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OPTICAL PROPERTIES OF $AgBiS_2$ THIN FILMS

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Thin films of $AgBiS_2$ were prepared by thermal evaporation in vacuum (at about 10^{-6} mbar). X–ray diffraction was used to determine the structural properties of the sample. The as–deposited films (at 300 K) were amorphous in nature and an amorphous–to–crystalline transition could be obtained by thermal annealing at 373 K. The degree of crystallinity increased with increasing temperature from 373 to 473 K. At 525 K, two–phase films with $AgBiS_2$ as a major phase were formed. Optical constants of amorphous and crystalline $AgBiS_2$ thin films were measured after various heat treatments. The analysis of optical absorption spectra revealed the existence of three optical transition mechanisms; allowed direct, forbidden direct and indirect transition, with optical energy gaps $E_d = 2.88$ eV, $E_f = 2.04$ eV and $E_i = 1.78$ eV at 300 K. These values were found to decrease at higher annealing temperatures.

1. Introduction

In recent years, the number of published papers on ternary thin films of various types, such as $A^{I}B^{III}C_2^{VI}$, $A^{II}B^{III}C_4^{VI}$, $A^{II}B^{IV}C_2^{V}$ and $A^{V}B^{VI}C^{VII}$, have increased remarkably. Considerable efforts have been invested to gain a better and deeper understanding of electronic, electrical and optical properties of these compounds. Little attention is paid to the compounds of the type $A^IB^VC_2^{VI}$ [1–4] including $AgBiS_2$. According to our knowledge, no studies have been published on the structure and optical properties of $AgBiS_2$ thin films and on the effect of heat treatment on these properties.

In the present work, the absorption coefficient (α), the optical energy gaps (E_d, E_f and E_i), the refractive index (n) and the dielectric constants ϵ' and ϵ'' were determined. The effect of annealing temperatures on these constants was also studied.

2. Experimental details

$AgBiS_2$ material was prepared by direct fusion of stoichiometric amounts of Ag, Bi and S (purity 99.9999%) in a sealed, evacuated silica tube (at 10^{-6} mbar). The tube was heated at 1100 K for 10 hours with continuous vibrational shaking to ensure homogeneity of the sample. The tube was gradually cooled to room temperature to obtain polycrystalline $AgBiS_2$. Thin films of amorphous $AgBiS_2$ were prepared by direct thermal evaporation of fine grained powder, from a molybdenium boat, on to ultrasonically–cleaned glass substrates under vacuum (at 10^{-6} mbar), using a Leybold Heraeus Univex–300 coating unit. The substrates were rotated during the deposition process. Multiple–beam Fizeau fringes [5] were used for measuring the film thickness. A Philips Pw 1373 X–ray diffractometer, using Cu radiation ($\lambda = 1.542 \times 10^{-10}$ m), operated at 35 kV and 20 mA, was used to investigate the structure. X–ray diffraction patterns were recorded automatically with a scanning rate of 2 deg/min in the scanning angular range 4–90°. The elemental compositions of $AgBiS_2$ crystals and thin films were determined by using atomic absorption GBC model 980 and Perkin Elmer model 1100 instruments. The transmittance T and the reflectance R at normal incidence for $AgBiS_2$ films were recorded using UV VIS NIR spectrophotometer type Schimatzu 3100 in the spectral range 500–2500 nm.

3. Results and discussion

The X–ray diffraction pattern of the prepared $AgBiS_2$ in powder form is shown in Fig. 1. Analysis of this pattern shows the polycrystalline nature of the cubic structure phase with $a = 5.646 \times 10^{-10}$ m. The values of the peak positions and their corresponding d values are in good agreement with the spacing reported in the A.S.T.M. card [6].

Typical X–ray diffraction patterns of the as–deposited (300 K) $AgBiS_2$ film of thickness 200 nm and that annealed in vacuum (at 10^{-3} mbar) for 1 hour at different annealing temperatures (373, 423, 473 and 525 K) are shown in Fig. 2. As can be seen from this figure, the as–deposited film (300 K) is amorphous in nature, whilst films heat treated at 373, 423 and 473 K are polycrystalline. It was found that the degree of crystallinity increases with increasing annealing temperature. Also, it is clear that the ternary $AgBiS_2$ film annealed at 525 K dissociates into two binary phases, namely α–Ag_2S and BiS_2, where $AgBiS_2$ was the major phase. X–ray and compositional analysis studies on the prepared $AgBiS_2$ powder, the as–deposited films and the corresponding annealed (at 373 and 473 K) films indicate that the composition was not perturbed during evaporation.

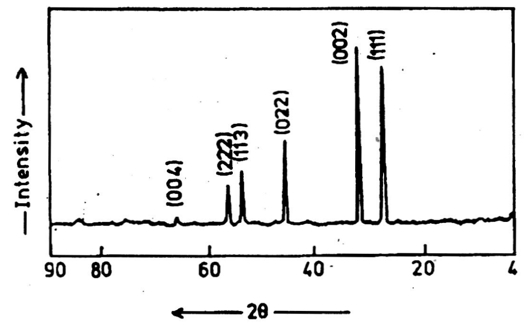


Fig. 1. X–ray diffraction pattern of the prepared $AgBiS_2$ *in powder form.*

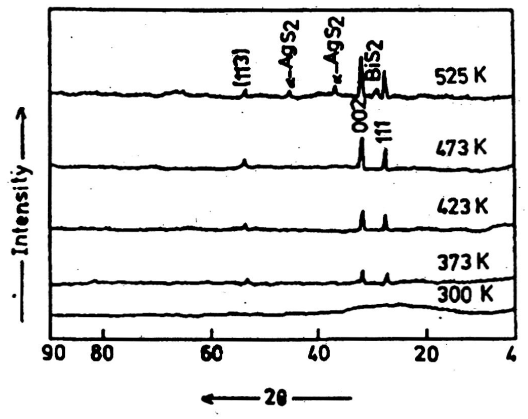
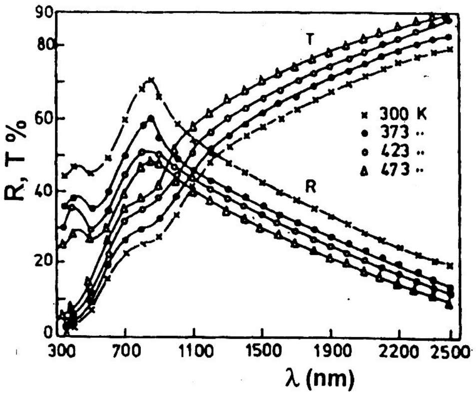


Fig. 2. X–ray diffraction patterns of $AgBiS_2$ *films of thickness* 200 nm*, annealed at different temperatures.*

To study the optical properties of $AgBiS_2$ thin films, the dependence of both transmittance (T) and reflectance (R) at normal incidence on wavelength, in the spectral range from 500 to 2500 nm, was recorded for $AgBiS_2$ films of the same thickness (200 nm). Figure 3 shows representative curves of transmittance and reflectance for the as–deposited (300 K) $AgBiS_2$ films and for films annealed in vacuum at different temperatures (373, 423 and 473 K). The absorption coefficient (α) could be calculated using the measured values of R and T from the relation [7]

$$T = \frac{(1 - R^2)\exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)},$$

where d is the thickness of the film.



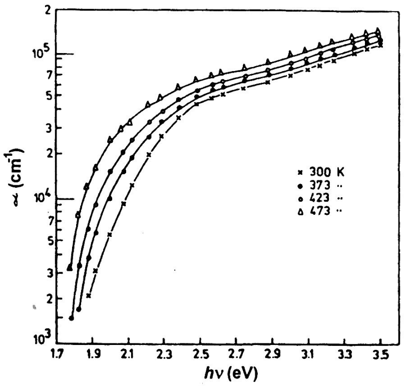
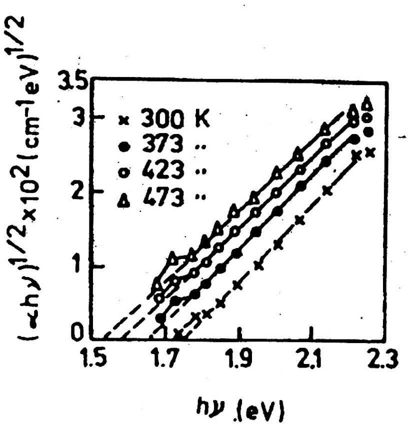


Fig. 3. Dependence of transmittance T and reflectance R on wavelenght λ for $AgBiS_2$ *thin films annealed at different temperatures.*

Fig. 4. Dependence of the absorption coefficient α of $AgBiS_2$ *films annealed at different temperatures on photon energy (right).*



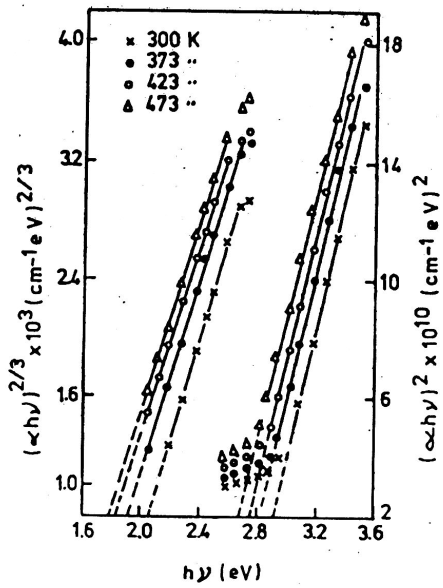


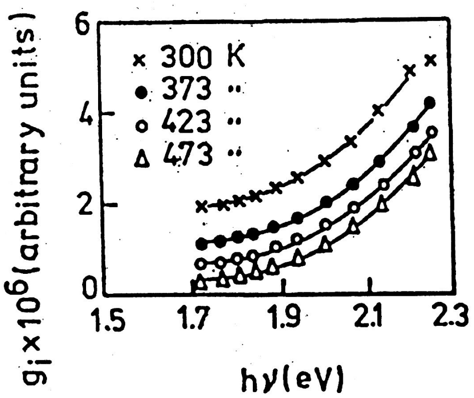
Fig. 5. Dependence of $(\alpha h\nu)^{1/2}$ *for* $AgBiS_2$ *thin films annealed at different temperatures on photon energy (left figure).*

Fig. 6. Dependence of $(\alpha h\nu)^{2/3}$ *and* $(\alpha h\nu)^2$ *of* $AgBiS_2$ *films annealed at different temperatures on photon energy (right figure). Left ordinate applies to the left set of four groups of data and the right ordinate to the right set.*

Figure 4 presents the variation of the absorption coefficient (α) with photon energy ($h\nu$) for these films. It is clear from this figure that all curves are characterized by the presence of three distinct absorption regions, possibly corresponding to three absorption mechanisms. It was found that the absorption coefficient for the $AgBiS_2$ films can be described by the relation

$$\alpha h\nu = A(h\nu - E)^p$$

where A is constant and p determines the type of transition. We found, $p = 2$ for the photon energy range $h\nu = 1.65 - 2.25$ eV, indicating indirect transition, $p = 2/3$ for the range of $h\nu = 2.25 - 2.75$ eV, indicating forbidden direct transition and $p = 1/2$ for the range of $h\nu = 2.75 - 3.55$ eV, indicating allowed direct transition [8]. For indirect, forbidden and allowed direct transitions, the energy gaps were determined by plotting $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^{2/3}$ and $(\alpha h\nu)^2$ as a functions of photon energy $h\nu$. Figures 5 and 6 show the variation of $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^{2/3}$ and $(\alpha h\nu)^2$ with the photon energy $h\nu$ for the as–deposited and for the heat treated films. The intercept of the extrapolations to zero absorption with the photon energy axis are taken as the values of the indirect, forbidden and allowed direct energy gaps E_i, E_f and E_d, respectively. It is clear from this figure that E_i decreases from 1.78 to 1.56 eV, E_f decreases from 2.04 to 1.79 eV and E_d decreases from 2.88 to 2.67 eV, with increasing the temperature of heat treatment from 300 to 473 K. The decrease in the indirect and direct energy gaps with increasing annealing temperature may be due to the broadening of electron and hole energy levels which results from the scattering of electrons and holes. Figure 7 shows the variation of the valence band density of states g_i [9] with photon energy $h\nu$ for $AgBiS_2$ films annealed at different temperatures.



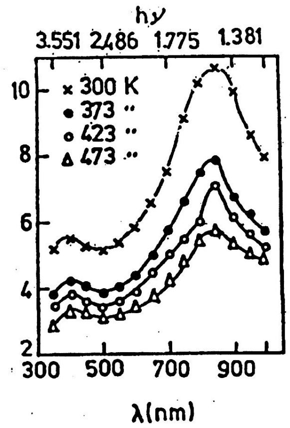


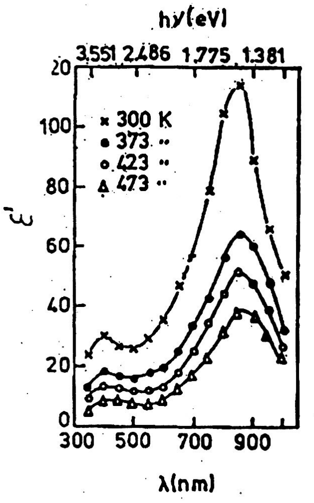
Fig. 7. Dependence of g_i of $AgBiS_2$ *thin films annealed at different temperatures on photon energy.*

Fig. 8. Dependence of n of $AgBiS_2$ *thin films annealed at different temperatures on photon energy (right).*

From the reflection (R) and extinction coefficient $k = \alpha\lambda/4\pi$, the refractive index (n) can be calculated using the relation

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}.$$

Figures 8, 9 and 10 show the dispersion curves of the refractive index n and the dielectric constants $\epsilon' = n^2 - k^2$ and $\epsilon'' = 2nk$ for the as–deposited $AgBiS_2$ thin films and for the films annealed in vacuum at different temperatures. It is clear from the curves that the general behaviour of these constants is the same for all films annealed at different temperatures. The high frequency refractive index n decreases from 8 to 5.9 when increasing the annealing temperature, which may be due to the change in the film structure.



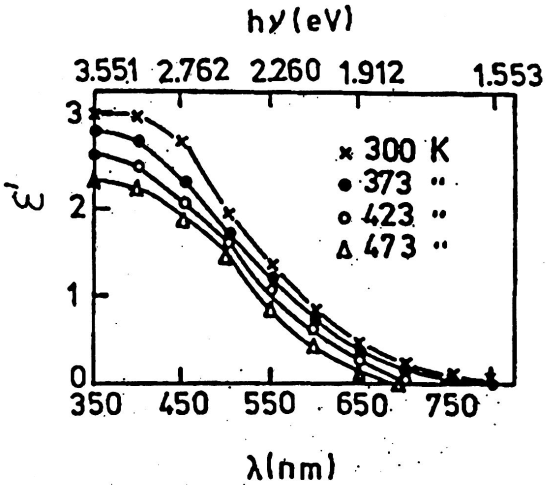


Fig. 9. Dependence of ϵ' of $AgBiS_2$ *thin films annealed at different temperatures on photon energy.*

Fig. 10. Dependence of ϵ'' of $AgBiS_2$ *thin films annealed at different temperatures on photon energy (right).*

4. Conclusions

It is concluded that the optical absorption spectra of $AgBiS_2$ thin films annealed at different temperatures revealed the existence of indirect, allowed and forbidden direct transitions. The derived values of the energy gaps were found to decrease with increasing annealing temperatures.

It can be also concluded that the as–deposited thin films of $AgBiS_2$ are amorphous in character, while films heat treated at higher temperatures are polycrystalline. At 525 K, two–phase films with $AgBiS_2$ as the major phase were formed.

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OPTIČKA SVOJSTVA TANKIH SLOJEVA $AgBiS_2$

Tanki slojevi $AgBiS_2$ načinjeni su naparavanjem u vakuumu pri tlaku 10^{-6} mbar. Strukturna svojstva određena su rendgenskom difrakcijom. Svježe pripremljeni slojevi (na 300 K) su amorfni. Prijelaz u kristalinično stanje postignut je toplinskim opuštanjem na 373 K. Stupanj kristaliničnosti se povećavao zagrijavanjem od 373 na 473 K. Na 525 K nastali su dvofazni slojevi u kojima je glavna faza bila $AgBiS_2$. Mjerena su optička svojstva amorfnih i kristaliničnih tankih slojeva $AgBiS_2$ nakon raznih toplinskih obrada. Analiza optičkih apsorpcijskih spektara pokazuje djelovanje triju procesa: izravnog i dozvoljenog, izravnog i zabranjenog te neizravnog, s energijskim procijepima $E_d = 2.88$ eV, $E_f = 2.04$ eV i $E_i = 1.78$ eV na 300 K. Te se vrijednosti smanjuju za više temperature opuštanja.