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Deposition of size-selected clusters at hyperthermal energies investigated by STM

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Abstract. We have studied the interaction of mass-selected antimony clusters (Sb_x^+, $x = 3$, 4, 8) with the (0001) basal plane of highly oriented pyrolythic graphite (HOPG) in the energy range from 40 eV to 410 eV by STM and STS. A threshold behaviour is observed for cluster implantation, which is dependent on cluster size. Below this threshold the interaction is characterised by neutralisation, adsorption, and diffusion of the incoming particles. STM and STS data suggest that some of these particles are intercalated in the graphite surface. Above this threshold the clusters are implanted into the surface, resulting in a strong distortion of the substrate and cluster structure.

The interaction of mass-selected clusters with surfaces has been of increasing interest during the last few years [1]. This is partly due to possible applications for surface modification and preparation, namely etching [2], thin film formation [3], cluster deposition [4–6], and collision induced reactions [7]. But up to now there are only a few experimental and theoretical data available. To characterise the processes taking place on the surface, the STM is ideally suited, because of its unique ability to give a real-space picture of small structures (a few Angstrom) in very low concentration. In this paper we present STM data on the interaction of mass-selected antimony clusters with HOPG for a broad energy range from 40 eV up to 410 eV kinetic energy.

1 Experiment

Details of the experimental setup have been given elsewhere [8]. In brief, it consists of a three-stage, fully UHV compatible, molecular beam apparatus, which is directly coupled to a surface science machine. Positively and negatively charged clusters are produced in a pulsed arc cluster ion source (PACIS) [9]. They are mass-selected by a pulsed mirror in a Wiley–McLaren-type [10] time-of-flight mass spectrometer arrangement and are directed onto the surface of graphite (HOPG) at an angle of 90° to the surface plane. The interaction energy of the charged cluster with the surface is controlled by the application of appropriate voltages to the substrate. Typical deposition times range from several minutes up to one hour. The substrate holder can then be transferred by a rotary-linear-motion feedthrough to the analysis chamber without breaking vacuum. Surface analysis is conducted at room temperature via a "Beetle" STM [11]. The graphite sample was prepared prior to the experiments by cleaving in air and heating in UHV.

2 Results and discussion

Figure 1a shows a STM scan of the sample after irradiation with Sb_4^+ clusters for 60 min at a mean kinetic energy of 70 eV. Only a few islands, showing up as white dots, can be observed. These islands are easily moved by the scanning motion of the tip. The picture changes completely when the mean kinetic energy of the cluster beam is increased to 230 eV; the result is depicted in Fig. 1b. A large number of hillocks with a mean diameter of about 20 Å are clearly visible (the general appearance of the STM pictures is qualitatively the same for all cluster sizes investigated). Compared to the islands observed at low kinetic energy, these hillocks are stable for days and are unaffected by the tip movement. The number density of the hillocks is strongly dependent on the mean kinetic energy of the cluster beam, which is plotted in Fig. 2 for Sb_3^+ and Sb_8^+ clusters. The threshold kinetic energy for stable protrusions in the STM image is located at a mean kinetic energy of 120 ± 25 eV for Sb_3^+ clusters and at 200 ± 25 eV for Sb_8^+ clusters. Below these values only very few instable islands can be found on the graphite surface; above, the number of stable hillocks increases drastically. The mean diameter of the stable structures is about 20 Å independent of cluster size. Therefore we suppose that these hillocks are formed by implantation of the cluster ions into the surface. A threshold behaviour has already been observed for the penetration of Kr^+ ions into a graphite surface, the minimum kinetic energy was found to be 45–50 eV [12].

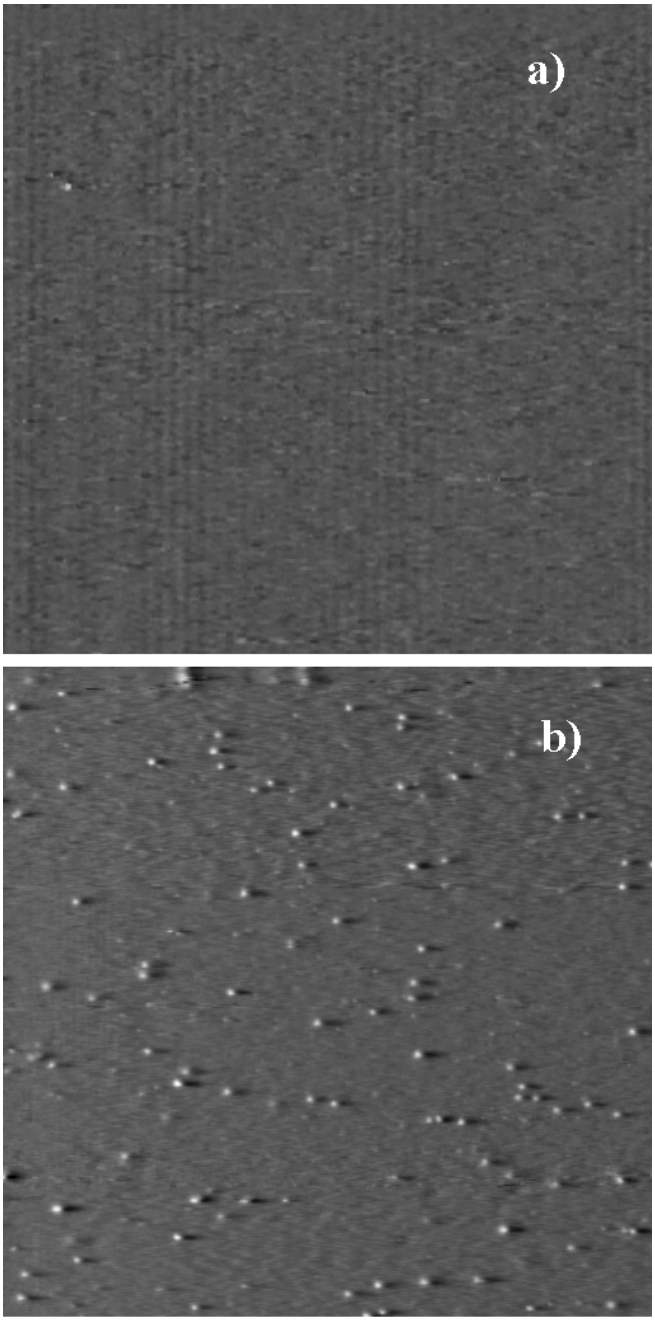

Fig. 1a,b. STM scan of the HOPG surface (248 nm × 248 nm) after irradiation with Sb_4^+ clusters for 60 min. **a** Mean kinetic energy 70 eV, $U = 500$ mV, $I = 0.5$ nA; **b** mean kinetic energy 230 eV, $U = 640$ mV, $I = 0.5$ nA

We find similar results for all other investigated cluster sizes (Sb_x^+, $x = 3$, 4, 8): Below a certain minimum energy no implantation of cluster ions into the graphite surface is observed. The exact value of the threshold itself is strongly dependent on cluster size (see Fig. 2). The increase in the implantation threshold with increasing cluster size is in qualitative agreement with the displacement energy concept, which states that the minimum energy necessary for the displacement of surface atoms increases with the mass of the projectile [13].

Only a very small number of fragile islands can be observed on the graphite surface at low kinetic energies

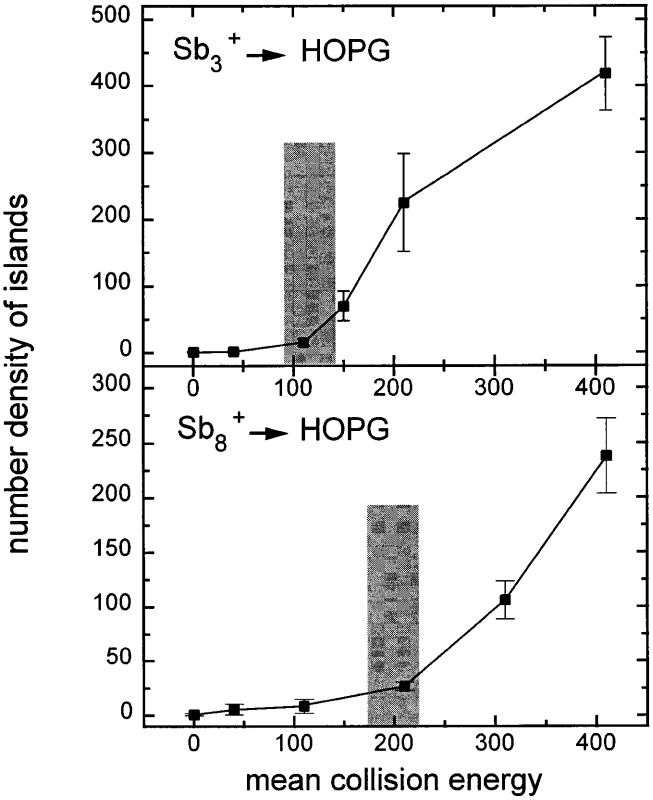

Fig. 2. Number of observed hillocks per μm^2 as a function of the mean impact energy for two different cluster sizes. The error bars give the standard deviation; shaded areas define the threshold region

(Fig. 1a). These are often found near step edges or at defect sites, which offer a higher binding energy for the clusters than the flat graphite surface. A cluster ion reaching the substrate will be neutralised near or at the surface, which is a highly efficient process for ion–surface interactions. Part of the kinetic energy of the projectile will be transferred to its and the surface's internal degrees of freedom. This may lead to fragmentation of the cluster. The cluster or its fragments are then free to move on the room-temperature graphite surface until they become weakly bound to a defect site. Figure 3a shows a stable structure observed for deposition of Sb_8^+ near its implantation threshold. The graphite lattice structure is visible with a protrusion in the center of the frame. Even on this protrusion the β-carbon atoms are clearly discernible in their expected lattice positions. This is even more obvious in Fig. 3b, which shows a cross section along the white lines in Fig. 3a. Spectroscopy curves (Fig. 3c) have been taken at positions A, B, and C in Fig. 3a. There are only small differences between the data taken on top of the protrusion and that on the undisturbed graphite surface (point A). The variations in the dI/dV curves are of the same order of magnitude as variations arising from STS data taken at different points on the clean graphite surface. From the above observations we conclude that the observed distortion may be due to an intercalation of the cluster or its fragments between the first and second graphite layer. Experiments with noble gas ions also showed similar results [14, 15].

Figures 4a,b are high-magnification scans of clusters deposited in the implantation regime. Near the hillocks the graphite surface is heavily distorted. The collision process is

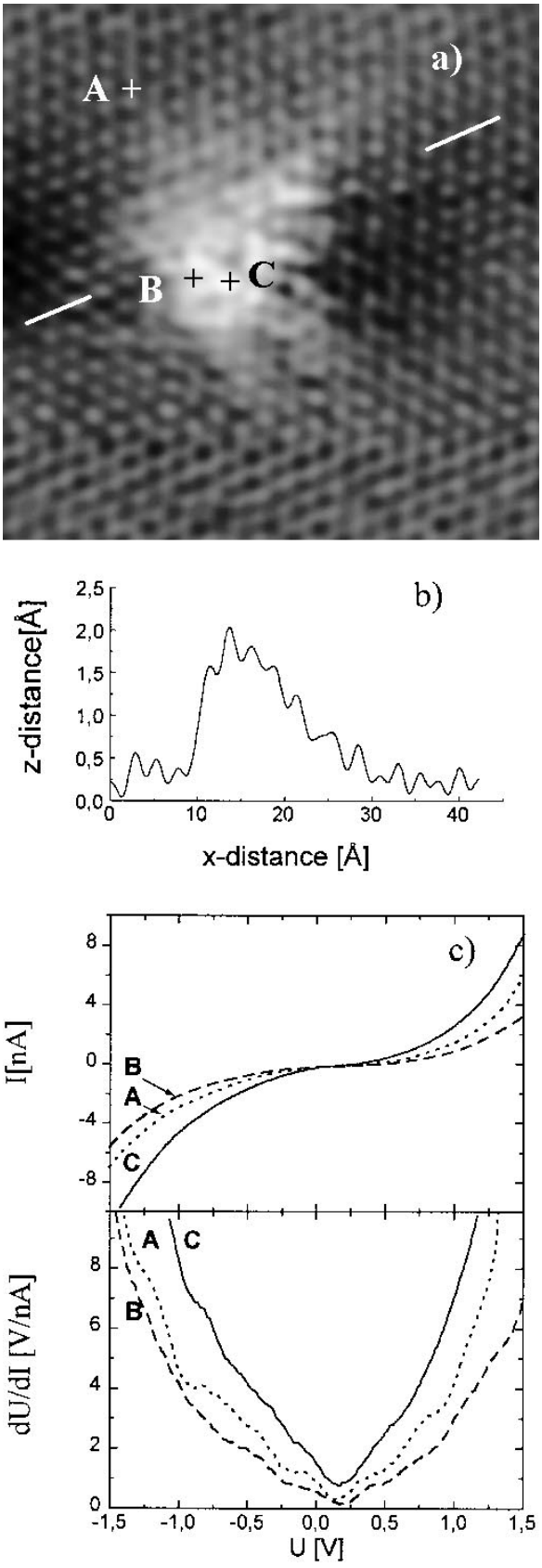

Fig. 3. a STM scan (4.6 nm × 4.6 nm, $U = 500$ mV, $I = 0.5$ nA) of a protrusion generated by irradiation of HOPG with Sb_8^+ at 210 eV mean impact energy. Lines mark the cross-sectional view (**b**). Tunnel spectra, depicted in **c**, were taken at points A, B, and C. STS data were measured at constant height

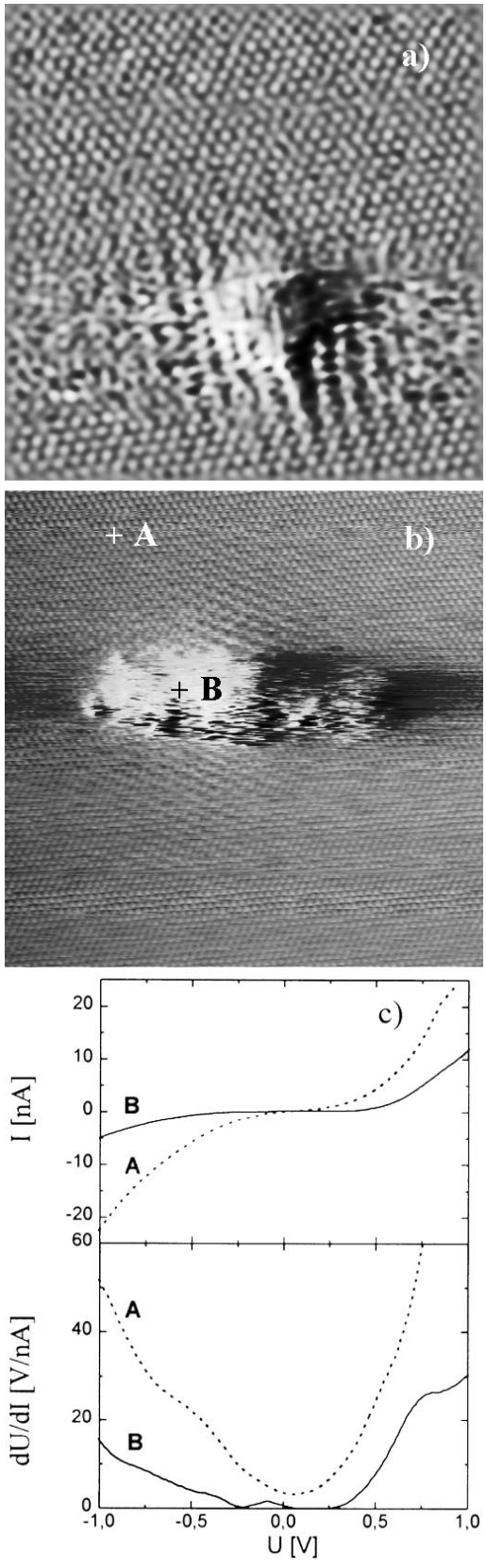

Fig. 4. a STM scan (7.2 nm × 7.2 nm, $U = 450$ mV, $I = 0.7$ nA) of a hillock generated by irradiation of HOPG with Sb_8^+ at 410 eV mean impact energy. **b** STM scan (14.3 nm × 14.3 nm, $U = 100$ mV, $I = 0.4$ nA) of a hillock generated by irradiation of HOPG with Sb_4^+ at 210 eV mean impact energy; A and B mark the points where tunnel-spectra, depicted in **c**, have been taken. STS data were measured at constant height

taking place on a very short timescale (≈ 100 fs), so the energy cannot be transferred away fast enough. This leads to extreme heating of the cluster and the surface, followed by melting. After an appropriate time, when all the heat has been dissipated, the system ends up in a highly amorphous, glassy state, which is in qualitative agreement with molecular dynamics simulations for different systems [4, 16]. The strong perturbation of the surface on the hillock is also obvious from the STS data, which are shown in Fig. 4c. Curve A shows the normal conductivity for the undisturbed graphite surface, whereas there is a significant depletion of electronic states near the Fermi energy directly on the hillock (curve B).

3 Summary

The interaction of mass-selected antimony clusters (Sb_x^+, $x = 3, 4, 8$) with HOPG has been investigated by STM and STS over a broad range of kinetic energies of the incoming ions. From the measurements, two basically different mechanisms are found: At low kinetic energy, neutralisation, adsorption, and diffusion, eventually followed by intercalation are the main processes, whereas at high kinetic energy the clusters are implanted into the surface. The minimum energy necessary for the implantation of the clusters depends strongly on the cluster size. Further work is directed towards the investigation of the influence of the kind of substrate on these processes.

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