JOURNAL OF MATERIALS SCIENCE 25 (1990) 1715–1718

Some physical properties of evaporated thin films of antimony trisulphide

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The optical properties of thin films of red Sb_2S_3 prepared by vacuum evaporation on amorphous substrates were determined from transmission measurements. The variation of the extinction coefficient, K, shows structures at energies of 4.4 and 5.4 eV. The band gap was found to be 1.7 eV for film of thickness 56 nm, and increase with thickness. The interpretation of structure was inferred from transmission electron microscopy and X-ray diffraction for thin films of antimony trisulphide. The investigated film thicknesses were from 46 to 64 nm.

1. Introduction

The optical properties of amorphous chalcogenides have been a subject of great interest for several years [1–3]. As_2S_3 and As_2Se_3 have received most attention [4–7], while materials like Sb_2S_3, which is widely used as the photoconductive target for the vidicon type of television camera tube [8], have not been thoroughly investigated. In this paper we report an investigation on the optical properties of amorphous thin films of Sb_2S_3, studied in the photon-energy range 1 to 6 eV.

In the amorphous material, due to disorder and consequent constraints of local topography, a large number of single coordinated negatively charged (C_1^-) and an equal number of triply coordinated positively charged (C_3^+) chalcogens may exist [9]. The creation of defect states affects the conduction and valence bands and also produces strong local distortion [10]. Amorphous (no translational periodicity over several interatomic spacings) and fine-grained (< 2 nm) structures cannot be distinguished on the basis of electron diffraction since the patterns in both cases consist of diffuse halos. Fujime [11] attempted to deduce radial distribution curves from the intensities of halo patterns. A fine-grained structure is expected to yield a continuous recrystallization. During the amorphous-to-crystalline transformation heat is produced which is nearly half the heat of fusion for the bulk [12].

An important parameter which determines agglomeration and film growth is the surface migration or mobility of an adatom. If the mobility is random, the adatoms and the embryos will execute a random walk on the surface, until they are either re-evaporated or chemisorbed [13].

2. Experimental procedures

High-purity antimony trisulphide was employed for the deposition of thin film in a vacuum of 10^{-5} Pa by evaporation from a tungsten boat onto crystalline mica and amorphous quartz substrates. The rate of deposition was estimated to be 2 nm sec^{-1}. The films were investigated by means of transmission electron microscopy (TEM) (10-Zeiss). The structure of the thin films deposited on mica was examined using a Seimens D-500 X-ray diffractometer. The optical transmittance in the UV was measured for films deposited onto quartz plates using a Beckman double-beam spectrophotometer (5260).

3. Results and discussion

The variation of the coefficient of absorption, α, the absorption index, K, and the transmittance of amorphous films are plotted against photon energy in the range of 1 to 6 eV (Figs 1–3). In Figs 1 and 2, the appearance of the exponential or Urbach's tail in the absorption coefficient (α) and extinction coefficient (K) is common with amorphous materials, particularly with the chalcogenides [14]. The optical coefficient α in amorphous materials usually follows a relation

$$\alpha E = \text{const}\ (E - E_o)^2$$

where E is the photon energy and E_o is the optical gap. This type of absorption is typical of interband transitions near the optical edge when transitions are indirect and the density of states $N(E)$ approximately equals $E^{1/2}$. The optical gap E_o represents the extrapolated zero of the density of states. Figure 4 shows the linearity of the plot of $(\alpha E)^{1/2}$ against E for a photon energy of about 2.3 to 3.5 eV, and that the optical gap obtained from extrapolation is 1.7 eV for a film thickness of 56 nm. This agrees with the results of Hall [15]. As the thickness increased to 64 nm, the optical gap increased to 1.95 eV. Figure 3 shows the transmitted light against photon energy for different thicknesses of Sb_2S_3 thin films. The transmittance shows a broad minimum at 4.4 eV and a minimum at 5.4 eV. These two structures were attributed to indirect transitions. This broad minimum has been observed before by Shutov *et al.* [16] in the investigation of polarization effects in the fundamental reflectivity

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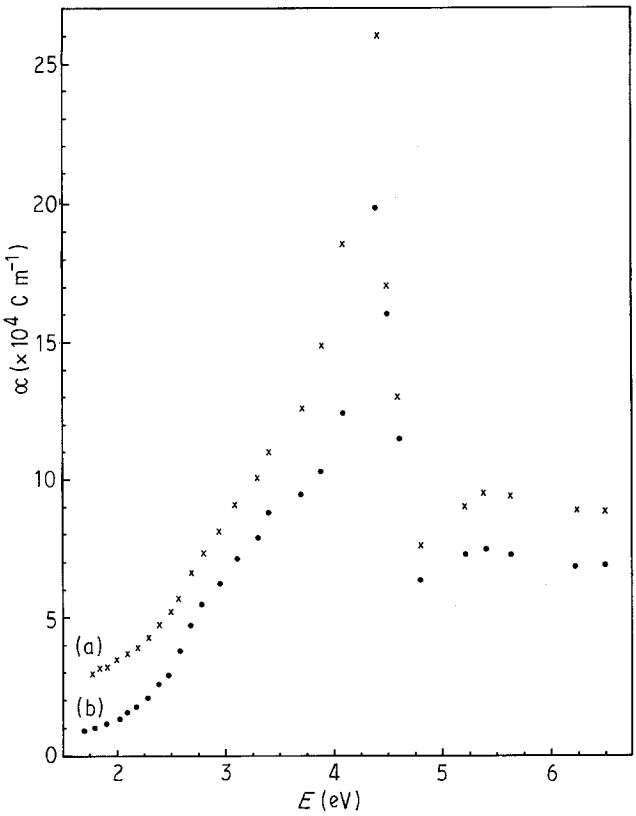

Figure 1 Absorption coefficient (α) against photon energy (E) for Sb_2S_3 films. Film thickness, d = (x) 56 nm; (●) 64 nm.

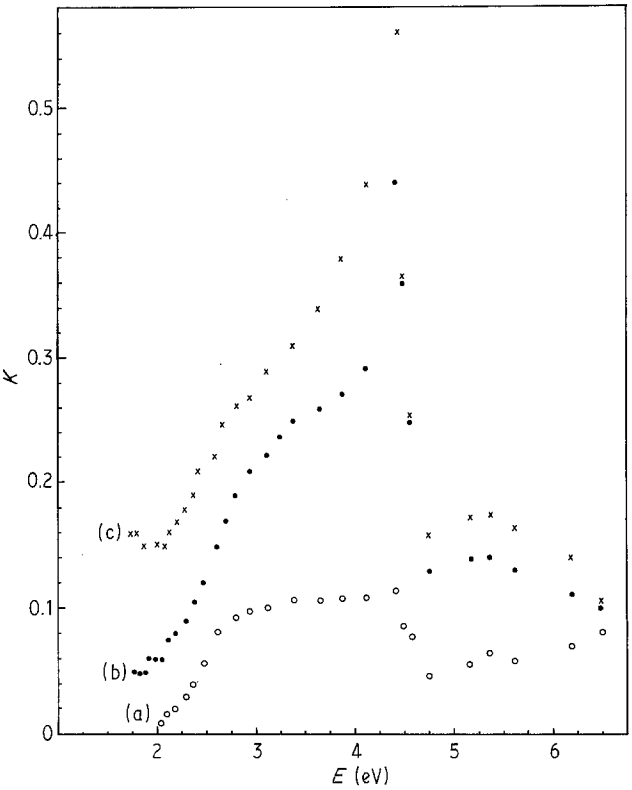

Figure 2 Dependence of extinction coefficient (K) on photon energy for Sb_2S_3 films of different thicknesses, d, (○) 46 nm; (●) 56 nm; (x) 64 nm, on quartz substrate.

spectra of Sb_2S_3 and Sb_2Se_3 crystals. The orthorhombic crystals Sb_2S_3 and Sb_2Se_3 are isomorphic and have a layered structure which leads to anisotropy of electrical conductivity and edge absorption.

The novel structural behaviour and properties of thin films can largely be ascribed to their growth process, which is therefore of basic importance to the science and technology of thin films. The details of nucleation and growth depend on the material being deposited, and on other parameters such as substrate temperature and material, and the angle of incidence of the evaporant onto the substrate [17].

Amorphous antimony trisulphide films evaporated on mica substrate, examined under the electron microscope, first show an amorphous halo structure, and then electron irradiation initiates rapid localized crystallization. The crystallization appears to be triggered by the high electric field set up by the charge gradients on the amorphous film. Once triggered, the heat released on crystallization accelerates the transformation process. Just how the oriented structure is obtained with the help of the electron beam is not clear. Such crystallization can also be obtained by means of an elevated annealing temperature ($\simeq$ 220° C

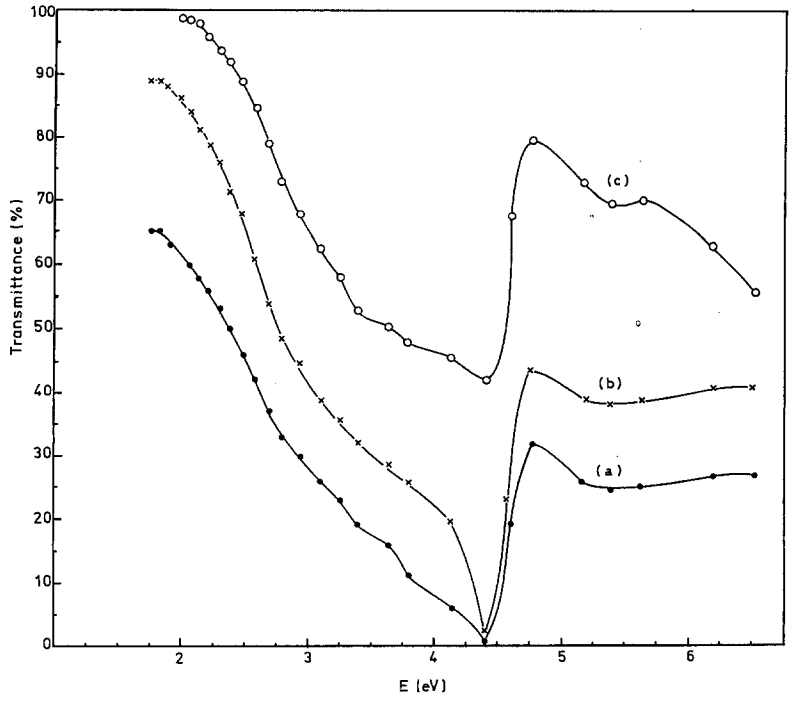

Figure 3 Dependence of transmittance on photon energy for antimony trisulphide films of different thicknesses, d, (●) 64 nm; (x) 56 nm; (○) 46 nm.

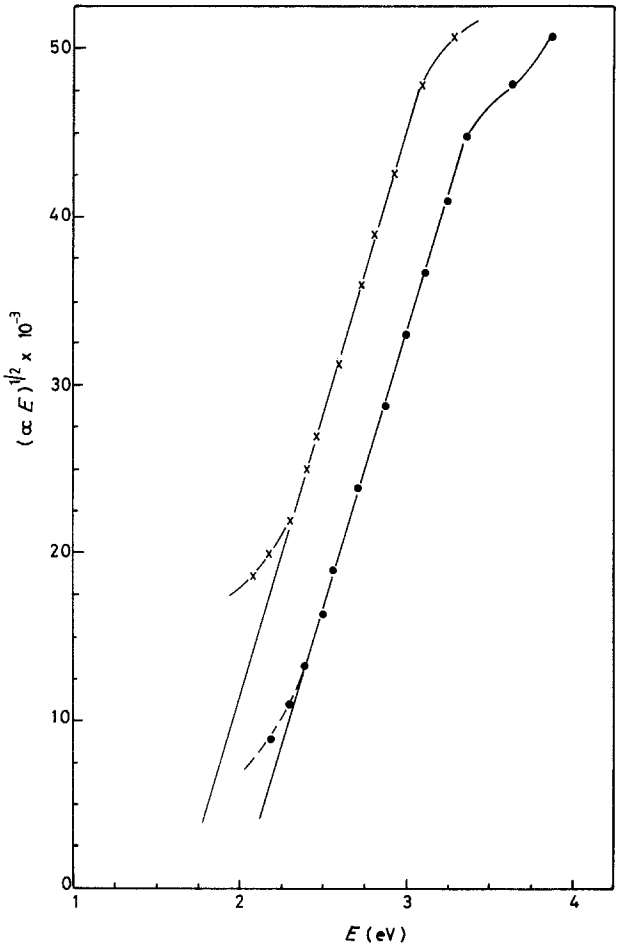

Figure 4 The plot of $(\alpha E)^{1/2}$ against photon energy (E) for amorphous Sb_2S_3 films. Film thickness, d = (x) 56 nm; (●) 64 nm.

for 3 h) leading to uniform growth over the whole film and a predominantly polycrystalline normal structure. These results agree well with the work of Shiojiri [18] who studied the crystallization of TiO_2 films prepared by evaporation onto rock salt at room temperature. He observed that a 50 keV electron beam set off rapid localized crystallization of the film, yielding polycrystalline rutile coexisting with large crystallites.

Let us emphasize that, depending on the system, the transformation via a metastable structure may be very rapid and thus difficult to detect with electron diffraction. Careful studies of changes in electrical resistivity on annealing are better suited to study the occurrence of metastable structures in amorphous systems.

Figure 5a shows a thin film of Sb_2S_3 with a thickness of 46 nm. Electron diffraction, taken at low beam intensity, indicated that the film is amorphous, while increasing the intensity of the beam caused crystal growth which is elucidated as a single crystal electron diffraction pattern. Increasing the thickness to 64 nm. Fig. 5b shows a polycrystalline pattern after being subjected to the electron beam.

Such a transformation was also confirmed by X-ray diffraction for Sb_2S_3 films of thicknesses 46, 56 and 64 nm. For the analysis of the structure of Sb_2S_3-evaporated films on mica, Fig. 6 reveals that only three orientations are obtained (1 0 1), (1 4 1) and (5 1 0). The figure also indicates a considerable change in intensity of X-ray-diffracted planes with increasing thickness. It is well known [19] that there are six factors affecting the relative intensity of the diffraction lines: polarization, structure, multiplicity, Lorentz

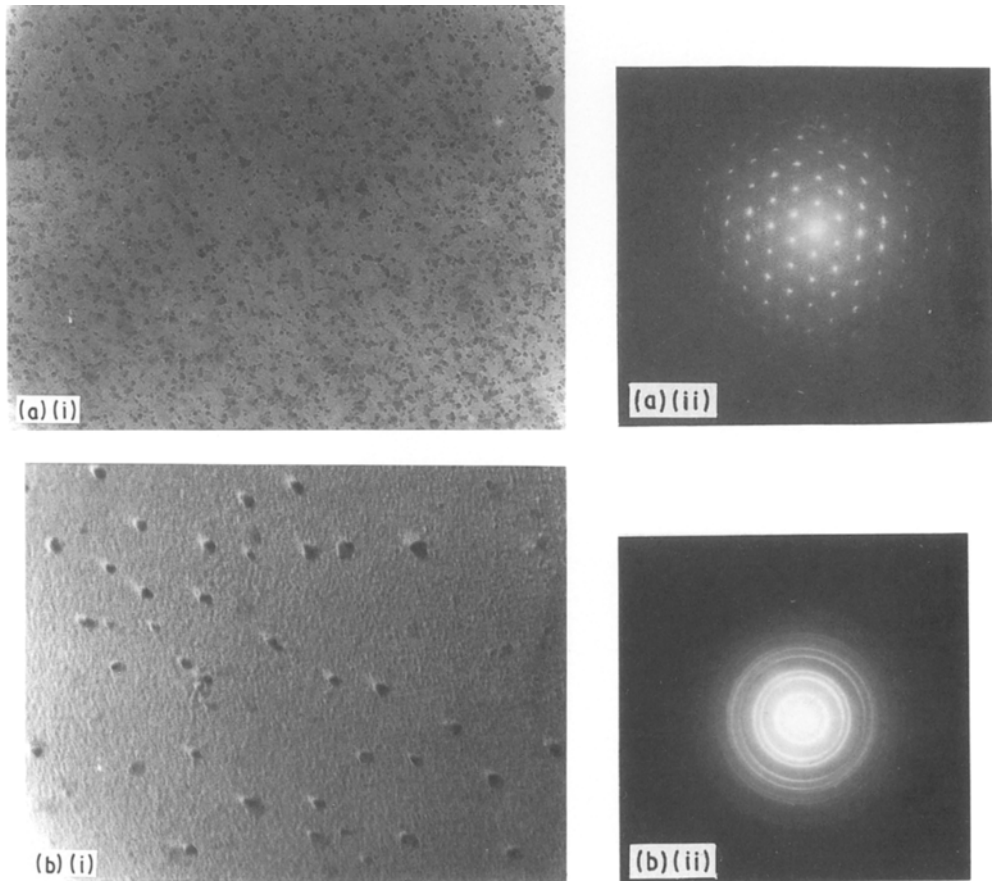

Figure 5 Transmission electron micrograph and transmission electron diffraction of Sb_2S_3 on a cleaved surface of mica. Thickness (a) 46 nm, (b) 64 nm. × 20 000.

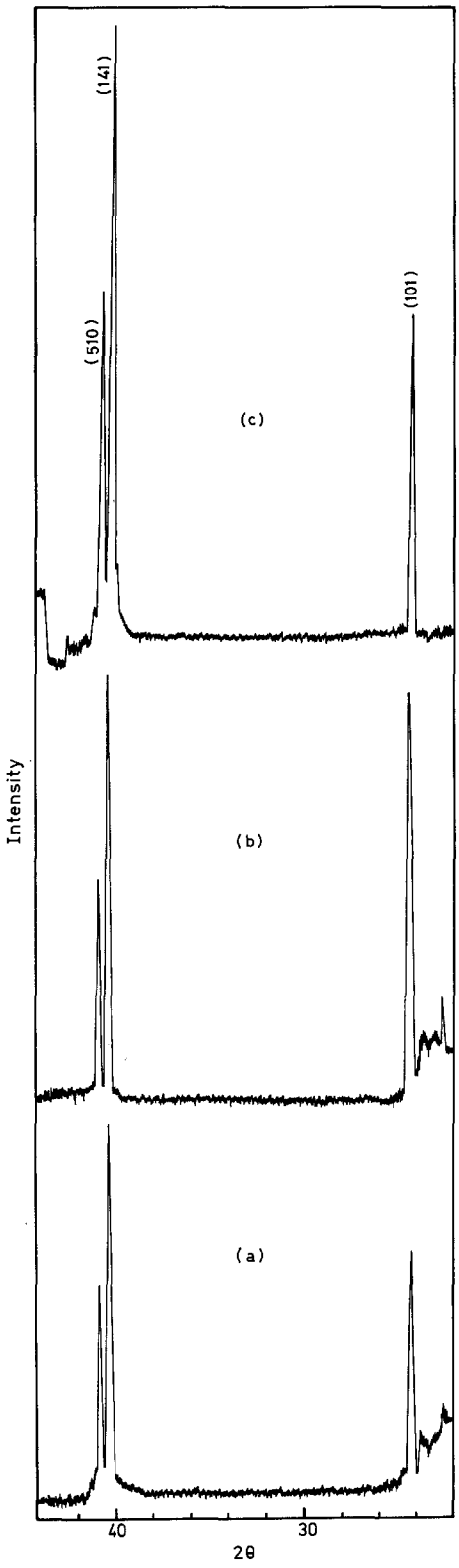

Figure 6 X-ray diffraction of Sb_2S_3 thin films for different thicknesses, d, (a) 46 nm; (b) 56 nm; (c) 64 nm.

polarization, absorption and temperature. Thus the substrate has a profound effect on crystal growth kinetics and morphology, and the crystallization behaviour of Sb_2S_3 is strongly temperature-dependent.

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Received 18 April 1989
and accepted 17 July 1989