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Rapid Communications

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Preparation and observation of Si_{10} clusters on a Au(001)-(5×20) surface

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Size-selected Si_{10} clusters have been deposited on a clean Au(001)-(5×20) surface and imaged using a scanning tunneling microscope in ultrahigh vacuum. The cluster images were found to depend on the sample bias voltage, and from tunneling spectroscopy measurements the clusters were found to have a band gap of ~1.0 eV wide. A wide variety of cluster images were observed even though size-selected clusters were deposited. When Si atoms were deposited on the surface flat islands were formed.

Virtually nothing is known experimentally about the structure of atomic clusters containing ≃4–100 atoms. One approach to this problem is to deposit clusters on a surface and then study them using one of the array of surface structure probes that have been developed. The direct imaging capabilities of the scanning tunneling microscope (STM) makes this a good choice. However, the interaction between the cluster and the surface could strongly perturb the cluster geometry so that the STM images may not be simply related to isolated gas phase structure. For example, Abraham *et al.* [1] and Baro *et al.* [2] have imaged Au, Ag, and Al clusters on graphite using STM, showing commensurate islands of higher order. To obtain the most information from studies of supported clusters, the experiment should be performed on size-selected clusters and under ultrahigh vacuum (UHV) to prevent contamination. It is also important that the clusters do not strongly interact with the substrate, but they should weakly chemisorb so that they do not diffuse and agglomerate. The Si-Au system was selected with these criteria in mind; thin layers of Au have been found to form an ordered structure on Si (Ref. 3) but compound formation does not occur in the bulk.[4] In this Rapid Communication we describe the first STM study of size-selected clusters. We have prepared and studied Si_{10} clusters on a Au(001)-(5×20) surface. STM topographs of Si_{10} and measurements of the band gap of the clusters by tunneling spectroscopy will be presented. We have also compared directly deposited clusters with the flat islands that result from depositing Si atoms.

There is currently considerable interest in silicon clusters.[5–11] Si_{10} has been identified as a particularly stable cluster in several experimental[5–7] and theoretical studies.[10,11] Two low-energy geometric structures for Si_{10} were proposed in a recent *ab initio* study:[10] a tetracapped octahedron and a tetracapped biprism. Theoretical studies of the chemisorption of atoms[12] and of a metallic dimer[13] on a metallic jellium surface have been performed, but the interaction of a silicon cluster with a metallic substrate has not yet been examined theoretically.

A detailed description of the cluster apparatus[7,14] and the STM (Refs. 15 and 16) can be found elsewhere. A clean, well-ordered Au(001)-(5×20) surface was prepared in the STM chamber (pressure $< 3\times10^{10}$ Torr) by ion sputtering and annealing. The sample was then moved by a mobile UHV transfer apparatus to the cluster deposition chamber. The sample transfer apparatus consists of two sections: a turbo-molecular and titanium sublimation pumped load-lock and a battery-powered ion pumped chamber in which the sample is held at a pressure $< 5\times10^{-10}$ Torr. The local pressure in the cluster deposition chamber was estimated to be better than 8×10^{-10} Torr during cluster deposition.

The silicon clusters were generated by pulsed laser vaporization of a silicon rod in a continuous flow of He buffer gas. Figure 1 shows a mass spectrum of the silicon cluster ions available from the source. A broad range of cluster sizes are generated, and Si_{10} is one of the dominant peaks in the spectrum. The quadrupole mass spectrometer was set to transmit only Si_{10}, and after mass analysis the ions were focused into a low-energy ion beam and deposited on the sample with an energy of approximately 5 eV. Molecular dynamics calculations suggest a threshold for cluster fragmentation of around 2 eV per atom,[17] well above the 0.5 eV per atom employed in these studies. A beam of $\sim10^7$ clusters/sec was focused to a 1-mm-diam spot on the Au sample, resulting in coverages of about 1×10^{12} clusters/cm^2 in 15 min. The sample was then transferred back to the STM chamber. During deposition, transfer, and measurement the sample was main-

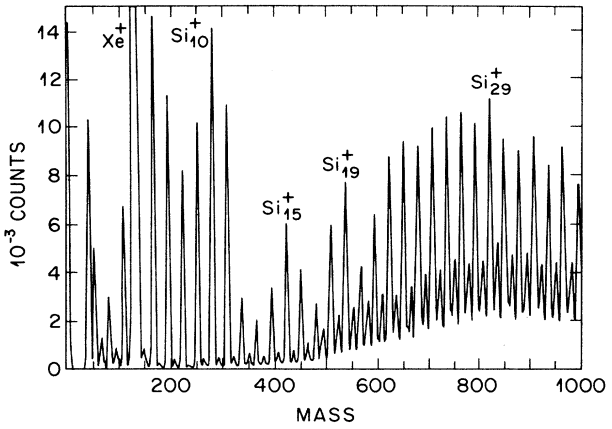

FIG. 1. Mass spectrum of silicon cluster ions available from the source.

tained under UHV conditions. Low-energy electron diffraction (LEED) patterns measured before and after deposition were virtually identical.

STM topographs were taken with a sample bias of between +2.5 and −2.5 V and with a tunneling current of less than 50 pA. Larger tunneling currents (which would normally provide higher resolution) often resulted in contact between the STM tip and a cluster. Figure 2(a) shows a 160×40 Å STM topograph of a Au(001)-(5×20) surface recorded outside the cluster-deposited area. Almost all of the individual Au atoms are imaged and show a distorted hexagonal structure with no trace of foreign impurities. Details of the Au(001)-(5×20) surface structure will be published elsewhere.[18] The major corrugations along the ⟨110⟩ are separated by 14.4 Å. This surface was selected for these studies because diffusion along the ⟨0$\bar{1}$0⟩ is inhibited by the corrugations. Figure 2(b) shows a large-area 280×220 Å STM topograph, recorded within the cluster-deposited area, as a curvature plot (this is essentially equivalent to the picture obtained with the light source from the left at 45°). Five clusters are visible on the surface. The observed cluster density is comparable to that estimated from the cluster ion current and the deposition time. As can be seen in Fig. 2(b), the STM tip changed several times as the area was scanned. However, the same clusters could be imaged several times and the individual cluster images showed the same general features. Closeup views of two typical clusters are shown in Figs. 2(c) and 2(d). In Fig. 2(c), recorded with a bias of −0.5 V, the cluster image appears as a dark hole, somewhat larger than the estimated cluster size (< 10 Å). Clusters always appeared dark when imaged with a bias between −0.8 and +0.5 V. Outside this range, the clusters are imaged as a white blob of < 10 Å diameter. Figure 2(d) shows a image recorded with a bias of −1.0 V in which the cluster appears as a white blob surrounded by a dark ring.

Some understanding of these images may be gained through tunneling spectroscopy measurements.[19,20] The inset in Fig. 3 shows plots of the tunneling current versus sample bias voltage measured with the tip situated over silicon clusters. These plots can be numerically differentiated to yield di/dV versus V (an approximate measure of the electronic density of states) as shown in the remainder of Fig. 3. The solid line indicates the average state density for the clean Au(001)-(5×20) surface, showing metallic behavior with peaks around 0.8, 1.2, and 1.8 eV (details will be published elsewhere[18]). The dashed line shows the measured electronic density of states for a cluster. While the locations of the peaks on the cluster density of states were not always reproducible, a band gap of ~1 eV between the empty and filled states

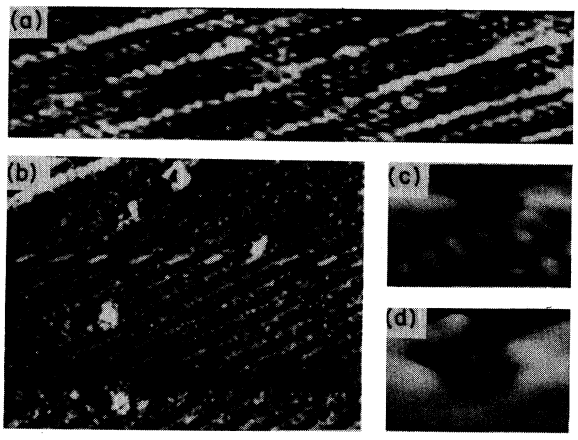

FIG. 2. (a) 160×40 Å topograph of Au(001)-(5×20) reconstruction measured with a sample bias of +0.5 V. All atoms in a distorted hexagonal array are shown (total gray scale range is 1.0 Å). (b) 280×220 Å curvature view of five Si_{10} clusters on a Au(110)-(5×20) surface measured with a bias voltage of +0.5 V. (c) 80×65 Å perspective topograph measured with a bias of −0.5 V. (d) 40×32 Å perspective topograph measured with a bias of −1.0 V. The total gray scale range in (c) and (d) is 2.4 Å.

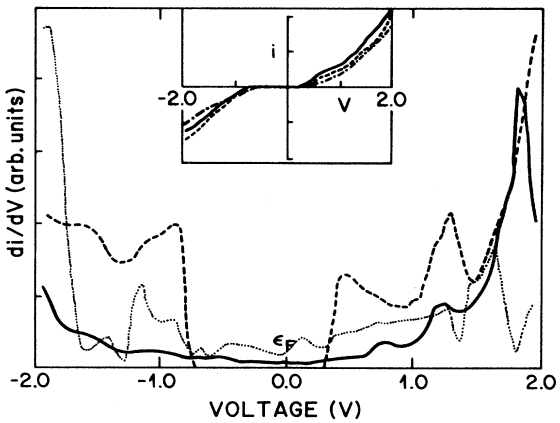

FIG. 3. di/dV as a function of sample bias voltage. The solid line shows the measured state density of the clean Au(001) surface, the dashed line is that for a Si_{10} cluster, and the dotted line is that of Au silicide islands. The inset shows plots of tunneling current against sample bias voltage recorded for three different clusters.

was always observed. The existence of the band gap suggests that the clusters do not strongly interact with the substrate and are not chemically altered during the transfer. Different tunneling channels on the clusters may give rise to the observed variation in the size of the band gap (0.95–1.15 eV) and in the locations of the peaks in the cluster density of states. The size of the band gap found here is very close to the value (1.2 eV) for the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap of Si_{10} deduced from uv photoemission studies[9] of the cluster anions in the gas phase. As can be seen from Fig. 3 the Fermi level of Au lies closer to the conduction band (or LUMO) of the cluster, indicating that the charge density is transferred from the substrate to the cluster. The position of the Si_{10} conduction band relative to the Au Fermi level varies (see inset in Fig. 3). As more charge transfer occurs, the Fermi level moves closer to the conduction band. The degree of charge transfer could be influenced by the structure and orientation of the cluster on the substrate.

The explanation for the different cluster images in Figs. 2(c) and 2(d) is now evident. STM images always contain electronic as well as geometric structure information;[21] where no states are available for tunneling, the STM image is dark. For Fig. 2(c), the sample bias lies in the band gap, so the cluster appears dark, while in Fig. 2(d), taken outside the band gap, the cluster is a white blob. The dark ring around the cluster in Fig. 2(d) indicates an area of lowered state density, apparently due to charge transfer from the surrounding metal substrate to the cluster. The large size of the cluster image in Fig. 2(c) is probably due to the combined effects of a dark cluster image and a dark ring on the substrate due to charge transfer.

To explore the differences between directly deposited clusters and clusters formed by aggregation of atoms on the surface, some experiments were performed in which Si atoms rather than clusters were deposited on the Au surface. When Si atoms were deposited the STM topographs showed flat islands that appeared to be one atom high. In tunneling spectroscopy measurements (Fig. 3), the islands shows metallic behavior, indicating the formation of silicide islands. The geometric and electronic structures of the silicide islands are clearly different from those of deposited clusters. It appears that, at least in this case, the three-dimensional structure of directly deposited clusters cannot be readily attained by aggregating atoms on the surface.

In summary, we have presented STM images of Si_{10} clusters on Au(001)-(5×20). The band gap determined from tunneling spectroscopy measurements was ~1.0 eV. A wide variety of different cluster images were observed even though size-selected clusters were deposited.

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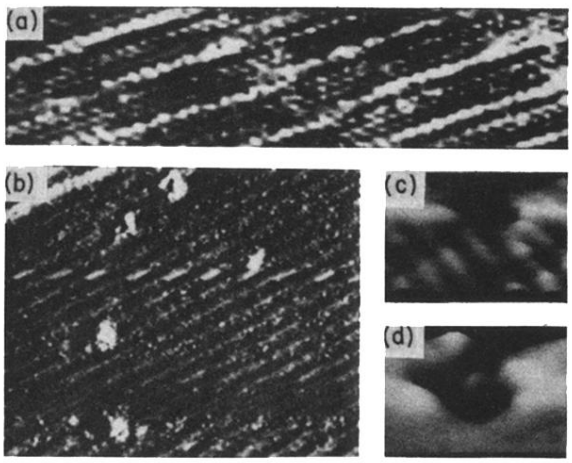

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