

OPTICAL PROPERTIES OF AMORPHOUS AND CRYSTALLINE Sb_2S_3 THIN FILMS

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The optical constants of amorphous thin films of Sb_2S_3 prepared by vacuum evaporation were determined. After deposition the films were crystallized by baking in a vacuum and their optical constants were re-determined. The amorphous and crystalline states of the films were determined by means of transmission electron microscopy. The amorphous material shows the exponential absorption tail characteristic of most amorphous materials. At higher photon energies near the absorption edge a linear dependence of $(\alpha E)^{1/2}$ on photon energy is observed from which the extrapolated optical gap is found to be 1.7 eV. The optical constants in the amorphous films are rather structureless but on crystallization several structures are observed in ϵ_2 at energies of 1.88, 2.88, 3.48, 3.86 and 5.25 eV. The band gap in the crystalline material is 1.88 eV and is considered to be direct. On crystallization the magnitudes of the optical constants ϵ_2 and n increase to a great extent. The establishment of long range order in the material is likely to increase the weaker bonding by the chalcogen p electrons. This would probably increase the effective number of electrons contributing to interband optical transitions and give rise to the observed change in optical properties.

1. INTRODUCTION

The optical properties of amorphous chalcogenides have been a subject of great interest for several years¹⁻³. Of all the amorphous chalcogenides As_2S_3 and As_2Se_3 have received most attention⁴⁻⁷ while materials like Sb_2S_3 , which is widely used as the photoconductive target for the vidicon type of television camera tube⁸, have not been thoroughly investigated. In this paper we report our investigations on the optical properties of amorphous thin films of Sb_2S_3 which were studied in the photon energy range 1–6 eV. The films were re-examined after crystallizing by baking in a vacuum. Such a study highlights the changes in optical properties when the long range order is destroyed in this material.

2. EXPERIMENTAL

Antimony trisulphide of 99.999% purity was evaporated from a tantalum boat onto polished silica substrates at room temperature. The evaporation was carried out in a bell-jar type of vacuum system at a pressure of approximately 1×10^{-5} Torr.

The thickness of the films for optical study was about 300 Å. Transmission and reflection from these films were determined in the photon energy range 1–6 eV using Cary 14 and Carl Zeiss M4 QIII spectrophotometers with reflectance attachments. The films were then baked at 220 °C in a vacuum of approximately 5×10^{-8} Torr for 3 h during which time the films crystallized. The transmission and reflection measurements were then repeated. The amorphous nature of the films as deposited on the substrates at room temperature and the subsequent crystallization on baking were determined using a Siemens Elmiskop 102 transmission electron microscope. The optical properties were calculated using a computer with the help of standard formulae⁹ which take into consideration the reflection from both sides of the film.

3. RESULTS AND DISCUSSION

The variation of the coefficient of absorption α , the real and imaginary parts of the dielectric constant ϵ_1, ϵ_2 , the refractive index n and the absorption index k of the films in amorphous and crystalline forms plotted against photon energy in the range of 1–6 eV are shown in Figs. 1 to 5. Figure 6 is the plot of $(\alpha E)^{1/2}$ versus photon energy.

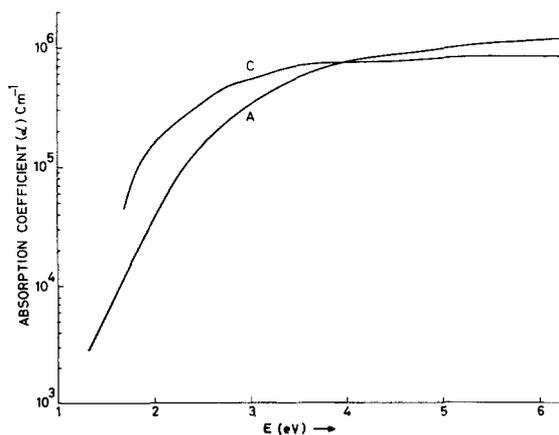


Fig. 1. A plot of the optical absorption coefficient α vs. photon energy E for amorphous (A) and crystalline (C) films of Sb_2S_3 .

The appearance of an exponential tail in the absorption coefficient, or Urbach's tail, is common with amorphous materials, particularly with the chalcogenides¹⁰. In the case of amorphous Sb_2S_3 this had been observed earlier by Hall¹¹. In the region above the exponential tail the optical absorption coefficient α in amorphous materials usually follows a relation

$$\alpha E = \text{const.}(E - E_0)^2 \quad (1)$$

where E is the photon energy and E_0 is the optical gap. This type of absorption is typical of interband transitions near the optical edge when the transitions are indirect and the density of states $N(E)$ approximately equals $E^{1/2}$. The optical gap E_0 represents the extrapolated zero of the density of states. Figure 6 shows that the

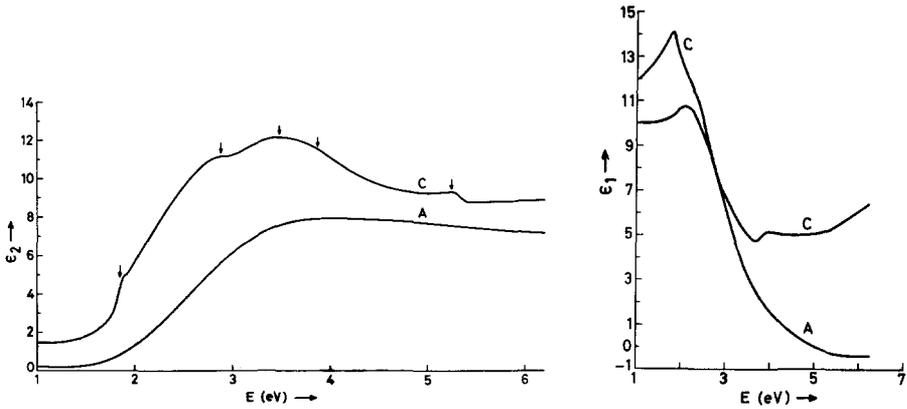


Fig. 2. A plot of the imaginary part of the dielectric constant ϵ_2 vs. photon energy for amorphous (A) and crystalline (C) films of Sb_2S_3 .

Fig. 3. A plot of the real part of the dielectric constant ϵ_1 vs. photon energy for amorphous (A) and crystalline (C) films of Sb_2S_3 .

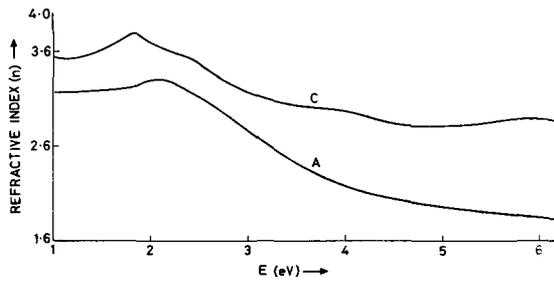


Fig. 4. A plot of the refractive index n vs. photon energy E for amorphous (A) and crystalline (C) films of Sb_2S_3 .

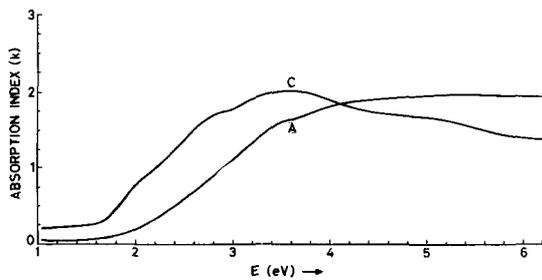


Fig. 5. A plot of the absorption index k vs. photon energy E for amorphous (A) and crystalline (C) films of Sb_2S_3 .

linearity of the plot of our results of $(\alpha E)^{1/2}$ versus E extends from an energy of about 2.3 eV to 3.5 eV and that the optical gap obtained from extrapolation is 1.7 eV. The absorption coefficient at the optical gap is about 10^4 cm^{-1} . Hall¹¹ determined the optical gap for Sb_2S_3 by a similar method to be 1.77 eV.

For amorphous Sb_2S_3 the ϵ_2 spectrum (Fig. 2) is quite structureless. It rises rapidly from an energy of about 1.8 eV to 3.6 eV, attains a maximum value at about 4

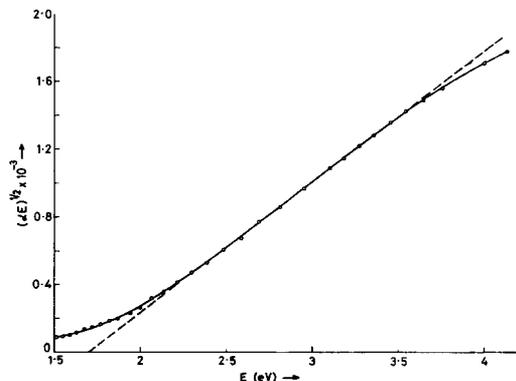


Fig. 6. A plot of $(\alpha E)^{1/2}$ vs. photon energy E for amorphous Sb_2S_3 films.

eV and then slowly decreases. The refractive index (Fig. 4) rises slowly from low energy to a broad peak at 2.1 eV and then falls. The absorption index (Fig. 5) rises quickly from 1.8 to 3.6 eV and then rises more slowly.

When the film is crystallized by baking the optical constants change markedly. In the region of interband transitions a number of structures are observed, in contrast with the rather structureless spectra of the amorphous material. The ϵ_2 spectrum, which follows the optical transition probability most closely, has structures at energies of 1.88, 2.88, 3.48, 3.86 and 5.25 eV. The reflectivity spectra from Sb_2S_3 crystals with polarized light were measured by Shutov *et al.*¹² They observed some structure in the spectra. Some of the prominent structures which were observed (at 1.88, 2.68, 3.48, 3.8 and 5.25 eV) are close to our observations. The structure at 1.88 eV which has been observed at the same energy in both cases is the first structure due to direct transitions observed. Although the extrapolated optical gap for amorphous material is 1.7 eV, the change of slope indicating interband transitions starts at around 1.9 eV. The disorder in amorphous materials is also likely to broaden the band edge and the onset of indirect transitions in the amorphous material appears to be at almost the same energy as the first structure due to direct transitions. Thus it appears likely that the band gap in this material is of the direct type.

The magnitudes of the optical constants n and ϵ_2 become very much higher when the material is crystallized. The maximum and minimum values of n in the amorphous material are 3.3 and 1.83 whereas in the crystalline state they are 3.8 and 2.83 respectively. For ϵ_2 the maximum values for amorphous and crystalline materials are 8 and 12.2 respectively. Such a large increase on crystallization can probably be understood if we look into the type of bonding that is observed in similar crystalline materials such as Sb_2S_3 and Sb_2Se_3 . The crystal structure of these materials is orthorhombic¹³ and there are two types of bonding. There is a strong short range bonding and also a weaker long range bonding provided by the p electrons of the chalcogen atoms. When the material is in amorphous form, the long range order is destroyed. From the optical sum rule¹⁴

$$\frac{2\pi^2 e^2}{m} n_{\text{eff}} = \int_0^{\omega_0} \omega \epsilon_2 d\omega \quad (2)$$

we find that if the effective number of valence electrons is increased ϵ_2 will increase correspondingly. On crystallization long range order is established and the effective number of electrons contributing to the long range bonds is likely to increase, thereby increasing the value of ϵ_2 .

The long range chalcogen p bonds make the largest contribution to the density of states at the top of the valence band and hence in the range of photon energies investigated we find large changes in the magnitude of the optical constants on crystallization. The increase in the optical absorption coefficient near the band edge on crystallization is probably caused by the increase in the density of states at the top of the valence band.

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