Comparison of molecular and cluster deposition: Evidence of different percolation processes

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Deposition of neutral antimony molecules Sb_n ($n=4$) and clusters ($n=1850$) on an insulator substrate has been used to study the percolation from conductance measurements and microscopy observations as a function of thickness. Cluster deposition is close to geometrical percolation, whereas molecular deposition seems to involve more complex mechanisms. The low mobility of the clusters makes it possible to explain these features.

Percolation theory and its related topics (fractal dimension, percolation threshold) have been extensively studied[1] and are of interest in many sciences such as mathematics, physics (phase transitions[2]), biology (growth of tumors[3]), and ecology (forest fires[4]). We recall that, in conventional site-percolation theory, "each site of a very large lattice is occupied randomly with probability p, independent of its neighbors" (Stauffer, Ref. 1). Computer simulations are performed by randomly paving a lattice.

However, most of the physical parameters diverge at the percolation threshold, making the experimental measurements difficult (for example, the viscosity increases very rapidly at the percolation threshold during the sol-gel transition[5]). On the other hand, conductance measurements and microscopy observations are easy to perform and give important information on the way the system percolates.[6-8] For two-dimensional microscopic systems, to our knowledge, these experiments have only been carried out on discontinuous metal films obtained by molecular-beam deposition (MBD).[9-12]

We have measured the electrical conductance of ultrathin films obtained by deposition of free antimony molecules and clusters on an insulator substrate as a function of the deposited thickness. The molecular and cluster beams are generated by the gas-aggregation technique in a source similar to that developed by Sattler.[13] The antimony metal heated at about 580 °C is vaporized in a cold helium (or argon) atmosphere (77 K) at a pressure which varies from 0 to 1300 Pa. The cluster size is determined by the helium pressure. A time-of-flight mass spectrometer is used in order to control the incident cluster size distribution. Previous results on fragmentation allows us to consider that the ionized-cluster mass distribution is a fairly good measure of the neutral-cluster distribution.[14] On the other hand, no mass discrimination has been detected for large masses ($n > 300$) by varying the nature and pressure of the inert gas. Further experimental details have been published previously.[15] The experimental cluster size distribution may be approximated by a Gaussian law with a mean cluster size $\langle n \rangle$ and a FWMH of about the same value. For the discussion, the size of the clusters will be identified with the mean size. These neutral clusters are deposited, at room temperature, on a glass substrate with two predeposited chromium electrodes and the applied potential is 1 V. (The fragmentation of the incident cluster during the impact on the substrate is unlikely. The excess energy of the cluster has two contributions: thermal energy and kinetic energy. Both contributions are smaller than the binding energy in the cluster.) The thickness is simultaneously controlled by a crystal quartz rate monitor. To measure the desorption rate on the substrate, the thickness of the deposit was checked by Rutherford backscattering spectrometry (RBS). The minimum measurable conductance with our device is about 2×10^{-14} s. For microscopy observations (Jeol 200CX microscope), copper microscopy grids are coated by 5-nm a-C film. A thin film (about 10 nm) of SiO_2 is deposited on the amorphous carbon. In these conditions, we have checked by electrical measurements that nucleation of antimony on Corning is similar to that on SiO_2. The image analysis is performed with a Quantimet 570 instrument.

For the Sb_4 deposition the main results are the following. The equivalent average thickness needed to reach the percolation threshold observed by the conductance measurement is about 37 nm [Fig. 1(a)]. The true percolation threshold is hidden by the tunneling current.[12] From TEM (transmission electron microscopy) observations, the mean size of the supported particles is about 200 nm [Fig. 2(a)]. Near the threshold the coverage is about 95%.

For the cluster deposition ($Sb_{\langle n \rangle}$, $\langle n \rangle = 1850$, 4.8-nm diameter) the main results are the following. The equivalent average thickness needed to reach the percolation threshold observed by the conductance measurement is about 2.2 nm (compare to the 37 nm needed in the case of the Sb_4 deposition). The true percolation threshold is well defined (typically ±0.05 nm) [Fig. 1(b)]. The mean size of the supported particles is about 9 nm [Fig. 2(b)]. Near the threshold the coverage is about 48% ($\pm2\%$). This value is reproducible.

In the following, we shall try to explain these differences by different nucleation and growth processes. The results will be analyzed in terms of percolation theory. Nucleation of antimony on Corning substrates

has not been investigated. However, some experiments have been made on amorphous carbon. In this case, the study of antimony deposits by TEM technique has shown clearly that the size of the incident clusters dramatically affects the morphology[16] of the films. The experimental study of the growth of supported particles clearly shows that the mode of film growth is in good agreement with a three-dimensional (3D) layer[17] and that the mobility of the particles strongly decreases as their size increases.

In the case of the Sb_4 deposition, owing to its high mobility, nucleation is governed by diffusion and occurs on preferential nucleation sites.[18] The supported particles have a spherical shape and their diameter increases along with matter deposition. These results are consistent with those obtained by other groups for atomic deposition. Let us analyze them in terms of percolation theory. Obviously, nucleation induces strong correlations between the deposited Sb_4 molecules. Then, the growth of the film should be compared to *bond* percolation between the supported particles. However, dynamic and static coalescences and Ostwald ripening induce correlations in the bond distribution, in opposition to conventional percolation as defined above. This will affect typical properties of percolation such as the threshold coverage. We have found a threshold coverage of about 95%. Beghdadi[19] finds, on Au films, values ranging from 59% to 65% depending on experimental conditions. Voss *et al.*[9] obtain thresholds around 74%. We recall that, for *random* percolation, the threshold coverage is around 50%. Qualitatively the spread of threshold coverages can be explained by changes in the size distribution of the supported particles or/and variations in the distribution of nucleation sites on the substrate. The stronger the nucleation is, the more sensitive the threshold becomes to the substrate surface state. For example, for circle-shaped particles in a square lattice, it can be shown that the threshold coverage is $\pi/4$. For a random distribution of sites, calculations are difficult. An analogy can be found with a Poisson size distribution on a random network and one finds a value close to 65% (Swiss cheese model, see Ref. 20). These preliminary results show that the interpretation of the growth of thin films from MBD in terms of percolation theory is faced with some difficulties.

In the case of free clusters, owing to their low mobility

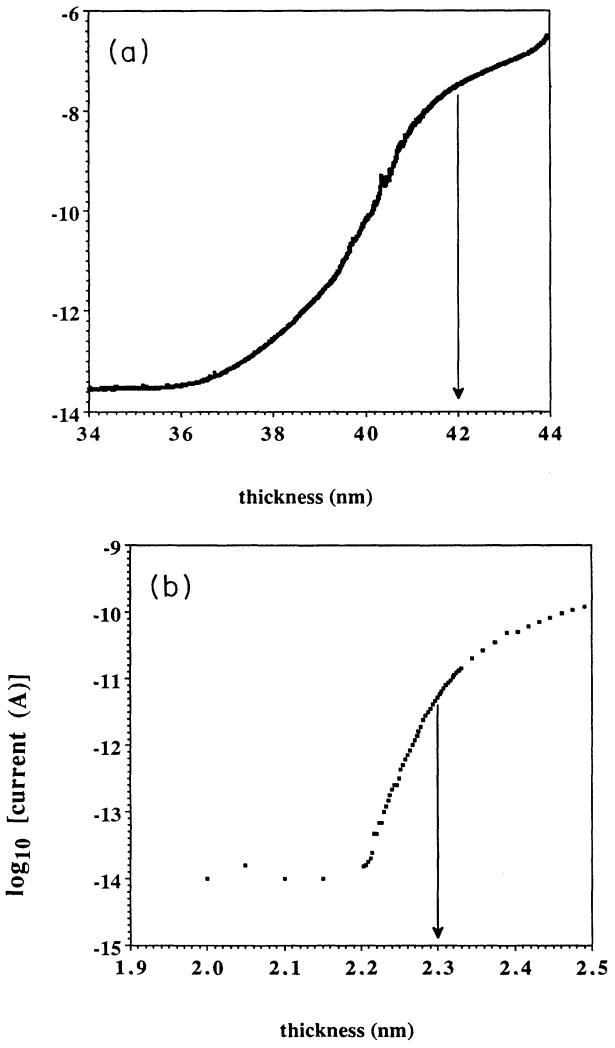

FIG. 1. (a) Plot of the observed current vs the film thickness in the case of Sb_4 deposition (deposition rate 0.003 nm s^{-1}). The arrow indicates the thickness of the micrograph [Fig. 2(a)]. The sample characteristics are the following: potential between the two electrodes, 1 V; length of the film (between the two electrodes), 3 mm; width of the electrode, 1.5 mm. (b) Plot of the observed current vs the film thickness in the case of free cluster deposition (deposition rate, 0.003 nm s^{-1}). The arrow indicates the thickness of the micrograph [Fig. 2(b)].

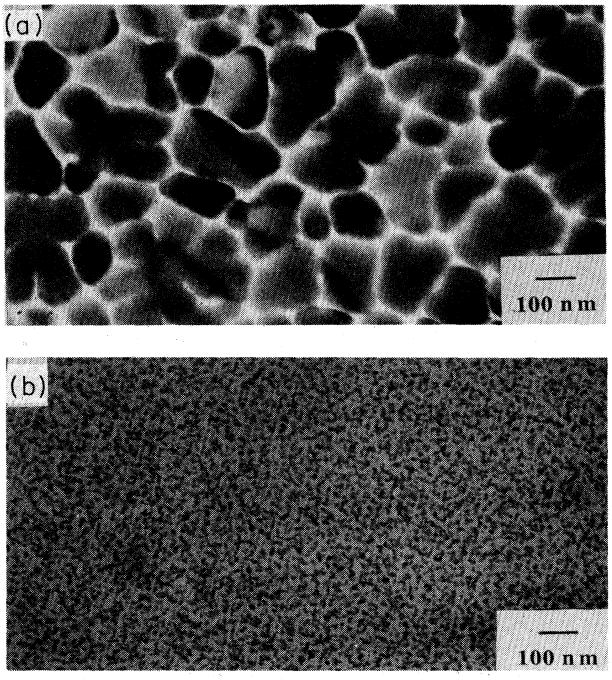

FIG. 2. (a) TEM micrograph of a film identical to that described in Fig. 1(a) (thickness 42 nm). (b) TEM micrograph of a film identical to that described in Fig. 1(b) (thickness 2.3 nm).

on the substrate, the growth is entirely governed by the impinging flux (desorption is negligible). Therefore, the film growth tends to be pseudo-2D. In this case the film is formed by the paving of the substrate by the incident clusters. To check this assumption, we have estimated the equivalent average thickness d_c at percolation threshold for a perfect 2D growth with spherical deposited particles, assuming a coverage rate of 50%:

$$d_c = \frac{1}{3}\Delta(f)^{-1/3}\langle n \rangle^{1/3} ,$$

where f is the filling factor of the antimony structure (0.43) and Δ the diameter of a Sb atom (0.292 nm). The experimental value is 2.2 nm, whereas the equation above gives 1.58 nm. The disagreement can be easily explained by supposing that a weak nucleation of incident clusters takes place. The measurement of the mean diameter of an isolated supported particle shows that the mean size corresponds to the accretion of about six incident clusters. In this case the theoretical threshold estimated by taking this accretion process into account gives 2.87 nm.

Then, it can be seen that, in the case of cluster deposition, neglecting the weak nucleation, the film grows by the paving of the substrate by the incident clusters. This is analogous to the filling of a two-dimensional lattice in conventional site percolation. As expected for continuum random percolation, the threshold coverage is close to 50%. For Sb_4 deposition, in contrast, nucleation is the important factor and the growth of the film seems to involve more complex mechanisms than random percolation.

Further comparison between the films obtained by cluster or atom deposition will be performed by studying the correlation lengths and size distributions of the deposited particles at the percolation threshold. Cluster deposition at low temperatures will also be performed in order to lower cluster diffusion and to get closer to "pure" percolation.

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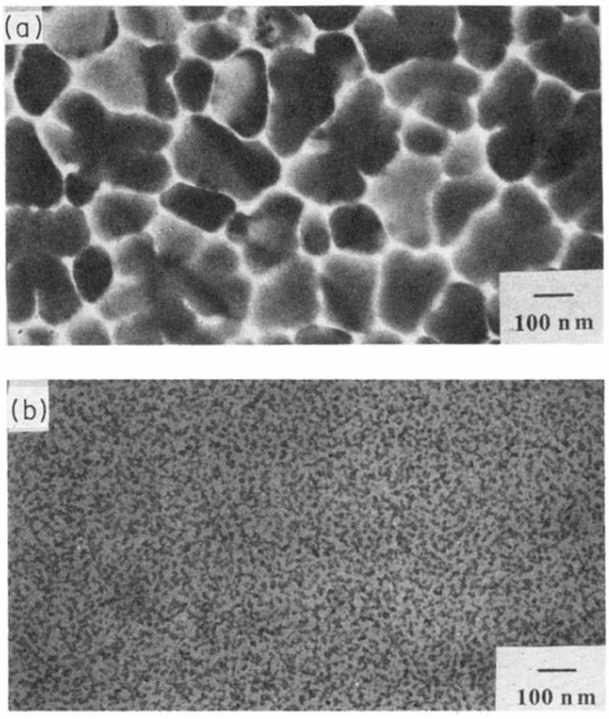

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