl chains by the STM tip has been previously observed in high current scanning over self-assembled monolayers on gold and GaAs surfaces.[14] Of course, STM does not provide the elemental analysis necessary to establish that the fragments consist purely of gold atoms.

In conclusion, we have demonstrated that coated clusters can be manipulated in a controlled way with the STM, given appropriate choice of tunneling parameters. For junction resistances of $\sim$50 MΩ, clusters can be removed from the surface to the tip. However, high density cluster films are resistant to this process, presumably a reflection of the restoring force exerted on a cluster by its neighbors. The cleared surface is speckled with cluster fragments resulting from a minority cluster dissociation process and these fragments can be laterally displaced by further high current tunneling, leading to the formation of flat (presumably metallic) platelets on the surface. Further investigations of the tip–nanocrystal interaction are needed to establish the precise thresholds for (i) removal and (ii) fragmentation of the coated clusters.

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