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Epitaxial growth and stabilization of the compound Ag_3Sb on silver {1 1 1}

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The vapour deposition of antimony on silver {1 1 1} under ultra-high vacuum conditions has been studied by means of reflection high-energy electron diffraction (RHEED) and Auger electron spectroscopy (AES). At room temperature, no evidence for sub monolayer structures was obtained and a deposit of an apparent thickness equivalent to six monolayers was necessary before any diffraction features typical of the overlayer could be detected. With increasing film thickness, the formation of islands with random rotational orientation was detected with Sb ⟨1 0 0⟩ normal to the substrate surface. Annealing of the deposit at 573 K led to the formation of the intermetallic compound Ag_3Sb in epitaxial relation to the substrate. Lattice parameters for pseudo-cubic antimony ($a = 0.613$ nm) and hexagonal Ag_3Sb ($a = 0.295$ nm and $c = 0.482$ nm) were obtained.

1. Introduction

In spite of the contemporary importance of thin films of certain elements in the fabrication of electronic devices and numerous experimental observations, there still seems to be no more than a modest number of systematic studies directed towards the obtaining of precise structural information about their nucleation, growth, and orientation. As an example, we may cite antimony. Following Görlich's discovery [1] of the alkali metal–antimony photocathode, the electronic applications of the Group V semi-metals has stimulated a considerable number of studies involving antimony. As a natural progression from early work of a more descriptive nature, to qualitative studies on the crystallization of the element on glass, the present trend towards studies of vapour and electro-chemical growth on single crystal substrates under precisely defined conditions is clearly appropriate.

A study of vapour deposition on the {1 0 0}, {1 1 0} and {2 1 1} crystal faces of tungsten [2–4] has shown that antimony can form a series of submonolayer-coverage structures, ordered in relation to the symmetry of the substrate surface. In this system, the miscibility of the components and their tendency to form compounds are both very small and, on annealing the deposits, thermal desorption of antimony reverses the growth process to regenerate the substrate surface. One may assume that the degree of adsorbate–adsorbate interaction is comparable with that of adsorbate–substrate interaction, both influencing the formation and orientation of the observed overlayer structures. In contrast, an early investigation of the deposition of antimony on a silver {1 1 1} [5] suggested a rather weak adsorbate–substrate interaction at room temperature. Diffraction data indicated that the antimony overlayer grows in a way similar to that on a non-crystalline substrate such as glass: an initial amorphous structure is succeeded by gradual crystallization of islands as a function of increased temperature and/or thickness of the deposit. These islands have random rotational orientation about a fibre axis corresponding to the pseudo-cubic ⟨1 0 0⟩ direction of antimony perpendicular to the substrate surface.

In view of the poorly-defined conditions in the previous antimony–silver {1 1 1} investigation, and in view of the commercially important electronic applications of antimony [6] and its use as a silver catalyst dopant [7], a closer examination of the system has been undertaken.

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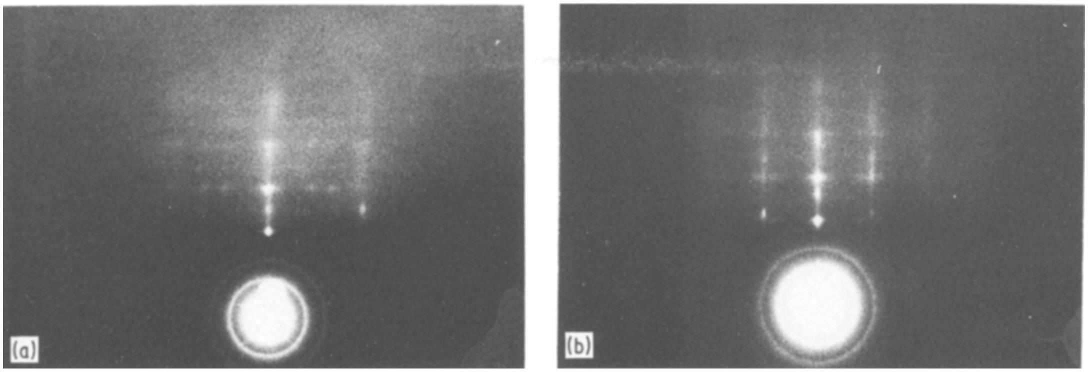

Figure 1 Diffraction pattern obtained from Ag {1 1 1} with a deposit equivalent to 6 monolayers of Sb. (a) ⟨2 1 1⟩ azimuth; (b) ⟨1 1 0⟩ azimuth.

2. Experimental details

The silver substrates were smooth epitaxial single crystals, grown on mica. They were prepared initially before the baking of the stainless steel diffractometer [8] and subsequently "refreshed" after bake-out by a further evaporation of silver. Antimony was evaporated *in situ* from a conical tungsten basket at an apparent rate of 1 to 3 monolayers per minute (assuming equal sticking probability at both the silver substrate and the quartz crystal monitor). The growth of the deposit was followed using the technique of reflection high energy electron diffraction (RHEED) and Auger electron spectroscopy (AES) at pressures less than 0.5 μPa.

3. Results

By evaporating antimony at room temperature in small quantities, controlled by a quartz crystal monitor, a search was made for ordered, low-coverage structures. This approach yielded no change in the streaked diffraction patterns from the silver surface and no evidence of adsorbed antimony as indicated by AES studies. Possible explanations of these observations are that either the sticking probability at silver {1 1 1} is very low, or that any deposit of antimony is rapidly desorbed during electron bombardment. In order to recognize any deposit of antimony by RHEED, the apparent equivalent of six monolayers of the element was necessary. At this stage some modulation of the intensity of the central diffraction streak and the development of new diffraction features were apparent (see Fig. 1) but, nevertheless, an Auger signal could still not be detected. With increasing antimony coverage, modification of the diffraction pattern was clearly apparent (see Fig. 2) and the invariance of those features associated with the deposit to rotation of the sample about the surface normal indicated that the antimony growth consisted of islands with one-dimensional order (I–O) texture about silver ⟨1 1 1⟩.

Annealing the deposits, of apparent thickness

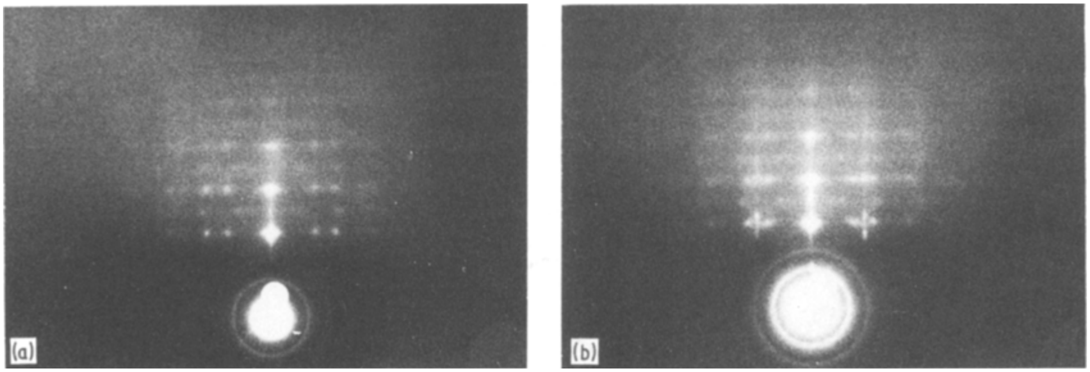

Figure 2 Diffraction pattern obtained from Ag {1 1 1} with a deposit equivalent to 10 monolayers of Sb; (a) ⟨2 1 1⟩ azimuth; (b) ⟨1 1 0⟩ azimuth.

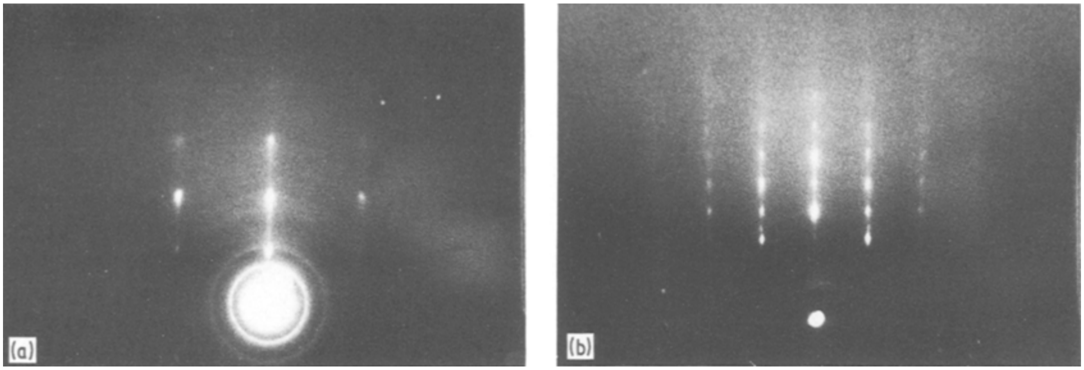

Figure 3 Diffraction pattern obtained from Ag–Sb alloy; (a) azimuth corresponding to Ag ⟨2 1 1⟩; (b) azimuth corresponding to Ag ⟨1 1 0⟩.

about 10 nm, to 573 K resulted in a change in their structure. Instead of the fibre orientation, the deposit assumed an alignment with the silver substrate, possessing identical azimuths corresponding to the same six-fold rotational symmetry (see Fig. 3). Close examination clearly indicated that the bulk antimony was not responsible for the diffraction pattern and, since this indicated a strong possibility of compound formation, further investigation was carried out by means of AES. Direct evidence for the formation of a silver–antimony alloy, as indicated by shifts in the positions of the Auger peaks, was unsuccessfully sought, since no changes were observed during the annealing process. Also, the relative surface concentrations of silver and antimony were followed as a function of the annealing temperature, the latter increasing at a rate of about 1 K min^{-1}. The plotting of the ratio of the peak height of the silver Auger signal to that of the antimony signal (Fig. 4) against temperature showed a constant value up to a temperature of about 450 K. At this stage, the ratio began to rise, the upper limit to these measurements being set by a dramatic broadening of the Sb (440 eV) peak above 610 K, which may have been the result of Auger electron emission by antimony evaporating from the sample surface, thus causing a reduction in resolution. The Ag (351/356 eV) peak remained unaffected. Prolonged annealing caused a reduction in both the antimony peak-width and its amplitude, but, even after annealing at 700 K for several days, evidence for the presence of surface antimony remained. In contrast, RHEED patterns at this stage were typical of clean smooth silver {1 1 1} and the likelihood of diffusion of antimony through the bulk host was qualitatively examined by the evaporation of 20 nm of silver at room temperature followed by annealing at 700 K. This procedure resulted in the reappearance of an antimony Auger peak.

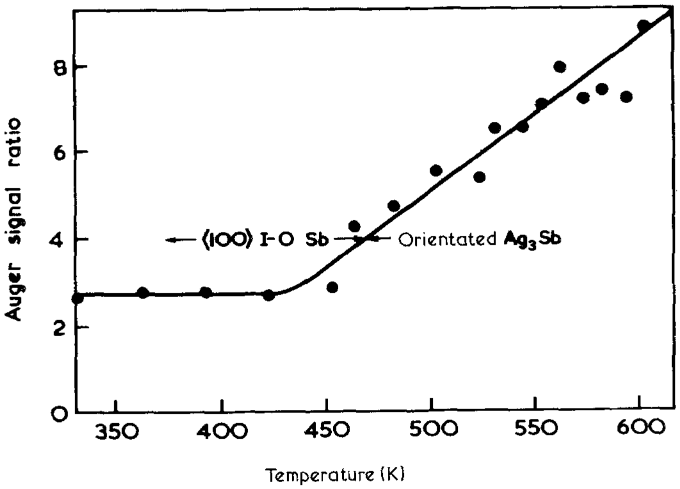

Figure 4 Plot of the ratio of Ag/Sb Auger peak-heights as a function of temperature.

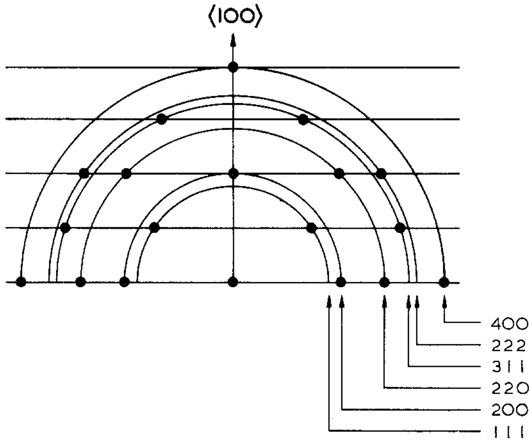

Figure 5 Diffraction pattern calculated for a ⟨1 0 0⟩ fibre-textures f c c crystal.

4. Discussion

In contrast with the results of Hopkins and Watts [2], no evidence for submonolayer structure was obtained in the present experiments. The possible causes for the apparent absence of ordering may be a consequence either of the relative magnitudes of the adsorbate–substrate and adsorbate–adsorbate interaction energies, or of the method of examination, since the crystallization of antimony is known to be sensitive to electron bombardment [8]. Presuming a genuine effect, it might be suggested that antimony should exist initially in the form of a two-dimensional gas until crystallization becomes possible with an increase in adsorbate concentration. At this point, the very low binding energy to the substrate leads to the formation of islands with random rotational orientation, but with a common crystal plane parallel to the substrate surface. The nature of the diffraction patterns (spots with no more than slight evidence of streaking) indicate that the antimony crystallites nucleate as three-dimensional units. Comparison of the rotationally-invariant diffraction pattern of antimony with that expected from a ⟨1 0 0⟩ fibre-textured f c c crystal (see Fig. 5) indicates the validity of the assignment of pseudo-cubic antimony to this orientation [9]. Further, since it is possible to observe diffraction both from the silver and from the overlayer, the lattice parameter of the former ($a = 0.409$ nm) may be used to calibrate internally a pseudo-cubic lattice parameter for antimony of $a = 0.613$ nm, a value acceptably in agreement with other observations [10]. The ⟨1 0 0⟩ I–0 growth of antimony was also noted by Newman [5] and it is noteworthy that antimony electrochemically-deposited on silver {1 1 1} also shows ⟨1 0 0⟩ perpendicular growth to the substrate surface, but in this case two types of single-crystal orientations were observed, such that antimony ⟨1 1 0⟩ was parallel with both silver ⟨1 1 0⟩ and silver ⟨2 1 1⟩ [11].

By the co-evaporation of silver and antimony on to a rock-salt substrate and the examination of the deposits by diffraction analysis, Pinsker and Li [12] have established the lattice parameters of several polycrystalline phases. In our present experiments, annealing always produced a transition from bulk antimony to a single intermetallic compound: the disappearance of diffraction features due to randomly rotated antimony islands, coincided with the appearance of those of a unique product. Close inspection of the diffraction pattern indicated that the compound, epitaxially orientated and of hexagonal structure with (0001) co-planar with silver {1 1 1}, was Ag_3Sb. Again it was possible, in the later annealing stages, to calibrate the overlayer diffraction pattern using diffraction maxima from silver. The measured lattice parameters for the compound Ag_3Sb were $a = 0.295$ nm and $c = 0.482$ nm, values in good agreement with X-ray data ($a = 0.299$ nm and $c = 0.482$ nm) [12] and electron diffraction data ($a = 0.292$–0.296 nm and $c = 0.477$–0.478 nm) [13].

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