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TEM and STM investigations of Antimony particles deposited on graphite by Molecular Beam Deposition and Low Energy Cluster Beam Deposition

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Résumé. — Les faisceaux d'espèces moléculaires ou d'agrégats de faible énergie sont utilisés pour l'élaboration de films minces supportés. Une caractérisation par TEM et STM de particules d'antimoine déposées sur graphite par les deux techniques (Molecular Beam Deposition et Low Energy Cluster Beam Deposition), a été réalisée dans le but d'étudier les premières étapes de la croissance. Selon la technique de dépôt utilisée, différents modes de croissance sont observés: dans le cas du dépôt par jet d'agrégats, le film se forme par juxtaposition de particules tridimensionnelles et amorphes tandis que dans le cas du dépôt par jet moléculaire une compétition entre une croissance 2D et une croissance 3D a lieu. Par ailleurs une mobilité des particules d'antimoine déposées sur le graphite est mise en évidence.

Abstract. — Molecular Beam Deposition and Low Energy Cluster Beam Deposition of antimony on graphite are used to produce small supported particles. Parallel TEM and STM investigations of these particles have been performed in order to characterize the first stage of growth. Differences in the growth modes are observed depending on the deposition technique: in the case of cluster deposition the film builds up by juxtaposition of 3D amorphous particles whereas molecular deposition leads to a competition between 2D and 3D growing mode. In addition mobility of the antimony supported particles on graphite surface has been evidenced.

1. Introduction.

Recent advances in the technology of thin films deposition allowed the growth of well crystallized, continuous and reproducible high quality films. Molecular Beam Deposition (MBD) of group V elements (P, Bi, Sb) on different substrates (InP, GaAs, a-C) has been particularly investigated [1,2]. It is well known that the process leading to the growth of high quality films is difficult to control. Recently the Low Energy Cluster Beam Deposition (LECBD) appeared as a new promising technique to produce thin films with specific properties [1,2]. Comparative studies pointed out differences between films produced by Sb cluster deposition and molecular Sb deposition [3]. The understanding of the mechanisms which determine the particular properties of a growing film requires investigations about nucleation modes and morphologies in the first stage of the growth. Characterizations of supported particles were done by Transmission Electron Microscopy and High Resolution Transmission Electron Microscopy (TEM and HRTEM). Some years ago Scanning Tunneling Microscopy (STM) emerged as a well complementary technique for getting more structural informations about supported particles [4-7].

This work concerns the first stage of growth of antimony thin films obtained by MBD and LECBD. We report TEM and STM investigations of antimony particles supported on high oriented pyrolitic graphite (HOPG) produced by the two deposition techniques.

2. Experiment.

Two kind of antimony deposition (MBD and LECBD) were carried out in the same apparatus which was described elsewhere [8]. The cluster beam is generated by gas aggregation technique in a thermal source similar to the one developed by Sattler *et al.* [9]. The metallic vapour obtained from an heated crucible is either used as it is to perform MBD, or first condensed in inert gas atoms (He or Ar) at liquid nitrogen temperature, before deposition. This procedure leads the metallic atoms to aggregate as clusters, whose size is monitored by the inert gas pressure. The cluster size distribution is obtained by a time-of-flight mass spectrometer. For low masses, previous results on fragmentation [10] demonstrated that mass distribution of ionized clusters and neutral ones are very similar. On the other hand no mass discrimination has been detected for larger masses. During evaporation deposited thicknesses were controlled by a crystal quartz monitor located near the substrate.

In the present work we used either a beam of Sb_4 molecular species (for MBD) or a beam of Sb clusters with a mean size of 1100 atoms corresponding to a diameter of 4 nm assuming a spherical shape (for LECBD). In both cases the deposition is carried out at room temperature on freshly cleaved High Oriented Pyrolitic Graphite. The deposition rate and the thickness are fixed respectively at 0.02 nm.s^{-1}(6.4×10^{13} atoms.cm^{-2}.s^{-1}) and 0.5 nm (1.6×10^{15} atoms.cm^{-2}). After deposition, graphite samples are observed by TEM on a JEOL 200CX operating at 100 kV and by STM in air with a "home built" microscope.

3. Results and discussion.

Figure 1 shows a typical TEM micrograph of the antimony supported particles on graphite surface produced by the LECBD technique. Individual particles with diameter in the 3 to 20 nm range are observed. They agglomerate without loosing their individuality to form larger conglomerates. Image analysis gives a density of 5×10^9 conglomerates.cm^{-2}. This image is representative of Sb particles distribution observed by TEM. STM images obtained from similar deposits do not reveal such an homogeneous distribution of the conglomerates on the surface. More often they show large aggregation of antimony near graphite defects. While isolated conglomerates were much more rarely observed by STM than it was expected from TEM analysis, it was occasionally possible to image some of them (Fig. 2). As for TEM micrograph, it can be seen that it is composed by several particles with diameter between 10 and 20 nm and a maximal height of 1.5 nm. Neither STM nor high resolution TEM revealed atomic structures on such particles. Indeed, no diffraction rings associated with crystallized antimony and no fringes in high resolution TEM images of particles were observed. Crystallized graphite could however prevents their observation. As atomic details were no more obtained from STM images, both the TEM and the STM data suggest that these particles are not well crystallised. Volumes of individual entities forming the conglomerate were estimated assuming a flattened hemispherical shape. Few entities have a volume comparable with the mean volume of free Sb-clusters in the beam. Most of the particles which form the conglomerate have a volume between twice and ten times the volume of beam clusters. These results suggest that the original clusters diffuse when deposited on the graphite surface and are inclined to coalesce in order to form larger particles. These last ones tend to regroup as shown by figure 2. Similar aggregation of Ag deposited particles on graphite were previously reported [4,11].

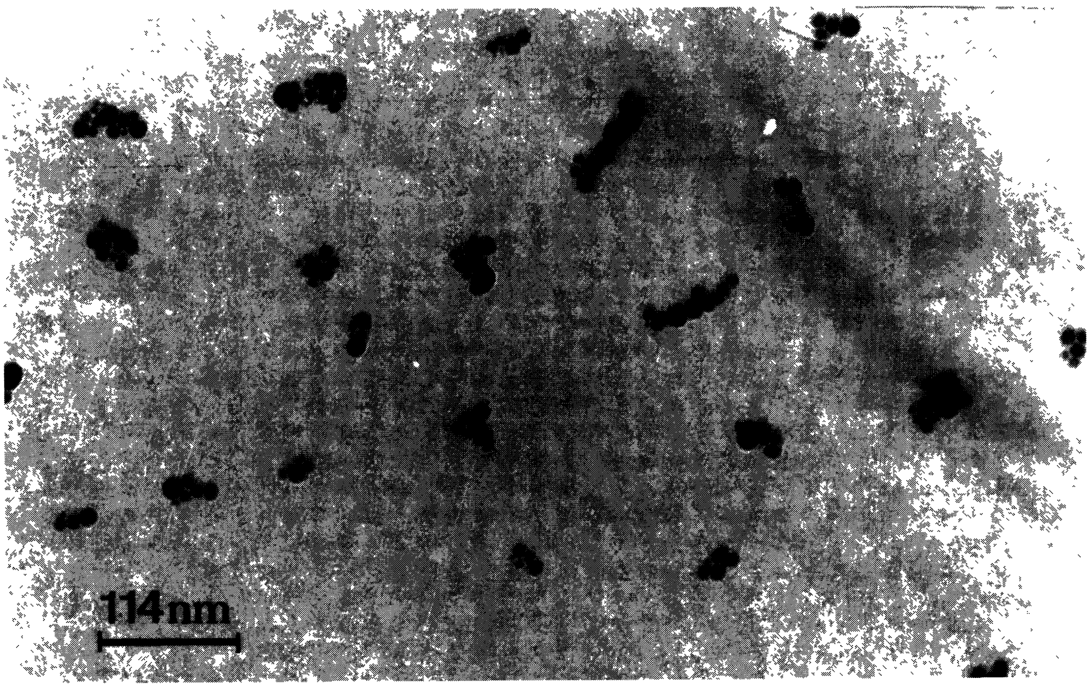


Fig. 1. — TEM micrograph of Antimony supported particles on High Oriented Pyrolitic Graphite obtained by cluster deposition.

In the case of antimony molecular beam deposition, very similar images of Sb particles arranged on graphite surface were recorded both by TEM and STM. Typical TEM and STM images are shown in figures 3-4. A density of 7×10^8 particles.cm^{-2} was deduced from TEM images. Two kinds of particles could be distinguished: individual ones with diameters ranging between 10 and 20 nm and larger ones which develop typical branched out shape. Particles appear to be formed by the stacking of layers. Their thickness ranges from one or two to several layers, and they appear quite flat on STM images (Fig. 5). In addition to these two kinds of particles, STM images display some crystallite-like features. One example is given in figure 6. The cross section (Fig. 6b) shows that a 3D structure has grown on a thin flat terrace with triangular shape (Fig.

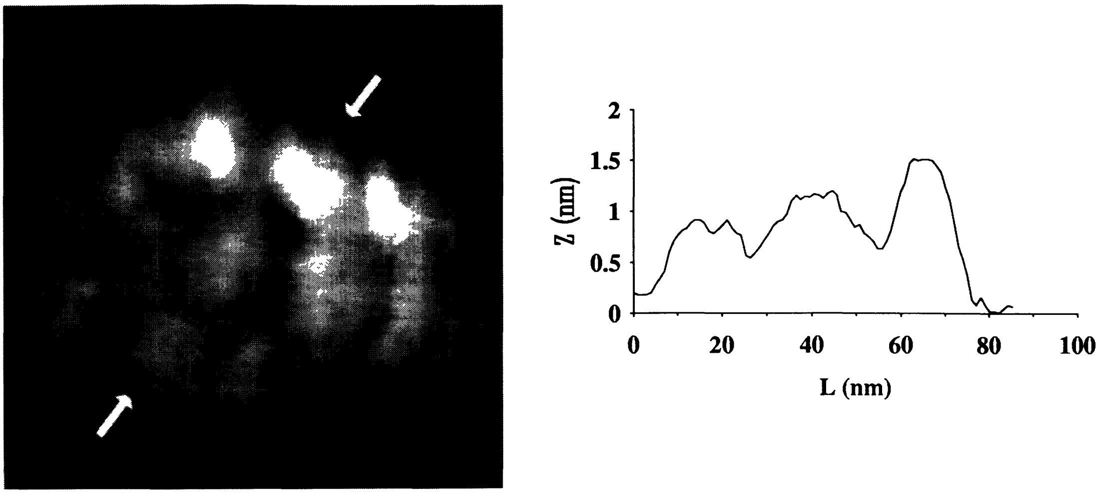


Fig. 2. — STM image (110 nm × 110 nm) of a conglomerate of Sb particles obtained by cluster deposition on graphite.

6a). High resolution image recorded in the middle of the flat terrace exhibits particular structures at atomic scale resolution (Fig. 6a insert). Superstructures are frequently observed on graphite surface, particularly in the neighbouring of supported particles [12]. Parts of the STM image in the insert of figure 6a appear reminiscent of these electronic perturbations, for example the typical misorientation [12] - relative to graphite lattice - can be found in the lower part. However there are elements which support the description of part of this image as a Sb layer growing in an organized way. First evidence comes from the triangular shape of the particle, which signifies that facets delimit a tiny crystal. Second, in the insert image, atomic or molecular dimension deposits of antimony are visible and mutual orientation of these entities are observable (center of the image). They have shape which seems to be more relevant of some dimeric antimony species than of the tetrameric species mainly present in the molecular beam. Then in the case of MBD, STM images evidence a competition between 2D and 3D growing mode. 2D limited layers are formed by atomic or molecular antimony beginning to self organize on the graphite surface. On these thin layers a 3D growing can start, which seems to be favoured by defects - like steps - on graphite.

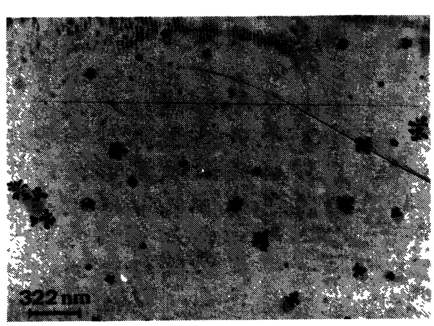


Fig. 3. — TEM micrograph of Sb particles obtained by Molecular Beam Deposition on graphite.

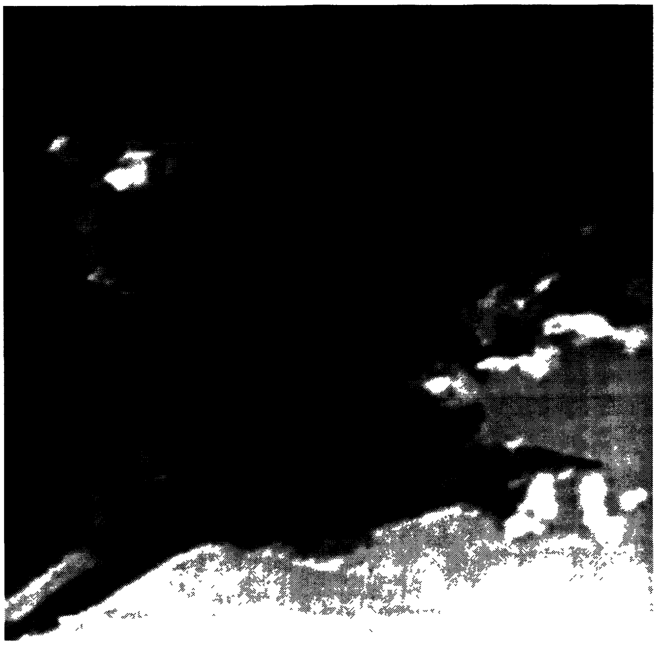
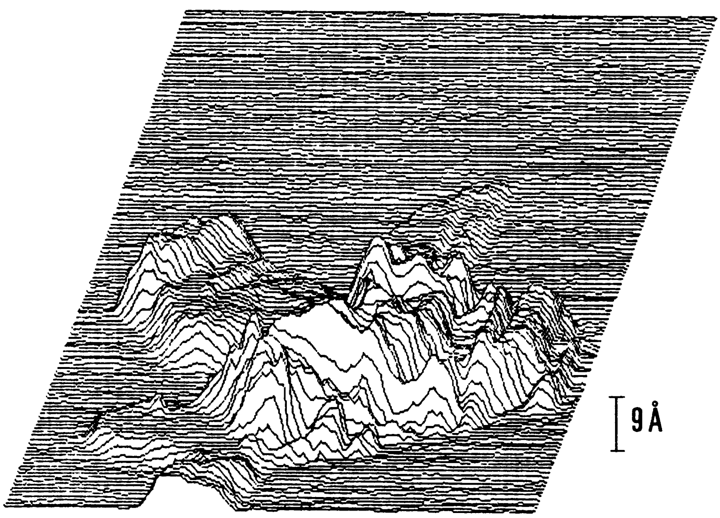


Fig. 4. — STM image (440 nm × 440 nm) of Sb particles obtained by Molecular Beam Deposition on graphite.

The structural difference in the first stage of growth observed between the two deposition methods (LECBD and MBD) is well evidenced from both STM and TEM observations. One can expect that for higher covering rate the two techniques will lead to the formation of thin films with different properties. Previous studies show structural and electrical differences between films obtained by Sb molecular deposition and Sb cluster deposition on amorphous carbon [3]. Though the substrate for this work was different - HOPG instead of a-Carbon - one can still expect that MBD will give more cristallized films than LECBD does.

TEM and STM are in quite good agreement for describing the morphology of the deposited particles. However a main discrepancy was revealed when we tried to compare the density of Sb particles imaged by the two methods. Densities obtained from STM measurements were badly reproductible from one experiment to another, and could vary in large proportions. Though the size of images used to determine the particle densities were different for STM and for TEM we think that size effects cannot take into account for so large differences. We rather suspect the mobility of Sb particles as the probable cause of discrepancy. It was already noticed that the supported particles obtained from Sb clusters deposition (LECBD) result from aggregation of several clusters from the beam. This means that deposited particles are mobile and diffuse on the surface to form larger entities. Indeed surface preparation is a key point in the process of aggregation and contamination influences the binding between particles and basal plane of graphite. In this experiment the surface was not specifically prepared except for the cleavage prior to the deposition. Grids for TEM observations were glued a short time after deposition whereas STM investigations were carried out several days later. Then one can think that antimony particles move on the graphite surface until they are stabilized by aggregation or by a surface defect (step, contaminant...). The figure 7 presents evidence for particle mobility. The three images presented comes

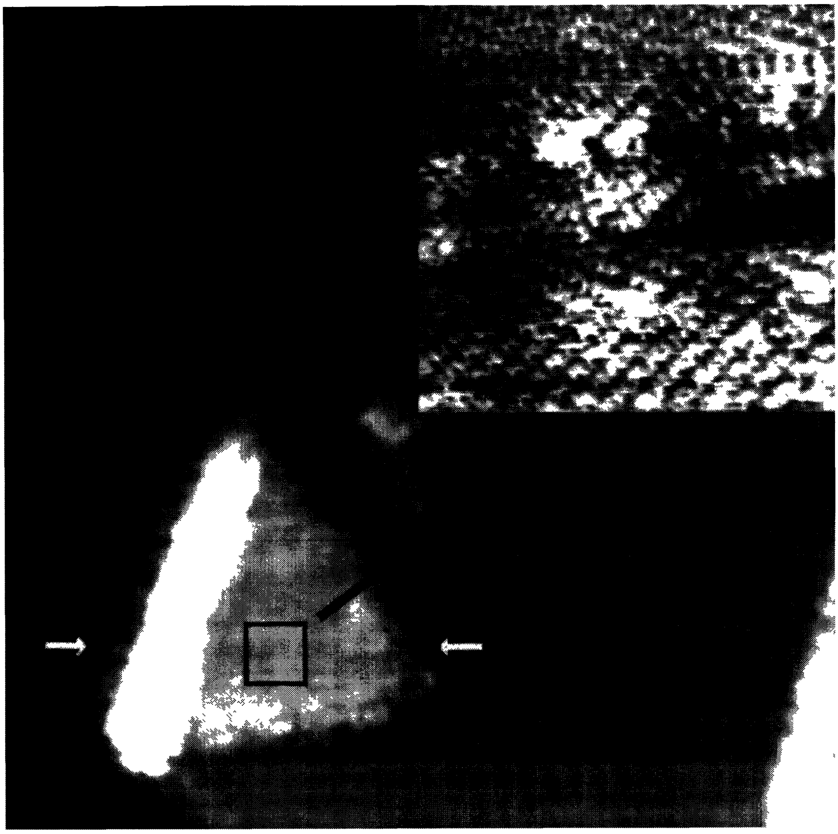
a)



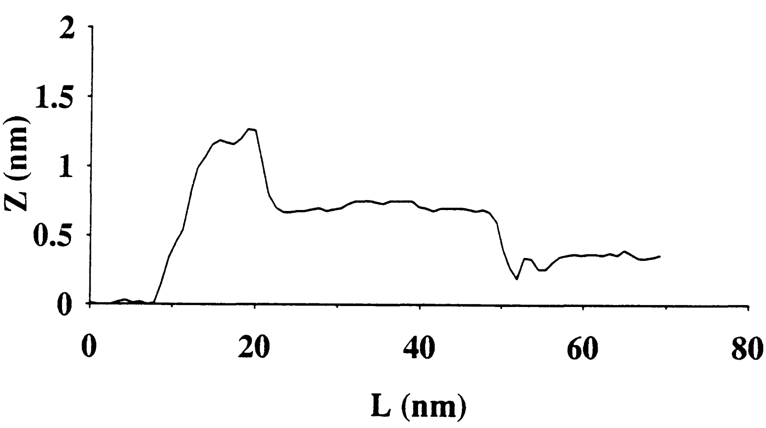
b)

Fig. 5. — STM image (110 nm × 110 nm) of a Sb branched out particle (MBD), a) grey scale top view, b) line drawing perspective view. The particle is formed by stacking of layers on which 3D growing occurs.

from a set of images recorded one after the other on the same area. Two individual particles and a decorated step give reference points for the third, central, particle (labelled A in Fig. 7) which moves with time. The tip can be suspected to displace the particle when scanning. We did not find any evidence of such a tip effect. The particle shapes are not modified along with scanning and no trace of material dispersion by the tip was observed. On the contrary the particle was displaced as



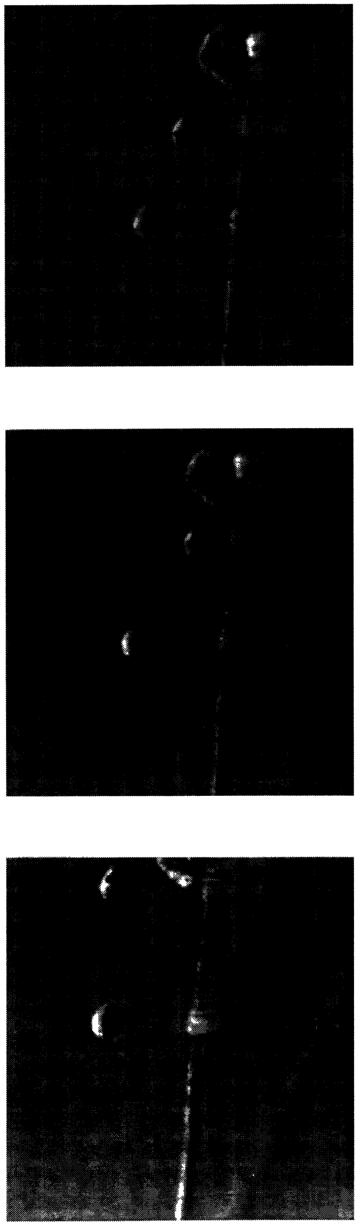
a)



b)

Fig. 6. — a) STM image (110 nm × 110 nm) of a triangular particle from Sb molecular deposit on graphite. b) Cross section through the particle exhibiting a flat terrace one monolayer high on which a 3D growing is visible. High resolution STM image recorded on the flat terrace is presented in insert: atomic structures superimposed on the graphite lattice are observable.

a whole entity from image to image. Morever the displacement was not in the scanning direction nor perpendicular to it. In fact between the first and the last images the displacement direction was changed: after an up and right shift of the particle labelled A towards the graphite step (Fig. 7b), the particle changed for an up and left shift away from the step (Fig. 7c).



a)

b)

c)

Fig. 7. — STM images of the same area (476 nm × 476 nm) exhibiting mobility of a Sb particle on the graphite surface. a) first image recorded, b) image recorded 2 minutes later: the particle labelled A shifted up and right towards the step, while two others particles stayed in place, c) image recorded 20 minutes after the first one: the particle A shifted up and left away from the step.

4. Conclusion.

Parallel TEM and STM investigations of antimony particles supported on graphite produced by molecular beam deposition (MBD) and low energy cluster beam deposition (LECBD) are presented. According to the deposition technique, different growth modes are observed. For the cluster deposition case, the growth results from juxtaposition of amorphous particles around anchoring sites. They should be formed by aggregation of several deposited Sb clusters. For the molecular deposition case, there is a competition between 2D and 3D growth which seems to belong to a Stransky - Krastanov mode, and the film gets more structural organization. The main discrepancy between TEM and STM images comes from particles numbering. Differences in particles density obtained from the two techniques have been attributed to antimony particle mobility on the graphite surface.

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