# Experimental Observation of Fast Diffusion of Large Antimony Clusters on Graphite Surfaces

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We present a quantitative study of the diffusion of spherical antimony clusters deposited on graphite surfaces. The experimental structures obtained during deposition are compared to predictions of recent computer models, and very good agreement is found. From this comparison we can obtain the diffusion coefficient of large antimony clusters containing around 2300 atoms moving on a graphite substrate: we find $D = D_0 \exp(-E_a/k_B T)$ with $D_0 \approx 1.6 \times 10^4$ cm$^2$/s and $E_a = 0.7 \pm 0.1$ eV. This large value of $D_0$ suggests that the diffusion cannot be explained by a simple atomic activated process, but may rather involve collective motions of the atoms of the cluster.

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How can a large cluster containing thousands of atoms move rapidly on a surface? Answers to this question are important from a fundamental point of view. They would also provide precious insights for a general understanding of diffusion processes on surfaces which are essential to control thin film growth and coarsening [1–3] or for controlling the growth of thin films prepared directly with cluster deposition [4,5]. Figures 1(a) and 1(b) show typical structures generated by random deposition of large clusters on graphite. It is clear that, in order to explain the aggregation of the clusters in those ramified islands, we have to admit that the clusters *move* on the surface. If we want to investigate the possible mechanisms that explain such a motion, an important first step is to *quantify* the diffusion. This is what we attempt to do in this paper. Quantitative data for atomic diffusion are now available in abundance thanks to "freeze and look" field ion microscopy observations [1,6] or indirectly by applying nucleation theory [2,3] to scanning tunneling microscopy studies of film growth [7]. Very recently, some data for cluster diffusion have been obtained for epitaxial systems [8] as well. The cluster diffusion studies find extremely

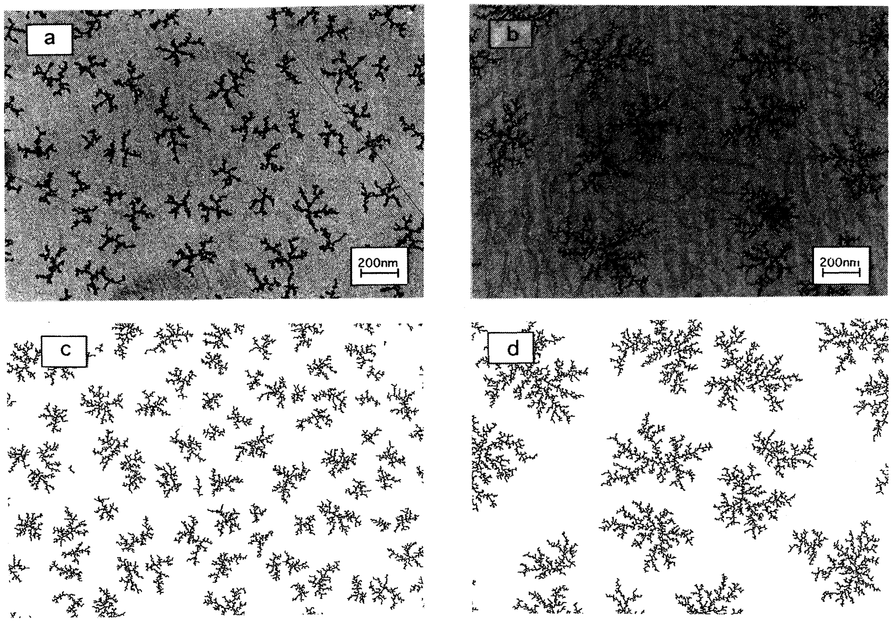

FIG. 1. Typical island morphologies obtained experimentally by transmission electron microscopy (a), (b) and from the model (c), (d). (a) $T_s = 298$ K and $F = 2.1 \times 10^9$ clusters cm$^{-2}$ s$^{-1}$, $N_{\mathrm{isl}} = 3.7 \times 10^{-4}$ per site; (b) $T_s = 373$ K and $F = 2.4 \times 10^9$ clusters cm$^{-2}$ s$^{-1}$, $N_{\mathrm{isl}} = 8.3 \times 10^{-5}$ per site, (c) $\phi = 8.9 \times 10^{-10}$ clusters per site per $\tau$; and (d) $\phi = 10^{-11}$ clusters per site per $\tau$. The size of the computer-generated images (437 × 437 sites) has been chosen to fit the scale of the experimental images. We have tried to quantify the agreement between the morphologies by measuring the fractal dimension $D_f$ of the islands for images (a)–(d): we find (a) $D_f = 1.7 \pm 0.05$, (b) $D_f = 1.9 \pm 0.05$, (c) $D_f = 1.8 \pm 0.05$, and (d) $D_f = 1.9 \pm 0.05$. The predicted fractal dimensions compare well with the experimental ones, even if the precision of the measurements does not allow a careful test.

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low values for the cluster diffusion coefficients (below $10^{-17}$ cm$^2$/s at room temperature), which is expected for *epitaxial* systems. Here we focus our attention on the diffusion of antimony clusters on graphite surfaces and we show that, in this nonepitaxial system, clusters are able to move much faster.

*Experimental details.*—Antimony deposits are obtained by low-energy cluster beam deposition [4] on highly oriented (0001) pyrolitic graphite. The antimony cluster beam is generated by the gas aggregation technique in a thermal source similar to that developed by Sattler [4]. The metallic vapor obtained from a heated crucible is condensed in an inert gas (Ar) and cooled at liquid nitrogen temperature. This leads to the formation of the beam of incident clusters, which are *neutral* and have low kinetic energy (less than 10 eV/cluster [9]). The cluster size, monitored by the inert gas pressure, is measured by a time of flight mass spectrometer. In the present work, the size distribution of the incident antimony clusters is centered on 2300 atoms, which corresponds to a mean diameter $d = 5$ nm assuming a spherical shape for the clusters. The half-width of the distribution is around 800 atoms or 1 nm (Fig. 2). The deposition rate and the thickness are controlled by a crystal quartz monitor located near the substrate. In this study, the thickness is fixed at 0.5 nm (i.e., $1.6 \times 10^{15}$ atoms cm$^{-2}$) for all the samples and only the deposition rate and the substrate temperature $T_s$ are varied. Further experimental details have been published previously [4]. In order to clean the surface, the graphite samples are freshly cleaved and annealed at 780 K for 5 h before deposition in the deposition chamber where the pressure is less than $10^{-4}$ Pa. This treatment results in atomically flat graphite surfaces extending over 2000 nm between steps. Image analyses are performed far from the steps which perturb diffusion. We emphasize that in these experiments *preformed* clusters are deposited directly onto the surface, contrary to Refs. [8,10] where clusters are formed on the surface by aggregation of previously deposited atoms. Moreover, Fig. 2 shows that the spherical clusters that we observe on the surface have the same size distribution as the incident ones, which excludes fragmentation or coalescence of the incident clusters on the substrate.

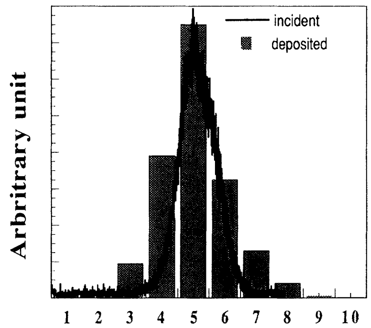

FIG. 2. Comparison of incident and deposited cluster size distributions. The size of the deposited clusters corresponds to the diameter of the spherical particles that compose the large islands seen in Figs. 1(a) and 1(b).

*Computer models.*—While Figures 1(a) and 1(b) demonstrate that clusters do move on the surface, a *quantitative* study of their diffusion needs the use of computer models which combine the dynamical processes simultaneously present in the experiments to simulate the growth of the ramified islands. The models, which have been independently implemented by several groups with small variations [3,11,12], include three physical ingredients:

(1) *Deposition:* Clusters are deposited at randomly chosen positions of the surface at a flux $F$ per unit surface per unit time.

(2) *Diffusion:* Each diffusion time $\tau$, all isolated clusters are chosen at random and moved in a random direction by 1 diam.

(3) *Aggregation:* If two clusters come to occupy neighboring sites, they stick irreversibly and form an island. Islands are assumed to be immobile (see below for an experimental justification).

It is useful to introduce the normalized flux defined as the number of clusters deposited per site per diffusion time (a site is defined as the projected area of a cluster on the surface). The normalized flux is then given by $\phi = F\tau\pi d^2/4$ and the cluster diffusion coefficient by $D = d^2/4\tau$, where $d$ is the cluster diameter. The model predicts that the surface density of islands reaches a maximum for coverages around 10% and remains almost constant in a large range of coverages, typically from 5% to 15% (the coverage is the portion of the surface covered by the clusters). The value of this plateau density $N_{\mathrm{isl}}$ depends on the normalized flux according to

$$N_{\mathrm{isl}}(\text{per site}) = 0.41\phi^{\chi} \quad \text{with } \chi = 0.336. \qquad (1)$$

*Experimental results and comparison with the model.*—In order to extract meaningful quantities from a comparison with the model we have to ensure that its main hypotheses are correct, namely, that (a) the diffusion of the clusters is Brownian, (b) clusters stick irreversibly upon contact, and (c) islands are immobile. While a direct experimental test of (a) is difficult (see the discussion below), we shall show in the following that (b) and (c) are correct. This is done by comparing two different predictions of the model with the experimental results:

*(i) Island morphology:* Typical morphologies observed for the cluster grown films at 10% coverage are shown in Figs. 1(a) and 1(b). The computer images are simulated at the same coverage, using a $\phi$ adjusted to reproduce the experimental island density [Eq. (1)]. Figures 1(c) and 1(d) show that the morphologies generated by the model strikingly resemble the experimental ones. Moreover, we have measured the fractal dimension of the islands and have found similar values (see Fig. 1). This actually

confirms point (b), i.e., that the clusters attach irreversibly upon contact, which seems physically reasonable since a bond between two clusters represents a large number of bonds between individual atoms. It seems difficult to break such a bond, contrary to what is usually observed for single atom bonds at high temperatures ("edge diffusion" [1,3,13]).

*(ii) Size distribution of the islands:* The model predicts that the only relevant length scale is the mean island size, and that different island size distributions obtained for different experimental conditions, when properly rescaled, should fall in the same scaling curve [3,11]. Moreover, the precise form of the scaling function can be calculated, and it is found to depend on the specific hypothesis made on the growth mechanisms [11,14]. Introducing dimer (islands containing two clusters) mobility [14,15] or reversible sticking [11] notably changes both the maximum and the width of the scaled island size distribution. Figure 3 shows that the experimental size distributions for different incident fluxes or substrate temperatures can be rescaled. The rescaled distribution is close to that predicted by the model when irreversible sticking is assumed [point (b)] and islands are immobile [point (c)].

*Diffusion coefficient.*—In the preceding paragraphs, we have shown that the simple deposition-diffusion-aggregation model reproduces our experiments remarkably well. We indicate that the dependence of the island density on the incident flux is also consistent with the model [14]. Then, from the experimental measure of $N_{\mathrm{isl}}$ we can confidently infer the diffusion coefficient by combining Eq. (1) and the definitions of $\phi$ and $D$. One gets

$$D = (0.41/N_{\mathrm{isl}})^{1/\chi} F \pi d^4/16 . \tag{2}$$

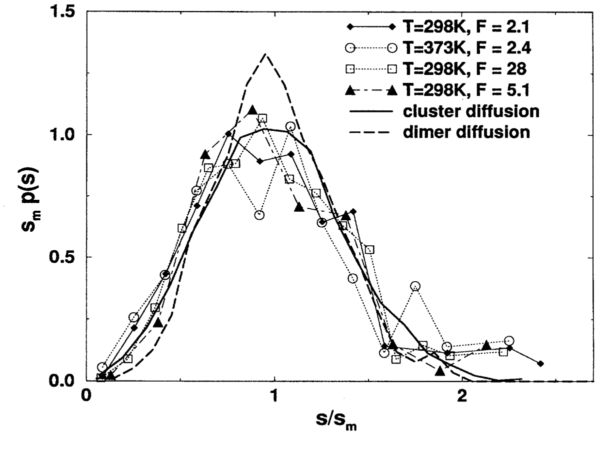

FIG. 3. Scaled island size distributions. The island distributions are transformed to $p(s)$, which represents the probability that a randomly chosen cluster belongs to an island containing $s$ clusters [3]. The island size $s$ is scaled by the mean island size $s_m$. Incident fluxes [$10^{-9}F$ (clusters $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$)] and substrate temperatures are shown in the figure. The solid line represents the island size distribution obtained from the model with only cluster diffusion, while the dashed line shows the results obtained when dimer diffusion is also included.

By changing the substrate temperature, we can study the temperature dependence of the diffusion coefficient (Fig. 4). We obtain $D = D_0 \exp(-E_a/kT)$ with $D_0 \approx 1.6 \times 10^4\ \mathrm{cm}^2\,\mathrm{s}^{-1}$ and $E_a = 0.7 \pm 0.1$ eV.

*Interpretation of the data.*—At room temperature, we find diffusion coefficient values $10^8$ higher than other studies of cluster diffusion [8,10]. A first explanation is that we are not studying an epitaxial system. Then, the clusters cannot find deep local minima of energy on the surface. The difference with the system studied in Ref. [10] lies in the nature of the substrate: graphite instead of NaCl. It is well known [16] that even atoms are weakly bound on graphite because the carbon-carbon atomic spacing is small (0.142 nm) compared to the bond length between carbon and the adsorbed atom. Then, the adsorbed atom sees a smooth potential surface and can diffuse rapidly. The situation is even more favorable in our case, since Sb clusters are formed by rigid $\mathrm{Sb}_4$ blocks of about 0.5 nm. Then it is clear that the clusters feel a smooth potential as they move and are not tightly bound in any configuration on the surface. In addition, the clusters are *amorphous*: this excludes any epitaxial arrangement on the surface which could stop diffusion as has been observed for gold crystallites [10].

It is difficult to prove that the motion of the Sb clusters is diffusive. We believe that the evidence given above on the agreement between the deposition model and the experiments is quite convincing. The only possible alternative, namely, some kind of linear transient mobility [17] just after deposition, is unlikely. The reason is that, in order to explain the low island densities observed, it should be assumed that the clusters can travel at least several thousand sites before being stopped by friction with the substrate [14]. This value seems unrealistic [17], unless we assume that the cluster has almost no interaction with the substrate. But then it seems difficult to explain the large changes observed in the island density when the

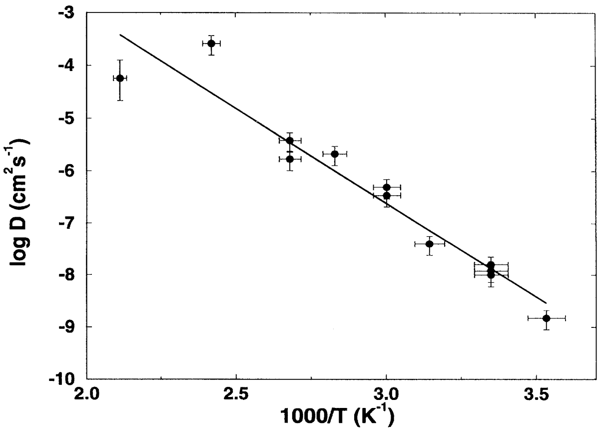

FIG. 4. Temperature dependence of the diffusion coefficient. The values are derived from the experimental $N_{\mathrm{isl}}$ and $F$ using Eq. (2). The solid line is a fit to the experimental data.

substrate temperature is changed. What might then be the mechanisms leading to such a fast diffusion? Let us first say that "evaporation-condensation" mechanisms—where single atoms evaporate from the clusters—analogous to what is suggested for epitaxial systems [8] are unlikely. The reason is that they would involve coexistence with a two-dimensional gas of $Sb_4$. This in turn would lead to a deposited cluster size distribution different from the incident one, which is not observed (Fig. 2). We conclude that the clusters move as a *whole*, as in Ref. [10]. This could be achieved by "periphery diffusion" of the $Sb_4$ at the surface of the clusters [18]. Then, the activation energy $E_a$ should be equated to the energy needed to move a "core" $Sb_4$ to the surface. The experimental value ($E_a = 0.7$ eV) is not absurd compared to the energy needed to *remove* a $Sb_4$ from the solid ($\approx 2$ eV). The problem with this suggestion lies in the large $D_0$ value found experimentally ($D_0 \approx 10^4$ cm$^2$/s). If diffusion is limited by the migration of one atom from the bulk to the surface, $D_0 \approx 10^{-3}$ cm$^2$/s is observed [8,18]. Possibly, the idea of a single activated process is too simple to account for the diffusion mechanisms of clusters containing 2300 atoms. Some alternative diffusion mechanisms for clusters have already been suggested [2,10]. These models assume collective motion of the atoms of the clusters, as opposed to the previous ones [8,18] where cluster motion arises from single atom evaporation or motion along the cluster edges. Further experimental data are needed to assess the precise kind of collective motion that might be involved here.

In summary, we have demonstrated that large antimony clusters move rapidly on graphite surfaces. Discovering the mechanisms which lead to such rapid motion is interesting to understand the interaction of nanoparticles with substrates, a field of promising technological interest. Certainly, much has to be done to understand the fundamental mechanisms of cluster diffusion. Experimental data are invaluable to discriminate between different diffusion mechanisms. In the future, we plan to study the size dependence of the cluster diffusion coefficient by changing the mean size of the incident cluster distribution.

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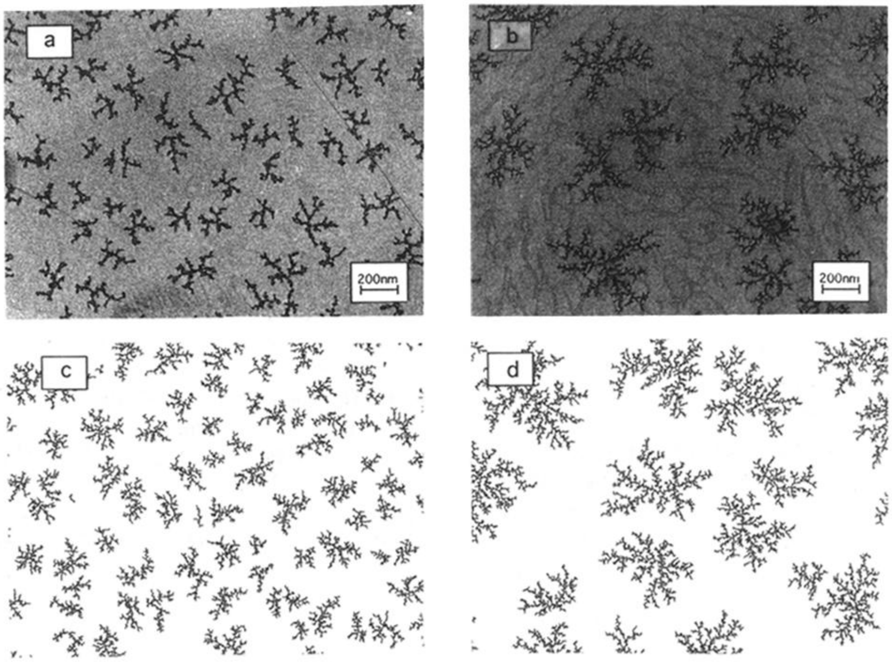

FIG. 1. Typical island morphologies obtained experimentally by transmission electron microscopy (a), (b) and from the model (c), (d). (a) $T_s = 298$ K and $F = 2.1 \times 10^9$ clusters $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, $N_{\mathrm{isl}} = 3.7 \times 10^{-4}$ per site; (b) $T_s = 373$ K and $F = 2.4 \times 10^9$ clusters $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, $N_{\mathrm{isl}} = 8.3 \times 10^{-5}$ per site, (c) $\phi = 8.9 \times 10^{-10}$ clusters per site per $\tau$; and (d) $\phi = 10^{-11}$ clusters per site per $\tau$. The size of the computer-generated images (437 × 437 sites) has been chosen to fit the scale of the experimental images. We have tried to quantify the agreement between the morphologies by measuring the fractal dimension $D_f$ of the islands for images (a)–(d): we find (a) $D_f = 1.7 \pm 0.05$, (b) $D_f = 1.9 \pm 0.05$, (c) $D_f = 1.8 \pm 0.05$, and (d) $D_f = 1.9 \pm 0.05$. The predicted fractal dimensions compare well with the experimental ones, even if the precision of the measurements does not allow a careful test.