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Electrical and optical properties of evaporated $Ag_{10}As_{30}Te_{60}$ thin films

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The temperature dependence of the electrical resistance and the spectral dependence of the optical absorbance of evaporated $Ag_{10}As_{30}Te_{60}$ thin films were studied. It was found experimentally that the heat treatments cause significant changes in the electrical resistance and the optical absorbance of the chalcogenide film. The results obtained were correlated with the X-ray analyses.

1. Introduction

In binary systems arsenic–chalcogen, replacement of selenium by tellurium sharply reduces the tendency of the alloys to vitrification as a result of enhanced metallization of the chemical bonds. In the system As–Te, when the melt was quenched with air, glasses with a tellurium content ranging from 45–55 at % were obtained [1]. When more rapid cooling was used, Cornet and Rossier [2] obtained the compound As_2Te_3 in the vitreous state. When a third component, copper, thallium, silver, was introduced into arsenic tellurides, relatively extensive vitrification regions were obtained [3, 4]. In the literature some information on the interaction of the components in the system Ag–As–Te are given [5, 6]. However, Wernick *et al.* [5] stated that in this system a ternary compound of the composition $AgAsTe_2$, with a melting point of 350 °C and a predominantly covalent bond, is formed. The compound has semiconductive properties with a forbidden band width of 0.8–1.0 eV.

Rykova *et al.* [1] determined the vitrification region in the Ag–As–Te system. They found that up to 28 at % Ag, from 15–50 at % As and from 50–75 at % Te can be incorporated into the vitreous alloys. The composition chosen for the present work belongs to the above-mentioned vitreous region. A characteristic feature of the behaviour of silver in vitreous arsenic tellurides is its relatively slight influence on the activation energy of the electrical conductivity of the glasses. The effect exerted by silver on the activation energy of the conductivity of vitreous arsenic tellurides is only about half that exerted by copper. In the system Cu–As–Te, a marked decrease in the activation energy of the electrical conductivity was observed when the first small portions of copper are incorporated.

2. Experimental procedure

Appropriate mixtures of 99.99% pure silver, arsenic and tellurium (7 g total) were sealed in quartz ampoules (8 mm diameter) in a vacuum of the order of 10^{-3} torr (1 torr = 133.322 Pa). The sealed ampoules were then heated in a furnace for 10 h at 1000 °C. Then they were air-quenched to room temperature. Thin films were made by thermally evaporating a fixed weight from the obtained composition under high vacuum $\sim 10^{-6}$ torr on top of chemically cleaned glass substrates. Using a low evaporation rate was helpful to keep the substrates temperature at around room temperature. Aluminium electrodes, 2 mm apart, were deposited on the thin films to measure the electrical resistance over the temperature range 300–500 K. The measurements were repeated on five pieces of parallel fusions. The discrepancy between the measured values was less than 0.1 order of magnitude.

The optical absorption of the semitransparent films was studied at room temperature with unpolarized light at normal incidence using a Cecil double-beam spectrophotometer in the photon energy range 1.5–2.6 eV. To eliminate the substrates absorption, a plain glass was kept in the reference beam. It is well known that the electrical and optical properties are strongly dependent on the thickness of the thin film. Therefore, to study the effect of the annealing temperature on these characteristics, all used specimens should have the same thickness. This was achieved by evaporating the same amount of the bulk material under the same conditions. Each specimen was annealed at the specified temperature for 1 h and then cooled to room temperature before taking any measurements. For the electrical study, aluminium electrodes were usually deposited after the annealing process to avoid metal diffusion into the material of the chalcogenide film.

X-ray diffractograms (XRD) for the Ag–As–Te films were obtained using Philips chart diffractometer. The radiation source used was CuK_α, of wavelength 0.154 nm. The X-ray investigation was carried out on the as-prepared films as well as on others annealed at certain temperatures.

3. Results and discussion

Variations of the electrical resistance with the ambient temperature of the as-prepared and annealed samples are shown in Fig. 1. Increasing the sample temperature, higher than the room temperature, causes a slight gradual decrease in the resistance of the chalcogenide glass. At high temperatures, a sharp decrease in the sample resistance is noticed. This sharp decrease of resistance with increasing temperature can be described by the exponential relation

$$R = R_0 \exp(\Delta E/KT) \qquad (1)$$

where ΔE is the activation energy for the electrical conduction and can be calculated from the slope of the $\log R$ versus $10^3/T$ plot. In the high-temperature range, the electrical activation energy for the as-prepared $Ag_{10}As_{30}Te_{60}$ thin films is about 0.68 eV. At low temperatures, deviations from the linear dependence of $\log R$ versus $10^3/T$ are expected because electron hopping between localized states at the band edges is the dominating mechanism [7–10]. Annealing the samples at different temperatures does not change appreciably the general trend of the R–T curve. At any measuring temperature, the resistance of the annealed sample is lower than that of the as-prepared one.

X-ray diffraction obtained for the as-prepared $Ag_{10}As_{30}Te_{60}$ film did not show any crystalline peaks indicating its amorphous state. Identical evaporated films annealed for 1 h at 100, 150, 175, 200 and 225 °C were X-rayed as shown by the diffractograms of Fig. 2. The film annealed at 100 °C still has the amorphous state, while those annealed at 150 °C and higher temperatures indicate the existence of crystalline phases. The appearance of different crystalline peaks after anneals means that phase separation and crystallization had occurred. Elemental tellurium and binary $AsTe_2$ crystalline phases were identified. The appearance of the As_2O_4 crystalline phase can be related to the oxidation of the chalcogenide film during the evaporation process. Unidentified crystalline peaks could originate from the formation of complex ternary structural units corresponding to ternary compounds of the type $AgAsTe_2$ [5].

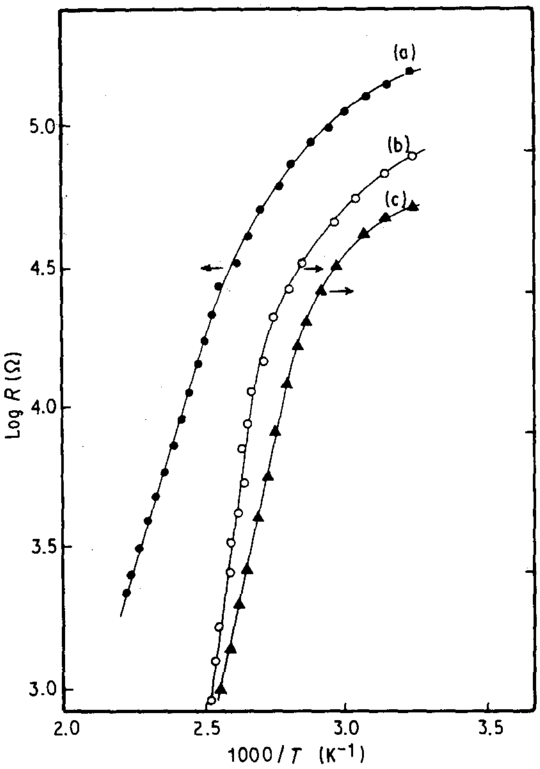

Figure 1 Log R versus $1000/T$ for the $Ag_{10}As_{30}Te_{60}$ film:
(a) as-prepared,
(b) film annealed at 100 °C,
(c) film annealed at 150 °C.

The amount of the crystalline phase was determined in terms of relative intensity I_C–I_G/I_G, where I_C is the peak intensity of the crystalline phase and I_G is the scattering intensity of the glass both determined at the same diffraction angle $2\theta = 29° 12'$; the results are shown in Fig. 3. It is found that the relative amount of the precipitated crystalline phase for $Ag_{10}As_{30}Te_{60}$ film increased with increasing annealing temperature. The same figure also shows the dependence of the activation energy for the electrical conduction on the annealing temperature. Increasing the annealing temperature higher than 150 °C, increases the amount of crystalline phases embedded in the chalcogenide glass and, consequently, decreases the activation energy for the electrical conduction.

Absorbance of the as-prepared and annealed $Ag_{10}As_{30}Te_{60}$ films versus the energy of the incident

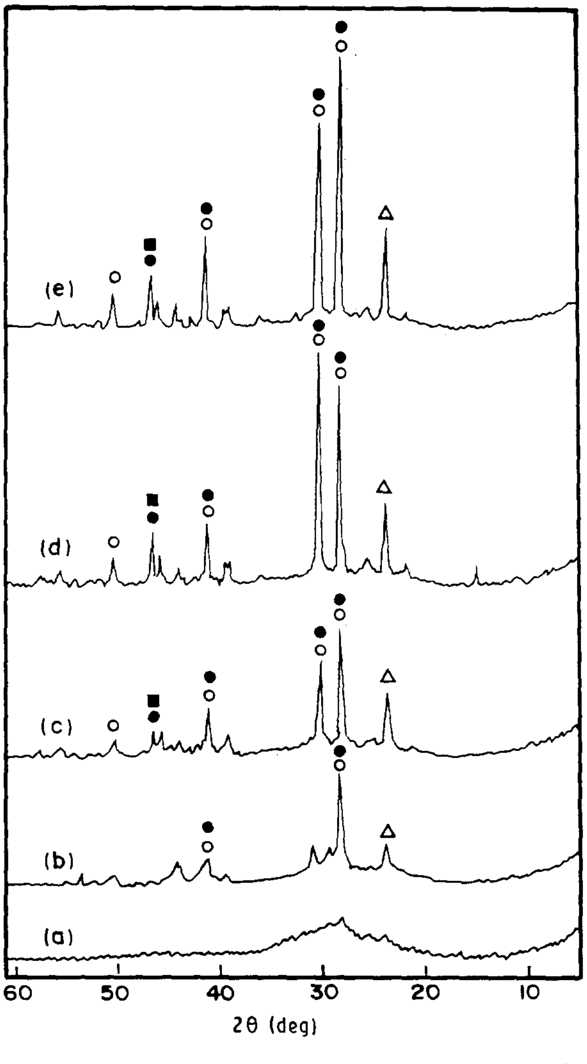

Figure 2 X-ray diffractograms for the $Ag_{10}As_{30}Te_{60}$ film annealed at (a) 100 °C, (b) 150 °C, (c) 175 °C, (d) 200 °C and (e) 225 °C. (○) As_2O_4, (●) $AsTe_2$, (■) Te, (△) unidentified.

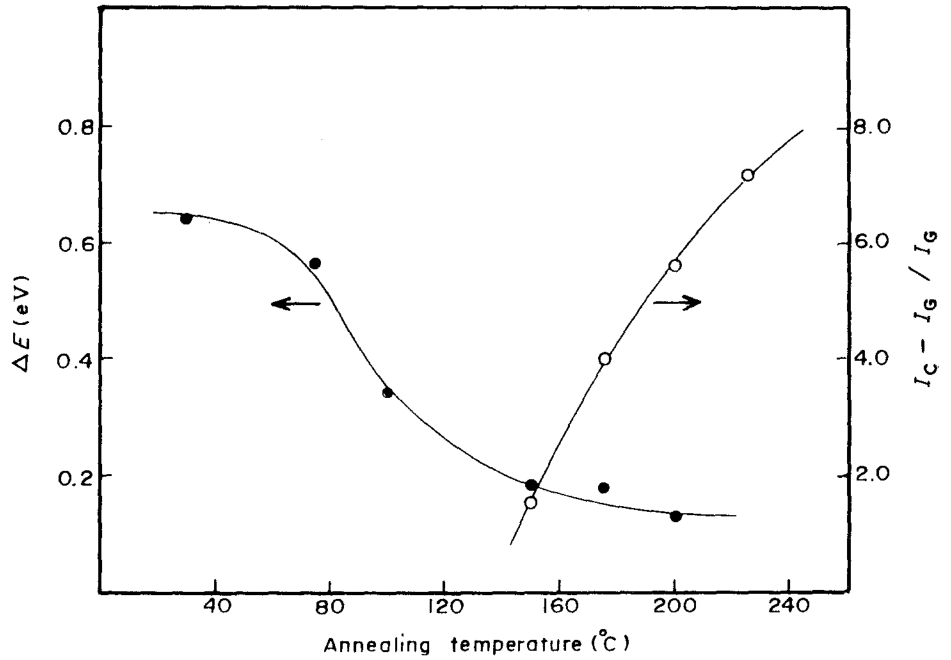

Figure 3 The dependence of (●) the activation energy for conduction, ΔE, and (○) the relative amount of the precipitated crystalline phase, $I_C - I_G/I_G$, on the annealing temperature of the $Ag_{10}As_{30}Te_{60}$ thin film.

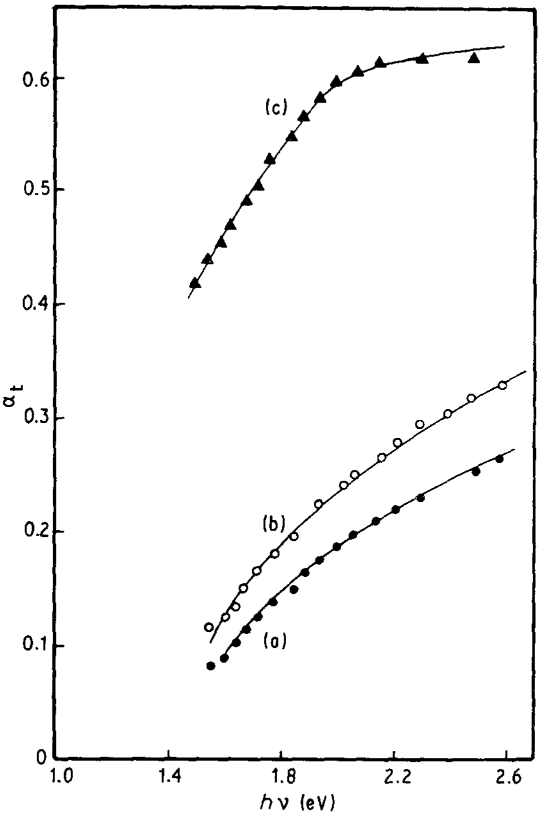

Figure 4 Optical absorbance versus photon energy relation of the (a) as-prepared film, (b) film annealed at 100 °C, (c) film annealed at 150 °C.

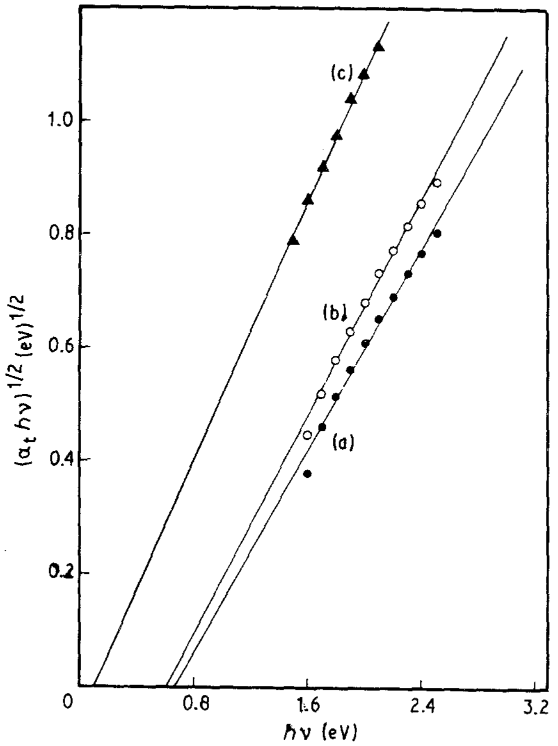

Figure 5 Plots of $(\alpha_t h\nu)^{1/2}$ versus $h\nu$ for (a) as-prepared film, (b) film annealed at 100 °C, (c) film annealed at 150 °C.

light curves are shown in Fig. 4. It is easily seen that the film absorbance depends on the energy of the incident photons in addition to the annealing temperature. Generally, it is well known that the amorphous films are more transparent than the crystalline ones [11, 12]. Therefore, the increase in the absorbance value of the chalcogenide film after anneals can be related to some transformations from glassy structure to crystalline phases.

The absorbance data were then replotted in the form of $(\alpha_t h\nu)^{1/2}$ versus $h\nu$ as shown in Fig. 5. The intercept of the straight line section of such plots with the energy axis gives the optical band gap, E_{opt}. This method has been suggested by Tauc [13] for amorphous semiconductors, for which K conservation is not an important selection rule. It is obvious that the fundamental absorption edge moves to lower energies with increasing annealing temperature.

A decrease in the optical band gap of the amorphous film can be caused by the increased tailing of the conduction band edge into the gap due to environmental contaminations during heat treatments [14]. On the other hand, the growth of the crystallization phases with increasing annealing temperature can lead to an increase in the film optical band gap. In the present work, the observed decrease in the film optical band gap after heat treatments can be interpreted by the higher effect of the environmental contaminations over that of the crystallization phases on the optical properties of the $As_{10}Te_{10}S_{80}$ chalcogenide films.

4. Conclusion

Crystallization phases resulting from heat treatments of the $Ag_{10}As_{30}Te_{60}$ chalcogenide glass were responsible for the decrease of the activation energy for the electrical conduction. On the other hand, the film optical band gap was controlled by two conflicting mechanisms: crystallization and environmental contaminations.

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