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Cluster-beam deposition for high-quality thin films

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Transmission electron microscopy studies have recently shown that low-energy cluster-beam deposition allows the formation of higher-quality films compared with the classical molecular-beam deposition. This work presents preliminary results obtained with antimony deposits.

The growth of reproducible high-quality films (well crystallized and continuous) has led to numerous recent advances in thin-film deposition technology. Among the most recent techniques developed in this field, ionized-cluster-beam deposition (ICBD) has been studied and used for metal, semiconductor, or insulating materials. Since the first results published by Takagi and co-workers,[1,2] some theoretical works have been published[3,4] in order to understand the specific aspects of such a technique. In this technique, it has been pointed out that an important criterion for obtaining high-quality thin films is that each cluster has sufficient energy to be dissociated on the substrate in order to spread out into a uniform layer.[4]

Nevertheless, very recent studies[5] have shown that differences between cluster-beam and molecular-vapor deposition still exists with nonaccelerated clusters. It has been pointed out that, in the first stages of the deposition, these low-energy clusters tend to form deposits that present significant differences with the ones obtained from molecular-vapor deposition. The calculated kinetic energy of these clusters has been estimated to be of the order of 1 eV. This value leads to an energy per cluster atom less than the bulk cohesive energy that prevents the cluster fragmentation on the surface.

The aim of this Rapid Communication is to present results obtained with a neutral antimony cluster beam. These results show that this technique allows the formation of high-quality thin films with regard to molecular-beam deposition (MBD). In exactly the same experimental conditions (vacuum, deposition rate, substrate temperature, etc.), thin films obtained from MBD and low-energy cluster-beam deposition (LECBD) are compared.

The cluster beam is generated by the gas aggregation technique in a source similar to that developed by Sattler.[6] The metallic vapor coming from a heated crucible condenses in an inert gas (helium) cooled at liquid-nitrogen temperature. The cluster size is monitored by the helium pressure; experimental results show that the increase of helium pressure induces a decrease of cluster size.[7] A time-of-flight mass spectrometer is used in order to measure the cluster size distribution before the deposition. For low masses, previous results on fragmentation[8] allow us to consider that ionized-cluster-mass distribution is nearly a good measure of the neutral cluster distribution. 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 previously published.[9] The results reported in this work deal with antimony deposits performed with 100 Pa of helium pressure, which correspond to a cluster mean size of 48 atoms (Fig. 1). These neutral clusters were deposited at room temperature on amor-

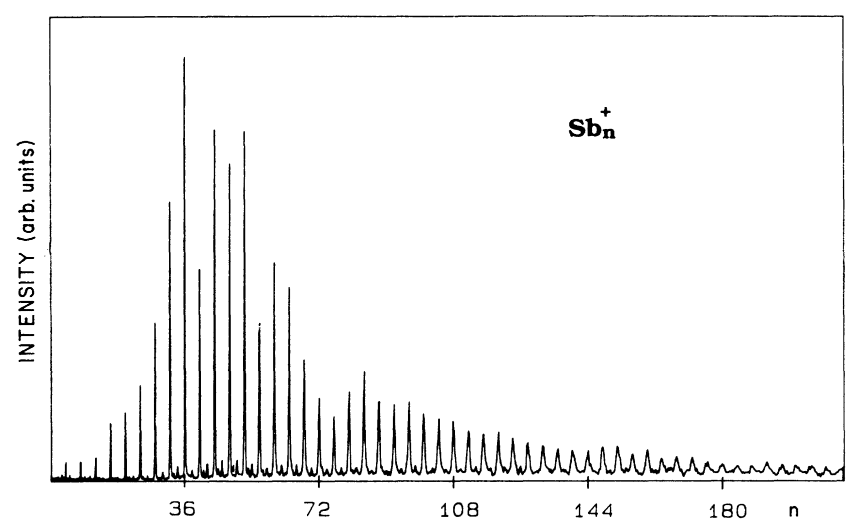

FIG. 1. Size distribution of ionized antimony clusters. Electron energy used to ionize antimony clusters is about 20 eV.

phous carbon films (5 nm thickness) supported on microscopy copper grids. The MBD experiment was performed in the same oven in absence of cold helium. It was checked that antimony vapor is formed essentially with Sb_4. During both experiments, the deposition rate was 0.03 $nm\,s^{-1}$ and the residual pressure was less than 10^{-4} Pa. After air transfer, thin films of 10 nm thickness were observed by TEM in a Philips EM300 electron microscope at 100 kV.

Typical TEM results are presented in Fig. 2. The difference between the 10-nm-thickness deposits obtained with LECBD [Figs. 2(a) and 2(b)] and MBD [Figs. 2(c) and 2(d)] can be clearly seen. With a low-energy cluster beam, the deposit is formed with very small aggregates (15 nm diameter) which have percolated in order to form a nearly continuous film. With MBD, the aggregates are isolated and their mean size is much more sizable (55 nm mean diameter). In addition, the diffraction patterns corresponding, respectively, to LECBD [Fig. 2(b)] and MBD [Fig. 2(d)] exhibit that the first technique tends to form well-crystallized thin films. The diffraction rings have been identified as being consistent with the α-antimony structure. It must be noted that numerous aggregates present the same crystallographic orientation on large areas of the LECBD deposit. It has been checked that the diffraction patterns performed on these large areas are similar to those obtained with α-antimony single crystal. In contrast, the diffraction pattern corresponding to the MBD deposit [Fig. 2(d)] presents only two diffuse rings, similar to an amorphous structure in agreement with previous results obtained by Levinstein.[10]

This work presents evidence of advantages for using the LECBD technique to obtain high-quality thin films. Very few results with TEM studies deal with deposits obtained with low-energy cluster beams.[5,11-13] In addition, all these results refer to ranges of low deposit thickness from 0.02 to 0.4 nm. In most of these cases, this range of thickness has been chosen to study mainly the first stages of deposition processes.

Antimony deposits have been chosen as a test system to compare the present results to those previously obtained with ICBD (Refs. 2 and 13) or MBD.[10,14,15] Even compared with the ICBD technique, the quality of LECBD antimony thin films seems to be ameliorated. The diffraction patterns performed on antimony deposits produced by accelerated ionized clusters[2] show a halo pattern indicating, as for a MBD deposit, a lack of long-range ordering. In contrast, the antimony films crystallize well with the LECBD technique.

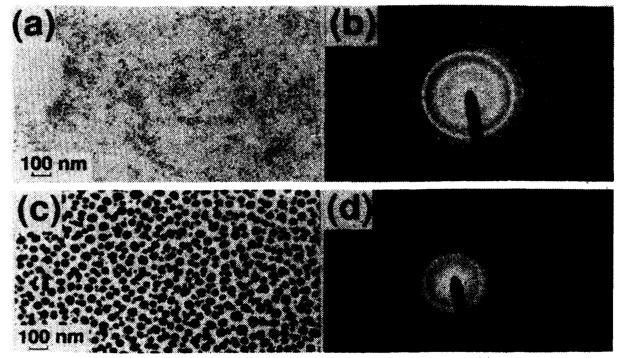

FIG. 2. TEM micrographs and diffraction patterns of 10-nm-thickness antimony deposits obtained with (a),(b) low-energy cluster-beam deposition and (c),(d) molecular-beam deposition.

Furthermore, it is well established that MBD antimony crystallizes at a thickness greater than a critical thickness d_c which depends on the nature and preparation of the substrate.[15-19] For MBD experimental conditions, the value of d_c is about 25 nm for collodion substrate.[19] We are now studying the optimum LECBD conditions to lower this value in the case of amorphous carbon substrate. These results are quite encouraging. Together with molecular physic studies on free antimony clusters,[8] electrical and optical properties of these films are now performed in our laboratory.

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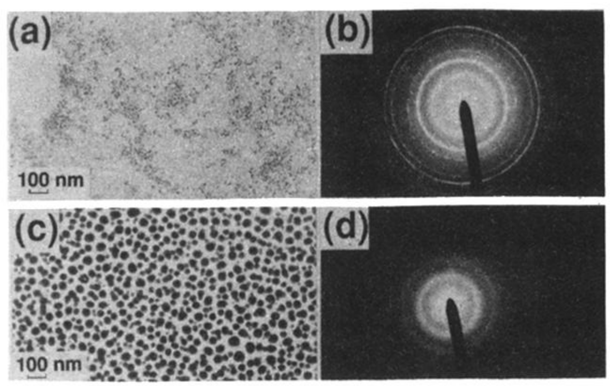

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