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Deposited microclusters and their interaction with substrate

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Abstract

Au, C and Sb clusters of nanometer size deposited on silicon and graphite substrates are investigated by means of a scanning tunnelling microscopy (STM). Both deposition and measurements were carried out in an ultrahigh vacuum (UHV) system at room temperature. The apparent height of the clusters, which reflects not only geometry but also their electronic density of states, changes markedly while scanning at different voltage biases. Such behaviour depends significantly on the cluster size, their chemical composition and the type of substrate. We discuss the properties of clusters in terms of their size and modifications by the substrate.

Keywords: Antimony; Carbon; Clusters; Gold; Scanning tunneling microscopy; Scanning tunneling spectroscopies

1. Introduction

Microclusters are small particles which consist of a few to several hundred atoms. It is expected that they will display characteristic properties because their atomic structure, bond length and bond character are different from the bulk crystal. As is typical for small particles, quantization of electron states [1] and single electron effects due to the Coulomb interaction [2–4] occur. Detailed investigation of these clusters allow us to solve the puzzle of how electronic band structure develops in solid state. Clusters of a few nanometers in diameter may find applications in nanolithography for the fabrication of various devices with a high degree of miniaturization. In addition, clusters are thought to form "inhomogeneous matter" [5] — bulk matter consisting of a huge number of small particles. Hence, considerable interest lies in determining the electronic structure of single clusters [6–10], the possibilities of manipulation and positioning them in the atomic scale [11–13], as well as in the interactions between clusters in densely packed many-cluster systems [14–16].

In this paper we present the preliminary results of the investigation of Au, C and Sb clusters deposited on silicon and graphite substrates, performed by STM. Scanning tunnelling microscopy is a unique and versatile tool that images the topography of analysed samples in real space and probes the local electronic states in a wide range of energy [17]. This means that STM is useful for the observation of irregular objects, such as deposited clusters. We clearly show that the electronic properties of the clusters are of a significantly different nature from the bulk material and are related to cluster size.

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2. Experimental details

Both deposition and STM measurements were performed at room temperature in a UHV system in a vacuum of 4×10^{-10} Torr. All types of clusters were deposited from the respective target element by KrF excimer laser irradiation. The purity of the target material was higher than 99.99%. The distance between the target and the substrate was kept to 1 cm during deposition. Au clusters were also deposited by applying a sequence of voltage bias pulses between the gold STM tip and the substrate. This technique allowed us to obtain clusters with controlled geometry and to position them in the desired way. Details of deposition from the tip are provided elsewhere [18]. Both highly oriented pyrolytic graphite (HOPG) and Si(111) wafers were used as substrates. The silicon wafers were chemically etched and heated several times in the vacuum chamber up to 1250°C. The rate of cooling did not exceed 20°C min^{-1} above 900°C and 60°C min^{-1} below 900°C. This method of substrate preparation resulted in a high surface quality with only a small number of structural defects. To avoid interpretation errors, only the substrates with very few contaminants (less than one particle per 5000 nm^2) were used in the experiment. Graphite substrates were heated up to 600°C. Both the Au and W tips, prepared by electrochemical etching, and commercially available PtIr tips were used for the STM investigations. The measurements were performed using the DI Nanoscope III with a UHV STM head. In our system the bias sample is measured relative to the tip, i.e. electrons tunnel from the STM tip towards the sample at the positive bias. All images shown in this paper were recorded in the constant current mode. The intensity of tunnelling current was kept below 100 pA (usually in the range 50–80 pA) to avoid dragging of clusters by the scanning tip. The scan under initial conditions was repeated after a series of scans at different biases to ensure that the analysed structure remained unchanged. Scanning tunnelling spectroscopy (STS) was also used to investigate the electronic states directly. The current/voltage (I/V) characteristics and their derivatives were acquired in constant tip-sample mode, usually in the range of bias between -2.0 V and 2.0 V. The STM tip was positioned over the desired point of the scanned area, the STM feedback loop interrupted and the I/V spectra recorded.

3. Results

Fig. 1 shows the sequence of images acquired at different bias voltages for five gold clusters arranged in a line on the Si(111) surface. Each of the clusters was deposited by applying a series of bias pulses between the tip and the substrate. Detailed analysis of the cross-sections reveals that cluster heights measured at the bias of 2.0 V are in the range 0.23–0.28 nm, which corresponds to the single atom diameter, whereas the cluster diameters vary from 4.8 to 6.0 nm. The group of deposited clusters is clearly visible at the biases of 2.0 V and 1.5 V. At 1.0 V the images of the lower clusters disappear. The three remaining ones are very weakly seen. It is worth noting that the atomic resolution of the substrate is still maintained.

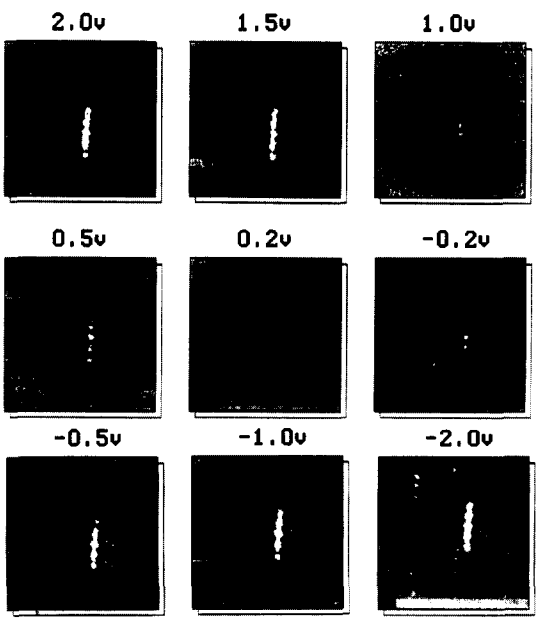

Fig. 1. The STM images of Au deposits arranged in a line on silicon obtained at various voltage biases. The size of the scanned area is 100×100 nm^2. The range of gray scale from black to white corresponds to 0.5 nm.

However, no Si adatoms can be resolved in these spots, where images of Au clusters are visible at higher voltages. The images become clearer at a bias of 0.5 V, but the clusters are worse resolved at 0.2 V. The cluster images become clearer as the bias changes towards negative values. In the range −1.0 V to −2.0 V contrast is very high and the measured height of the clusters does not change. However, weak additional satellites appear in the picture recorded at −2.0 V bias. These are the result of the multitip effect. It is worth emphasizing that the stability of these Au deposits on the silicon substrate is very high. Their arrangement did not change during several scans over 40 min.

Fig. 2 depicts the sequence of STM scans of another Au cluster, also deposited from the STM tip, which is different in size from the previous ones. It has a dome-like shape, 3.6 nm in diameter and 1.1 nm in height (at 2.0 V). Rough estimation reveals that this cluster consists of a few hundred atoms. Again, we followed the measurement procedure of scanning at various biases, ranging from 2.0 V to −2.0 V. Interestingly, the cluster is seen clearly at all biases without any considerable change in its height. This behaviour is significantly different from that presented in Fig. 1. Here atomic resolution of the substrate is high as well.

Fig. 3 depicts a typical I/V spectrum and its logarithmic derivative acquired for a small cluster, comparable in size to those shown in Fig. 1. The

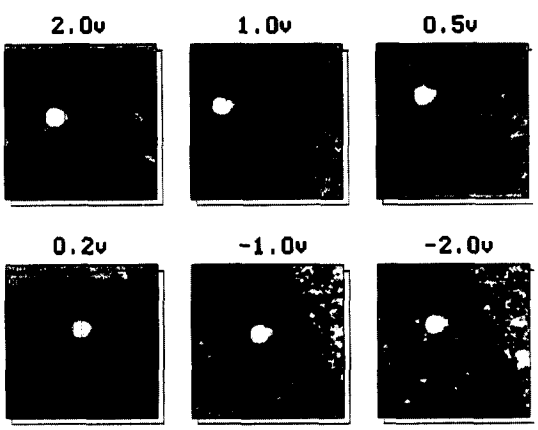

Fig. 2. The tunnelling images of dome-like shaped Au deposit on silicon at various voltage biases. The scanned area is 41.5×41.5 nm^2.

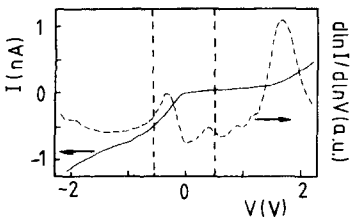

Fig. 3. I/V (solid line) and $\mathrm{d}\ln I/\mathrm{d}\ln V$ (dashed line) spectra acquired for a small cluster, one atom diameter in height. The energy gap is evident between 0 and 1.1 V. For comparison, the position of the energy gap of clean silicon is marked by two vertical dashed straight lines.

I/V curve (solid line) exhibits a well-resolved, slightly sloped, plateau between 0 and 1.1 V. In the $\mathrm{d}\ln I/\mathrm{d}\ln V$ spectrum (dashed line) two peaks, below 0 V and above 1.1 V, are clear. They are separated by a flat part of the curve which has relatively weak features. For comparison we performed similar measurements on a clean silicon surface. Generally, the shape of both the I/V and $\mathrm{d}\ln I/\mathrm{d}\ln V$ spectra is similar to that obtained for small clusters, although the curve is shifted towards negative voltage by about 0.5 V. The range of the plateau of the I/V curve for the clean surface is marked on Fig. 3. by two perpendicular dashed lines.

We also analysed Au clusters on silicon substrate, produced by laser ablation, to compare the influence of various deposition techniques on cluster size and properties. The scans at different voltages reveal again that the images of small clusters disappear in the same range of biases as for those deposited from the STM tip, shown in Fig. 1. The $\mathrm{d}\ln I/\mathrm{d}\ln V$ spectrum also takes the same shape with two highlighted peaks separated by a flat region, as for clusters deposited from the gold STM tip. Therefore we conclude that the mechanism of cluster deposition does not produce any difference in the behaviour of the observed clusters.

Au clusters were also deposited by laser ablation on graphite (HOPG) to investigate the influence of the type of substrate on cluster properties. We followed the same measuring procedure of recording scans at different voltages in the range −1.5 V to 1.5 V. Particular attention was paid to cluster behaviour in the range of biases between 1.0 V and 0 V, where the images of Au clusters deposited

on silicon substrate were less resolved. Au clusters of different sizes are clearly visible for the HOPG substrate in the whole range of applied voltages. Even the smallest particles, consisting of several atoms, are seen as protrusions. We did not notice any significant changes in their apparent height with the bias, contrary to the experiment performed on Si.

It was found that the size distribution of clusters deposited on silicon substrate depends on deposition technique. The size of clusters obtained by field emission from the tip varies with the process parameters, i.e. the distance between the tip and the sample, and the amplitude of applied pulses. Clusters produced by this method are located in desired positions and have a relatively wide distribution of sizes (from one atomic diameter in height to a few nanometers). It seems that clusters formed by laser ablation from the gold target are smaller than those deposited from the tip and consist of only a few to several tens of atoms. Their height is usually smaller than three diameters of an atom. Their size distribution is therefore narrower. The positions of these clusters on the substrate is random, not dictated by the structure of the surface, existing defects or the steps of terraces.

Clusters grown by laser ablation on the HOPG substrate appear to show a wider size distribution than those deposited by the same technique on silicon. We have observed small particles, which were composed of several atoms, as well as objects of a few nanometers in size. Although the laser ablation process is not well controlled, it is plausible that much weaker bonding to the HOPG substrate allows coalescence of small clusters into bigger ones, whereas this process is hampered on silicon surface. We also observed that deposited objects are much more stable on silicon substrate.

Besides Au clusters, we also analysed carbon clusters deposited by laser ablation. A graphite (HOPG) was used as the carbon target. These clusters are also small and consist of a few to several atoms, like the Au particles deposited by the same technique. The STM images of C clusters recorded at various biases in the range 2.0–0.25 V are shown in Fig. 4. The images are unadorned and numerous spikes from the tunnelling signal appear, especially at lower voltages. The heights

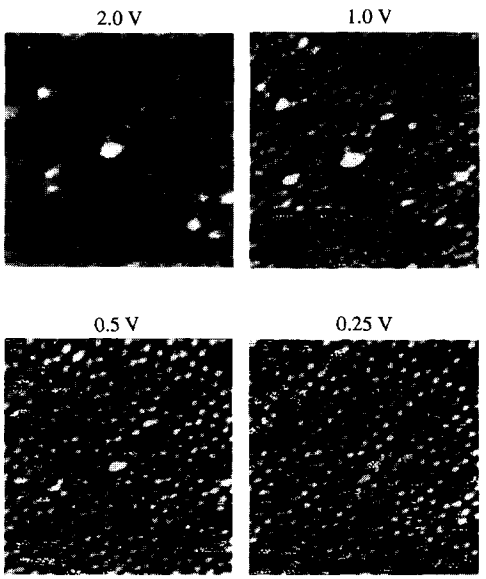

Fig. 4. The tunnelling images of carbon clusters on silicon at different biases. The biggest cluster is located in the centre of the image. The smaller ones are visible in the left side and lower right corner. The size of the scanned area is 13.3×13.3 nm^2. The range of gray scale from black to white corresponds to 0.6 nm.

of all clusters measured at the bias of 2.0 V are comparable with the diameter of a single atom. The cluster, elliptical in shape, which is located in the centre of the scanned area consists of the biggest number of atoms (longer axis is *c.* 1.1 nm, shorter axis is -0.8 nm). The smaller clusters are distributed in the left part of the picture and in the lower right corner. All deposited particles are very clearly visible as protrusions at the bias of 2.0 V. The images of the clusters become less clear as the bias voltage decreases from 2.0 V. The measured height of the smaller adsorbates decreases more rapidly with decreasing bias, i.e. only the biggest cluster can still be recognized at the bias of 0.5 V. Finally, the images of all clusters disappear at the bias of 0.25 V. It is worth mentioning that no Si atoms can be resolved at this bias within areas, where carbon clusters are visible at higher biases. On the other hand, reconstruction of the clean silicon surface is clearly evident at all biases. Decreasing the bias to negative values results in an increase in apparent cluster height and therefore

in the distinctness of their images, similar to the effect observed for Au particles.

Sb clusters, deposited by laser ablation, are the third type of particles analysed in this paper. Fig. 5 shows two STM images of the same area acquired at different voltages. The silicon surface shows typical reconstruction although relatively large numbers of surface defects are found. Sb clusters are visible as protrusions at a bias of 1.6 V. They consist of a few to several tens of atoms. The biggest cluster is 0.4 nm in height and 2.2 nm in diameter. The position of all clusters on the surface is random. The images of the clusters disappear in the image recorded at 0.83 V. Only Si atoms on clean parts of the substrate are still well resolved. Similarly, as for previous cases, Si atoms are not resolved at the bias of 0.83 V in these spots, where Sb clusters are located.

The Sb particles deposited on HOPG by laser ablation are larger than those deposited on silicon, as in the case of Au. The size of the biggest clusters reaches 4 nm in diameter and 2 nm in height. The topography measurements at different voltages reveal that the cluster images become less visible or even disappear, depending on their size, in the range of biases between −0.2 and 0.2 V. Beyond this range Sb clusters are clearly visible as protrusions both at positive and negative biases. Fig. 6 depicts the STM images of the same area with two clusters, different in size, recorded consecutively at 0.77, 0.10 and 0.70 V. The longer axis of the bigger cluster is 2.2 nm and its height is 0.5 nm. The size of the smaller cluster is 0.4 nm (height) and 1.4 nm (diameter). Its image disappears at the bias of 0.1 V, and the larger cluster is only very weakly visible.

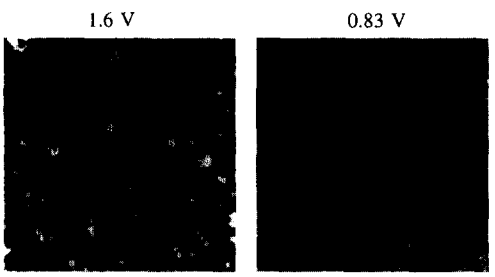

Fig. 5. The tunnelling images of Sb clusters on Si(111) obtained at voltage biases 1.6 V and 0.83 V. The size of the scanned area is 40×40 nm^2.

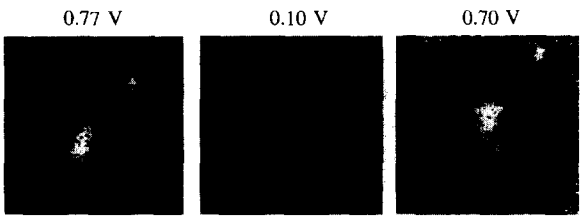

Fig. 6. 9×9 nm^2 consecutive STM images of the same area of HOPG containing two Sb clusters acquired at biases 0.77 V, 0.10 V and 0.70 V. The image of the smaller cluster disappears at the lowest bias. The height is displayed in a gray scale ranging from 0 (black) to 2 nm (white).

Comparison of the two scans taken at 0.77 V and 0.7 V shows that the shapes of the clusters are slightly changed. It is probable that the STM tip deformed them during scanning at the bias of 0.1 V.

4. Discussion

At any bias voltage only the electronic states between the Fermi levels of the tip and the sample contribute to the tunnelling current. In theoretical considerations Lang [17] has shown that the apparent height of the adsorbed atom on a flat surface measured by STM at various voltages in constant current mode is determined by the density of electronic states in that adsorbate in the corresponding range of energy. Therefore, topography measurements at constant current mode at different bias voltages is the simplest way to detect the surface states in the real space. Although this method is limited as a spectroscopic tool, the use of I/V data allows qualitative conclusions to be drawn on the electronic structure of investigated objects. On this basis we discuss the property dependence of Au, C and Sb clusters in terms of their size and the influence of the substrate, on which they are deposited.

If one compares the images of clusters of different sizes deposited on silicon substrate, a common feature is easily found: the images of very small clusters become less clear or even disappear. In constant current mode the tip, scanning above these clusters, does not follow the topographic profile of the sample. It has to decrease the width of the tunnelling barrier in order to maintain the

constant intensity of the tunnelling current. As a consequence, the height of observed objects is reduced. This may be a result of the lowered electronic density of states in clusters. We assume that the disappearance of cluster images is a result of direct electron tunnelling between the STM tip and the substrate. The reason for this is the occurrence of an energy gap in the cluster in the corresponding energy range. This may originate from quantized, discrete electronic states or from modifications induced by the substrate. Usually, in the case of topography recording, the electronic structure of the tip appears to be relatively unimportant, contrary to I/V data collection [19,20]. The contribution of tip electronic states to tunnelling current remains unchanged while scanning at fixed bias voltage in constant current mode.

Our suggestions, that in small Au clusters the remnant of an energy gap occurs, are confirmed by I/V spectra acquired for such clusters. The plateau in the middle part of the curve is typical for samples which exhibit the energy gap. The logarithmic derivative highlights this feature very well. The two peaks below 0 V and above 1.1 V are associated with valence and conduction bands, respectively. They are separated by a region which displays a much lower density of states. The width of the observed energy gap is the same as for the clean substrate. However, its position, relative to the Fermi level (which corresponds to 0 V), is shifted by about 0.5 V. It is worth noticing that the images of clusters become less visible, and some of them even disappear, in the same range of biases, i.e. between 0 and 1.1 V.

We also performed measurement in the constant height mode. This method is extremely sensitive to protrusions located on the flat surface because of the exponential dependence of tunnelling current on tip-sample separation. As in constant current mode, the images of small clusters disappear in the same range of applied biases, again suggesting direct tunnelling between the STM tip and the substrate, and therefore a lack of states in the cluster for the corresponding energy.

The images of all analysed, very small clusters (Au, C and Sb) deposited on silicon substrate disappear or become less visible in the same range of biases (Figs. 1, 4 and 5). Because this is a common feature, we assume that, in a similar way to Au particles, induction of the energy gap also takes place in C and Sb clusters. The surface of Si(111) exhibits metallic character and suppresses the semiconducting properties of the bulk. As a consequence, the characteristic 7×7 reconstruction of the clean surface is well resolved at all applied voltages. In the deposition sites the dangling bonds of silicon adatoms are coupled with the bonds of atoms and clusters are formed. The free Si dangling bonds therefore no longer exist and this is one reason why Si adatoms are not observed in these sites when the images of the clusters disappear. It is thought that the metallic character of the Si surface is suppressed in these spots and energy gap is induced in clusters by the proximity of the semiconducting substrate. The bigger the cluster, the weaker the modification of its properties by semiconducting substrate is observed. Large clusters do not show dependence of their apparent height on applied voltage. The image of the Au cluster shown in Fig. 2, with an estimated volume of 10.6 nm^3, does not change at all, suggesting that its height, and therefore density of electronic states, does not vary with the bias. Such behaviour is expected for particles of metallic character for which the density of states is does not change with energy.

Significant changes in the STM imaging of clusters of different sizes, deposited on silicon, suggest that metal–nonmetal crossover occurs. As we have shown, the images of small clusters disappear at certain biases, whereas bigger clusters are clearly visible in the whole range of applied voltages. The critical height of Au clusters is found to be comparable to the diameter of a single atom. Above this height clusters are imaged as typical metallic particles. The behaviour of the smallest ones resembles semiconducting material. On the other hand, the energy levels are expected to be quantized in small clusters which consist of several atoms. Thus, the question arises of whether the observed energy gap is the result of the proximity effect of semiconducting substrate or of the reduced size of the adsorbates. To answer this question we deposited Au and Sb clusters on graphite substrate. The van der Waals bonding to HOPG surface is much weaker than the bonding to silicon, therefore it is expected

that the graphite surface will not disturb the inner electronic structure of deposited clusters as much as the silicon surface.

The images of both Au and Sb clusters deposited on the graphite substrate are well resolved in the range of biases, for which they disappear on the silicon substrate. The apparent height of all Au clusters, even of the smallest ones, does not change significantly, suggesting a relatively smooth dependence of electronic states with energy. Similarly, Sb clusters on HOPG are well resolved at 0.77 V, the voltage at which their images disappear on the silicon surface. Therefore, we favour the explanation that the nonmetallic behaviour of small clusters on the silicon substrate, revealing a lowered density of electronic states, is induced by the semiconducting substrate.

An interesting result was acquired for Sb clusters deposited on HOPG. The images of smaller clusters disappear in the narrow range of biases between −0.2 V and 0.2 V. This effect can be explained by direct electron tunnelling between the tip and the substrate. This occurs when no electronic states, which contribute to the tunnelling current, are available in the cluster in the corresponding range of energies. If it is assumed that the influence of the weakly interacting HOPG substrate is negligible, it is reasonable to expect that the energy gap observed in these clusters is due to their reduced size. Sb is a semimetal in the bulk, therefore the overlap in the energy of the conduction and valence bands is very small. This overlap diminishes and bands become separated, giving rise to energy gap occurrence as the size of the Sb particle decreases. Further investigations are in progress.

5. Conclusions

We have analysed by means of STM the electronic structure of clusters which are different in composition and size. The common feature observed is that images of small clusters (Au, C, Sb) deposited on silicon become less visible or even disappear at the bias between 0 and 1 V. Our explanation is that the reduced apparent height of clusters reflects their lowered density of states, which is induced by a semiconducting substrate. This remnant of the energy gap is clearly seen in I/V spectra obtained for small Au clusters. Such nonmetallic behaviour is observed only in clusters of one atom diameter in height. Larger clusters are not affected by the semiconducting substrate and exhibit metallic character with a continuous density of states over the energy range. The shift of the energy gap in the cluster, relative to a clean silicon substrate of about 0.5 eV, suggests that deposited objects act as Fermi level pinning centres and bend the energy bands of the silicon substrate.

The comparison with results acquired on HOPG substrate shows that the observed remnant of the energy gap in clusters deposited on silicon is due to the semiconducting substrate. All Au clusters, deposited on HOPG, exhibit metallic character. However, the evidence of narrow energy gap occurrence in Sb clusters deposited on HOPG is clear. Because the graphite surface is inert, we believe that energy band separation is due to the reduced size of this type of cluster.

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