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LETTER TO THE EDITOR

The impact of size-selected Ag clusters on graphite: an STM study

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Abstract. We have used the scanning tunnelling microscope (STM) to investigate the deposition of size-selected $(Ag_n)^+$ clusters, in the size range 50–400 atoms, on highly oriented pyrolytic graphite (HOPG). The cluster morphology has been explored as a function of impact energy. For high deposition energies (∼10 eV/atom) the clusters are pinned to the surface and flattened on impact. For lower impact energies (∼1 eV/atom) the footprint of the cluster on the surface is significantly reduced. By controlling the deposition parameters clusters have also been selectively sited at surface steps. Larger particles, arising from diffusion and aggegation of deposited clusters, are visible with the scanning electron microscope (SEM) but not the STM; we find definite evidence that the interaction with the STM tip disturbs these particles.

The production of clusters is an exciting and growing research area, enabling investigations of the physics and chemistry of truly nanometre scale systems. Experimental and theoretical investigations of clusters over the last decade have revealed many interesting properties, the majority of which are size dependent [1]. This research effort has still to find fruition in the development of industrially useful processes, though important progress is currently being made, e.g. in the use of high-energy cluster beam deposition for producing thin films [2]. Moreover, if clusters are to be exploited as nanoscale components for electronic devices then they must be deposited onto a substrate. Hence an understanding of the deposition and interaction of the cluster with the substrate is paramount to the development of industrially useful cluster-based technologies.

Studies of the creation of clusters, or islands, by the evaporation of metal atoms onto surfaces, such as graphite [3–5], have yielded important insights into the growth and diffusion of clusters on the surface. One of the appealing aspects of the graphite surface is the existence of surface steps on the cleaved basal plane, which have enabled us to explore the site-selective nucleation of clusters at prototype line defects on the surface [5]. Scanning electron microscope (SEM) studies of the deposition of size selected clusters on graphite have recently been reported by our group [4, 6, 7]; these results indicate that clusters (in the size range 20–300 atoms) deposited at low energy (∼50 eV) are able to diffuse across the surface and tend to aggregate. Clusters deposited at higher energy (∼400 eV) are *pinned* to the substrate, thus limiting diffusion and aggregation.

In this work we use the scanning tunnelling microscope (STM) to explore the relationship between the morphology of the cluster and the deposition energy, as well as the selective trapping of size-selected clusters at surface steps. We also consider the origin of differences between SEM and STM images of the same samples, with particular reference to interaction between the STM tip and the deposited clusters.

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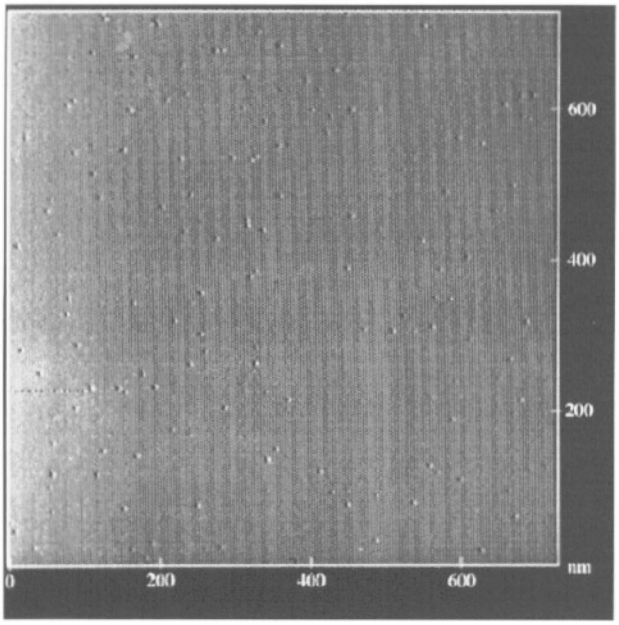

Figure 1. STM micrograph of an array of Ag_{50} clusters deposited on graphite with an impact energy of 500 eV (coverage, 2.5×10^{10} clusters cm^{-2}; deposition rate, 3×10^{8} clusters cm^{-2} s^{-1}). The tunnelling current was 1 nA, with a 200 mV bias. This micrograph was produced in differential imaging mode.

The size-selected silver clusters were produced in a gas aggregation cluster source, which is described elsewhere [8, 9]. In brief, silver is evaporated into a room-temperature stream of helium gas which cools the silver atoms, causing nucleation and hence cluster growth. The mixture of carrier gas and metal clusters expands through a nozzle and is ionized by a magnetically confined plasma before passing through a skimmer. The cluster ion beam is focused and steered by a set of electron optical lenses, before passing through a mass filter. Size-selected clusters are deposited onto the highly oriented pyrolitic graphite (HOPG) substrates in a high-vacuum chamber with a background pressure in the range 10^{-7}–10^{-6} mbar; during deposition the pressure of helium in the chamber rose to 10^{-5} mbar. The clusters produced in the aggregation process had a mass range from $\sim$100 to 1000 atoms/cluster. Two mass filters were used: a Wien filter was used to produce clusters containing 50 atoms, with a resolution of ±8 atoms at this size. A newly developed time of flight mass filter, operated with a resolving power of $M/\Delta M = 20$, was used to select the larger clusters. The cluster coverage was determined from the sample drain current during ionized cluster deposition.

The kinetic energy of the ionized cluster when it lands on the substrate is controlled by simply biasing the substrate to the appropriate voltage. The substrates were cleaned before deposition by heating to 500 °C *in vacuo*. The samples were analysed using a benchtop STM (Nanoscope II) and a Hitachi S900 high-resolution SEM. Samples have been studied up to a month after deposition and no major change in the appearance of the sample was observed. Thus the morphology of the film produced by cluster deposition appears to be largely ‘frozen’ by exposure to the ambient.

Figure 1 is an STM image of size-selected Ag clusters on a graphite (HOPG) substrate.

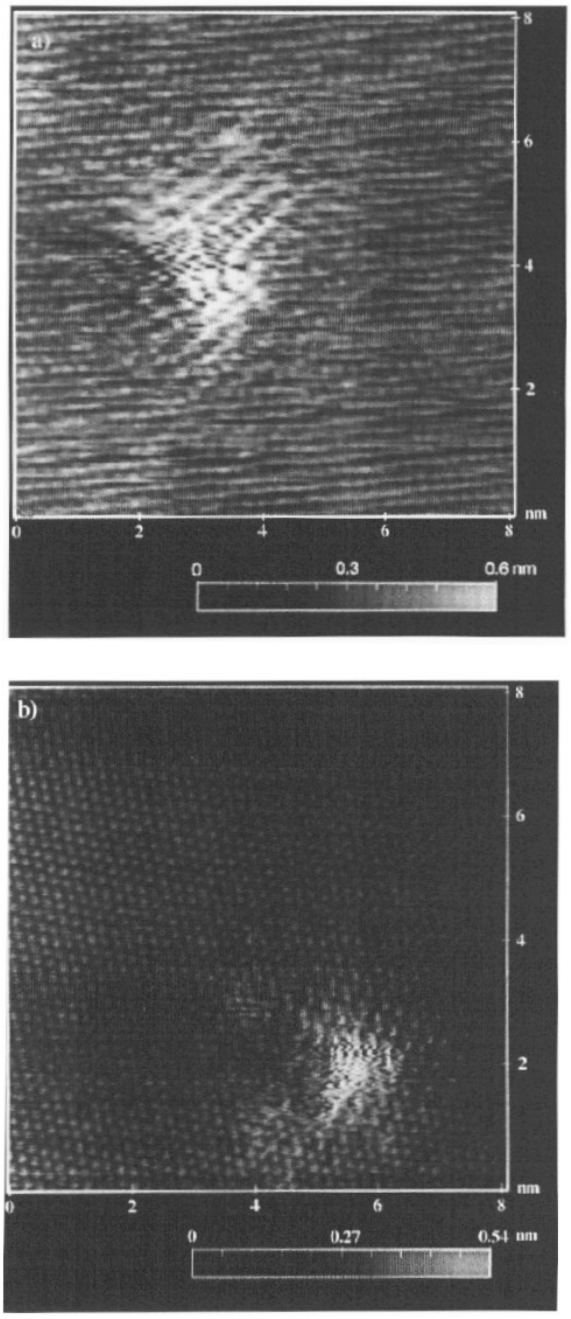

Figure 2. (a) An STM micrograph of a single Ag_{50} cluster deposited on graphite with an impact energy of 500 eV (coverage, 3×10^9 clusters cm^{-2}; deposition rate, 1×10^8 clusters cm^{-2} s^{-1}). The tunnelling current was 0.5 nA, with a 350 mV bias. (b) An STM micrograph of a single Ag_{50} cluster deposited on graphite with an impact energy of 50 eV (coverage, 4×10^9 clusters cm^{-2}; deposition rate, 1×10^8 clusters cm^{-2} s^{-1}), imaged with a tunnelling current of 2 nA and a bias of 200 mV.

We shall term the cluster coverage, 3×10^{10} clusters cm^{-2}, 'low coverage' (the deposition rate was 3×10^{8} clusters cm^{-2} s^{-1}). The clusters contain 50 ± 8 Ag atoms, and were deposited at 500 eV (i.e. 10 eV per atom). The uniformity of the cluster size in figure 1 is noteworthy. Figure 2(a) shows a close-up view of a cluster of the same size deposited at the same energy (coverage, 3×10^{9} clusters cm^{-2}; rate, 1×10^{8} clusters cm^{-2} s^{-1}); the diameter of the cluster is approximately 2–3 nm This diameter is consistent with the clusters being flattened out to a monolayer as a result of the impact on the surface. There is no evidence of aggregation of clusters on the surface; it is probable that the clusters have been deposited with sufficient energy to become pinned to their point of impact, e.g. by damaging the surface beneath them. This regime of cluster impact energy will be referred to as 'high-energy' deposition, and the results are in broad agreement with our previous SEM studies of this high energy regime [4, 7]. Moreover, the explicit observation that clusters with a deposition energy of ∼10 eV/atom flatten on impact parallels work done using the same energy per atom to produce smooth films by cluster deposition [2].

We have also investigated the relationship between the size and shape of the cluster on the substrate and the deposition energy. This is illustrated by the STM micrographs shown in figures 2(a) and (b). In figure 2(b), like figure 2(a), the Ag clusters contain 50 ± 8 atoms (coverage, 4×10^{9} clusters cm^{-2}, rate, 1×10^{8} clusters cm^{-2} s^{-1}), but the deposition energy has been reduced to 50 eV. In contrast with figure 2(a) (deposition energy, 500 eV), where the cluster diameter is approximately 2–3 nm, the cluster diameter in figure 2(b) is approximately 1 nm. In this latter case the footprint of the cluster is consistent with a hemispherical shape on the surface, compared with the single layer of Ag atoms at 500 eV. These two observations confirm our intuitive expectations; as the deposition energy increases the cluster becomes more flattened upon impact. It is interesting to note that the clusters deposited at 50 eV (i.e. 1 eV/atom) still show some flattening compared with the (presumably) roughly spherical shape in the gas phase. The mechanism by which the shape of the cluster is deformed on the surface is intriguing; one possibility would be surface melting of the cluster when it impacts on the substrate. Cheng and Landman have modelled the impact of a copper cluster, with ∼2 eV/atom, on a Cu(111) surface; the cluster was found to undergo internal melting [10].

We have also explored the trapping of deposited clusters at surface steps. Samples prepared with a deposition rate (3×10^{8} clusters cm^{-2} s^{-1}) and a low coverage (1×10^{10} clusters cm^{-2}) are depicted in figure 3. In this case the clusters contained 400 ± 30 atoms, and were deposited at 50 eV onto the graphite surface (the kinetic energy per atom, 0.125 eV, is particularly low in this case). The STM micrograph, figure 3(a), shows clusters arrayed along a step edge. The sizes of the clusters in figure 3(a) range from ∼3 to 6 nm; this size range is larger than would be expected of the clusters incident on the surface (see below). No clusters were found on the terraces near step edges, revealing that in this deposition regime clusters landing near a step had sufficient mobility to reach the step, allowing the production of samples featuring organized cluster arrays.

Francis *et al* [5], in their study of atomic vapour deposition of silver on graphite, found evidence that both atoms and clusters are more mobile on the terraces than on the steps. This suggests two possible explanations for the distribution of cluster sizes on the step in figure 3(a). (i) Clusters diffuse to the step after which further diffusion only takes place along the step edge, leading to some aggegation of the incident clusters. (ii) There is some aggregation of diffusing clusters on the terraces, but when clusters, or small aggregates of clusters, meet a step they are trapped. In this latter picture the size distribution of clusters on the step represents a series of 'snap-shots' of the cluster aggregation process on the terraces.

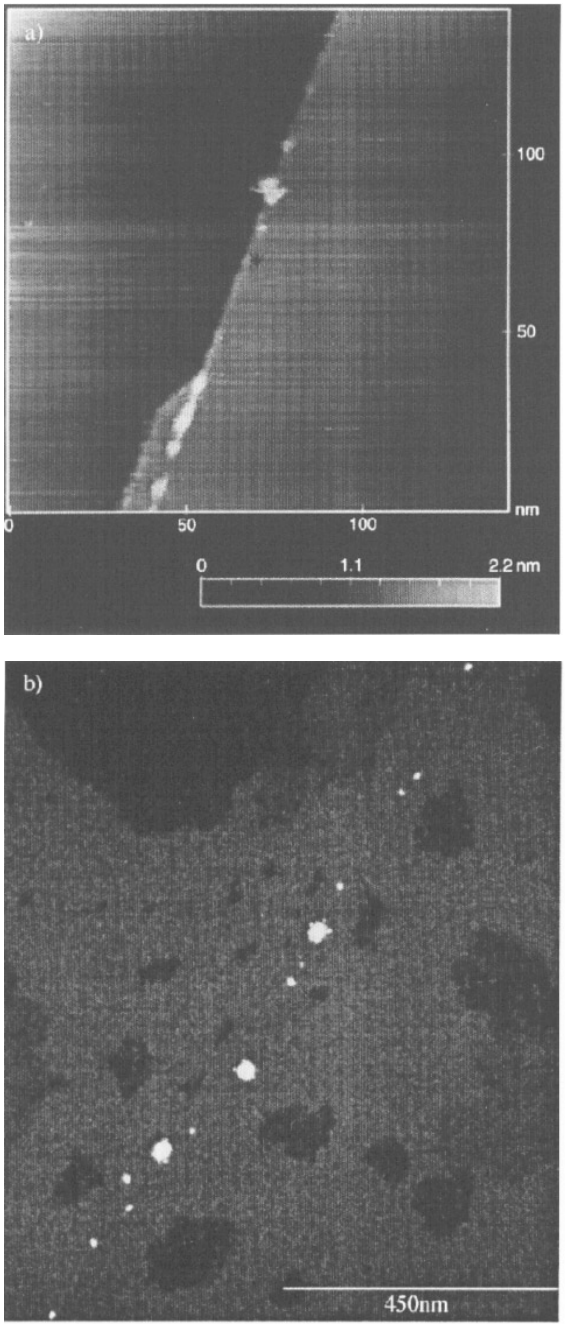

Figure 3. (a) An STM micrograph obtained after deposition of Ag_{400} clusters onto graphite at 50 eV (coverage, $\sim 1 \times 10^{10}$ clusters cm^{-2}; deposition, rate $\sim 3 \times 10^{8}$ clusters cm^{-2} s^{-1}), showing the accumulation of small particles along a step edge. The tunnelling current was 0.1 nA, with a bias of 1.3 V. (b) SEM micrograph of the same sample as (a).

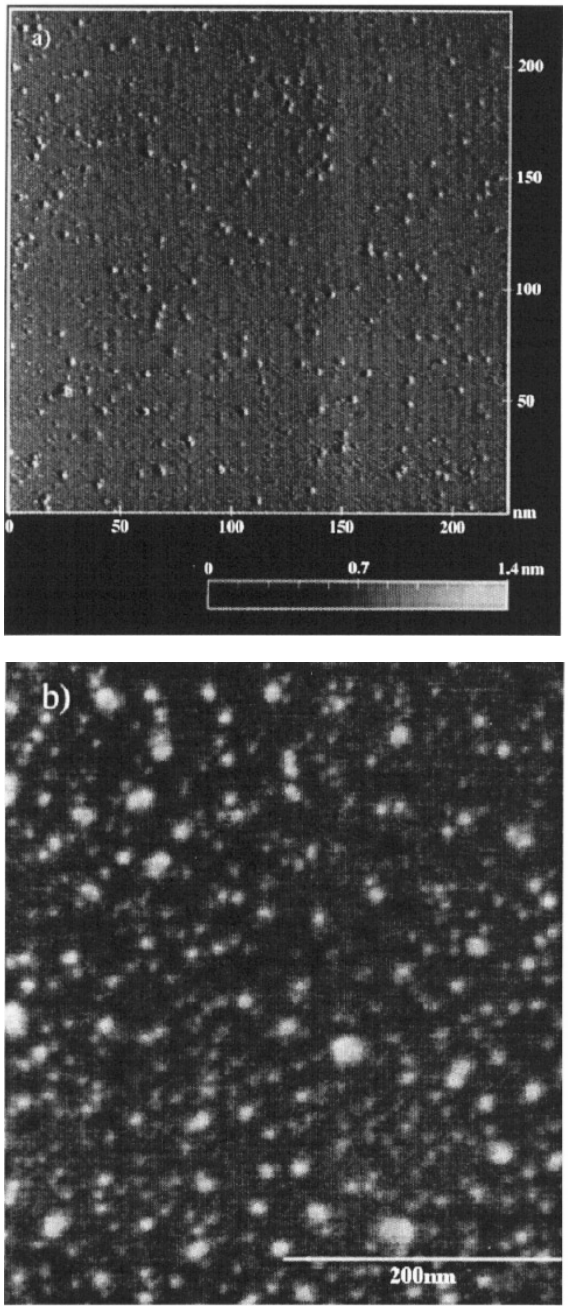

Figure 4. (a) An STM micrograph obtained after deposition of Ag_{100} clusters onto graphite with an impact energy of 200 eV (coverage, 2×10^{12} clusters cm^{-2}; deposition rate, 2×10^{9} clusters cm^{-2} s^{-1}). The tunnelling current was 0.6 nA, with a bias of 200 mV. (b) An SEM micrograph of the same sample as in (a).

Figure 3(b) is an SEM image of the same sample as shown in the STM image of figure 3(a). Again, clusters are shown decorating a step, and no clusters were found on the

terrace in the area near the step. However, the size range of the clusters in figure 3(b) is 5–30 nm. One would expect that the techniques of SEM and STM would be complementary for smaller particles, because the superior resolution of the STM would reveal clusters too small for the SEM to image easily. However, it also seems that the STM fails to detect clusters larger in size than approximately 10 nm; no clusters above this size were observed in the STM images of the sample, but they are clearly visible in the SEM pictures. A possible explanation for this effect is an interaction between the tip of the STM and the cluster, such that, for example, larger particles are displaced by the tip during STM scanning.

In order to explore this effect further, another set of complementary STM and SEM images of a given sample is shown in figure 4(a) and (b). In this case, the coverage of clusters was 'high' (2×10^{12} clusters cm^{-2}), while the deposition rate was 2×10^{9} clusters cm^{-2} s^{-1}. The clusters contained 100 ± 50 atoms and were deposited at 200 eV. The STM image, shown in figure 4(a) reveals clusters of diameter $\sim$3 nm. The SEM micrograph, figure 4(b), shows a much broader range of cluster sizes, from $\sim$5 to 20 nm. The SEM images indicate that diffusion and aggregation occur. The differences between what is seen in the STM and the SEM thus mirror the results of the low-coverage study (figure 3). Again, the 'discrepancy' is consistent with the tip–cluster interaction suggested above. It is interesting to note that the maximum size of the clusters observed on the terrace with the STM is smaller in figure 4(a) than that observed at the step (figure 3(a)). This could be explained if clusters are more strongly bound to the step than to the terrace (as one would expect); in this case, the force required to displace a cluster from the step would be larger.

In summary, we have studied the deposition of $(Ag_n)^+$ clusters ($n = 50$–400) on a graphite substrate using both the scanning tunnelling microscope and the scanning electron microscope. The effects of varying the cluster size and coverage, and especially the impact energy, have been explored. A study of the morphology of the deposited clusters as a function of impact energy has revealed that the clusters flatten out at higher deposition energy ($\sim$10 eV/atom), and are most likely pinned at their point of impact on the surface. At lower impact energies ($\sim$1 eV/atom), the footprint of the deposited clusters is smaller, consistent with an approximately hemispherical shape. We have also found that by control of the deposition parameters (low deposition rate and coverage) it is possible to deposit clusters at specific locations on the surface, in this case at surface steps. Finally, complementary STM and SEM images of the same samples show definite differences; in particular, large particles (aggegates) visible with the SEM do not appear in STM images. It was suggested that these large clusters are moved around by the STM tip. Future investigations will need to explore in more detail the effect of the cluster impact energy, e.g. to find the critical energy for pinning of the clusters on impact. We also hope to deposit the clusters in an ultra-high-vacuum environment and perform spectroscopic studies of deposited clusters as a function of their mass using electron energy loss spectroscopy.

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