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Optical properties of ternary $AgSbS_2$ thin films

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Abstract. Structural and optical properties of amorphous and crystalline ternary $AgSbS_2$ thin films as well as the effect of annealing temperature on these properties have been investigated. From the study of x-ray diffraction patterns, it is clear that the as-deposited films (300 K) are amorphous in nature, whilst those heat treated under vacuum at moderate temperatures (373 K) for 1 h have been transformed from the amorphous structure to a crystalline structure and the crystallinity increases with increasing temperature. At 500 K a new crystalline plane, (200), appears, characteristic of the binary α-AgS_2 besides $AgSbS_2$.

The optical constants, absorption coefficient α, reflective index n, optical energy gap E_g, valence band density of states g_i and dielectric constants ε' and ε'', were computed for amorphous and crystalline $AgSbS_2$ films of thickness 169 nm. The analysis of the absorption coefficient data revealed the existence of two optical transition mechanisms, indirect and direct transitions, depending on the value of wavelength range. These energy gaps were found to have the values (1.38–1.17 eV) and (2–1.77 eV) in the temperature range from 300 to 473 K for indirect and direct energy gaps respectively.

1. Introduction

The $AgSbS_2$ compound has potential use for a wide variety of applications. Pyrargyite (Ag_3SbS_3) is a very promising material for non-linear optics (Nikogosyan 1977, Bardsley *et al* 1969) and moreover, it exhibits piezoelectric (Morozovskii 1981) and pyroelectric (Semak *et al* 1975) properties. However, the optical properties of pyrargyrite have been largely neglected and the limited available information is some what contradictory. The preparation (Valyukenas *et al* 1979) and crystal structure of α-$AgSbS_2$ have been investigated (Davies *et al* 1969, Alekseeva *et al* 1978, Rice *et al* 1974). The results of a spectroscopic analysis indicated that the concentration of impurities in this crystal did not exceed 10^{-2}%. The dependence of the electrical conductivity of α-$AgSbS_2$ crystals was $\sigma = 6.3 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$ and increased exponentially with rising temperature at a rate corresponding to an activation energy of $\Delta E = 0.89$ eV. Near $T = 476$ K there was an anomaly of σ and a change in the activation energy. At $T > 476$ K, they found that this energy was $\Delta E = 1.64$ eV. From the study of the current–voltage characteristics, they found that at room temperature the ionic conduction mechanism appeared in α-$AgSbS_2$ crystals in fields above the critical value $E_c \geqslant 280\ V\ cm^{-1}$; the electronic component of the conductivity in fields $E \geqslant E_c$ at $T = 300$ K was 32%. In a field $E = E_s$ (E_s was called the switching field) there was S-type switching of α-$AgSbS_2$ from a high-resistivity to a low-resistivity state. At $T = 300$ K, the switching field was $E_s = 2.2 \times 10^3\ V\ cm^{-1}$. The structure and optical properties of $AgSbS_2$ thin film and the effect of heat treatment on these properties have not been yet investigated. It is, therefore, of interest to investigate the structure and optical properties of $AgSbS_2$ thin films.

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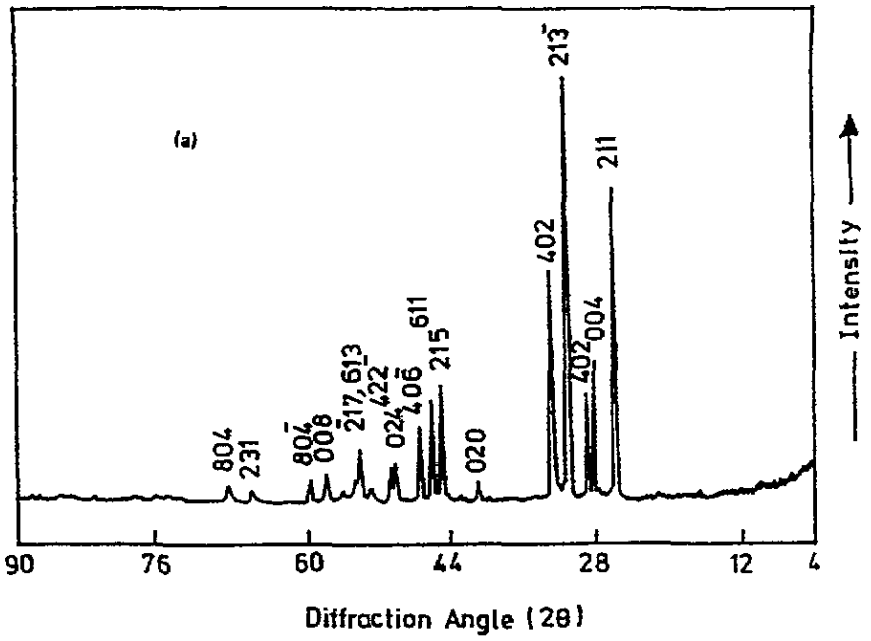

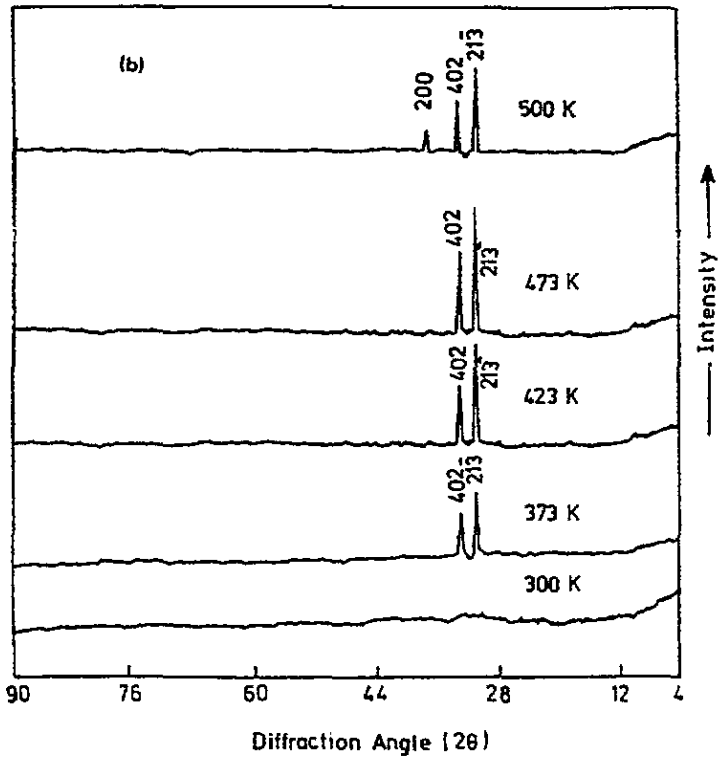

Figure 1. The obtained XRD (a) powder and (b) thin films annealed in vacuum at 473 K for 1 h.

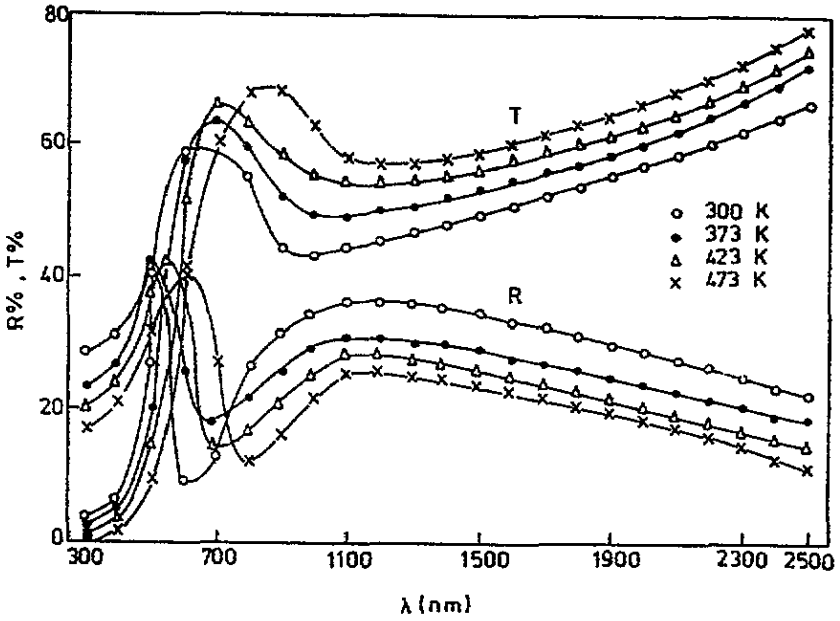

Figure 2. The spectral distribution of both T and R for $AgSbS_2$ thin films for different annealing temperatures.

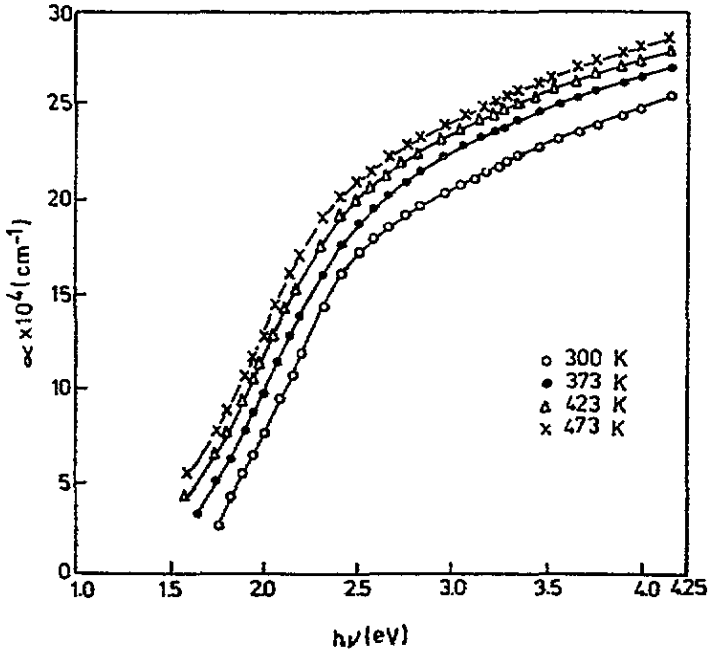

Figure 3. The absorption coefficient α as a function of photon energy $h\nu$ for $AgSbS_2$ thin films for different annealing temperatures.

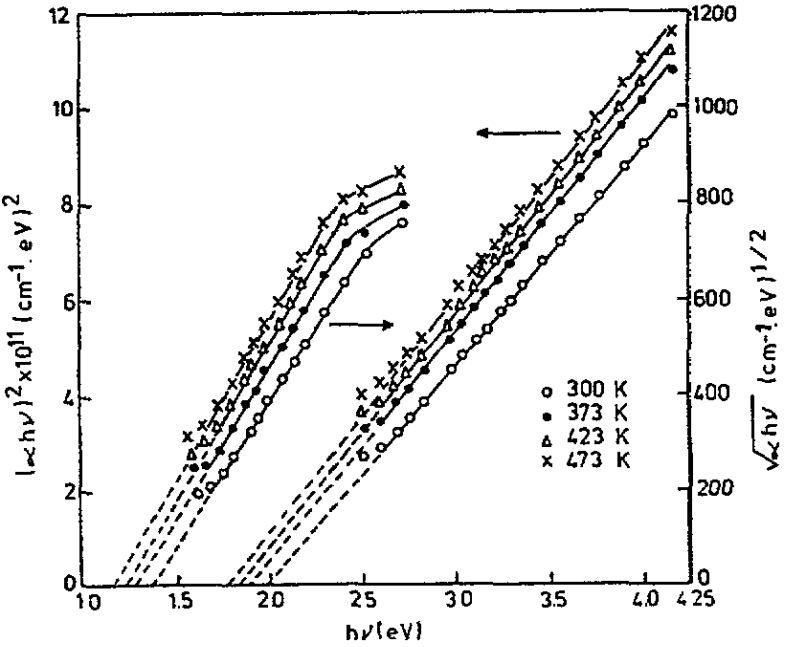

Figure 4. $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ against photon energy $(h\nu)$ for $AgSbS_2$ thin films for different annealing temperatures.

2. Experimental procedure

$AgSbS_2$ has been prepared by direct fusion of a mixture of silver, antimony and sulphur (purity, 99.9999%) for 24 h at 900 °C in a sealed, evacuated (10^{-6} Torr) silica tube. The tube was shaken throughout the melting operation to ensure mixing of the elements. The temperature was then reduced gradually to room temperature to obtain crystalline $AgSbS_2$. Thin films of $AgSbS_2$ were prepared by direct thermal evaporation of fine-grained powder from a molybdenum boat on ultrasonically clean glass substrates under vacuum (10^{-6} Torr) using a Leybold Heraeus-Univex 300 coating unit. The substrates were rotated during the deposition process. The deposition rate was fixed at 10 nm s^{-1} and was kept the same for all the films investigated. The thickness of the films was measured using multiple-beam interferometric methods. X-ray diffraction (XRD) patterns were obtained for samples in the powder form and thin films by x-ray diffractometry (Philips PW 1373) with a nickel filter and copper target. The transmission T and the reflection R at normal incidence for $AgSbS_2$ films were recorded using a UV–VIS–NIR UV 3101 PC Schimadzu (Japan) spectrophotometer in the spectral range 300–2500 nm. The optical absorption coefficients α of $AgSbS_2$ films heat treated in vacuum (10^{-3} Torr) at 373, 423 and 473 K for 1 h were measured. The valence band density of states was calculated in the same manner as that for InSe (Kenawy *et al* 1991). The results shown in this work are the mean values of five samples under the same conditions.

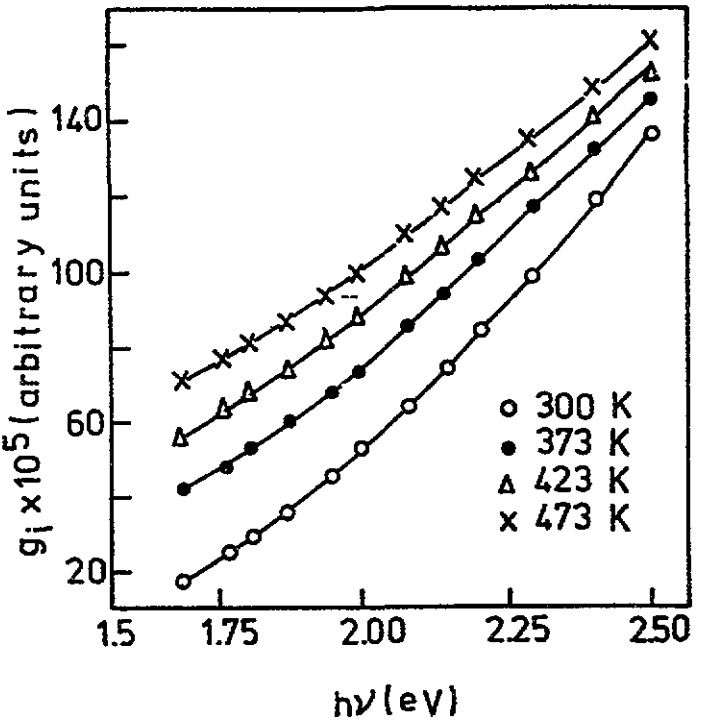

Figure 5. Density of states (g_i) as a function of photon energy ($h\nu$) for $AgSbS_2$ thin films for different annealing temperatures.

3. Results and discussion

3.1. Structural properties

The recorded typical XRD patterns of the prepared $AgSbS_2$ in powder form and the as-deposited films annealed in vacuum at different temperatures are shown in figure 1. Analysis of the obtained patterns shows the crystalline nature of the monoclinic structure. The calculated lattice constants were found to be $a = 13.2$ Å, $b = 4.4$ Å and $c = 12.86$ Å. These results are in good agreement with the results obtained by Graham (1951). It is observed from figure 1(b) that the as-deposited $AgSbS_2$ thin films of thickness 169 nm are amorphous, whilst those heat treated under vacuum at moderate temperatures (373 K) for 1 h are transformed from the amorphous structure to crystalline structure with preferred orientation for the crystalline planes $(21\bar{3})$ and (402) and the degree of crystallinity increases with increasing annealing temperature (373–473 K). A new crystalline plane, (200), appears in the XRD at 500 K, which is characteristic of α-AgS_2.

3.2. Optical properties

The most accurate method for determining the energy band structure of semiconductors is based on investigation of the spectral distribution of both the reflective index n and the absorption index k and hence the absorption coefficient α. To investigate the effect of the annealing temperature on $AgSbS_2$ thin films, the transmission T and the reflection R at normal incidence in the spectral range 300–2500 nm were measured for thin films of thickness 169 nm, subjected to different annealing temperatures (300, 373, 423 and 473 K) for 1 h under a vacuum of 10^{-3} Torr, and are illustrated in figure 2.

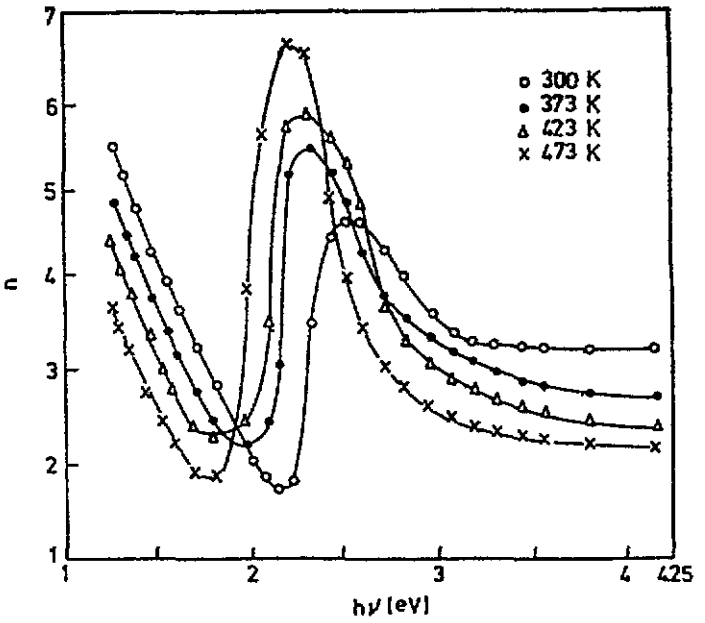

Figure 6. n as a function of photon energy ($h\nu$) for $AgSbS_2$ thin films for different annealing temperatures.

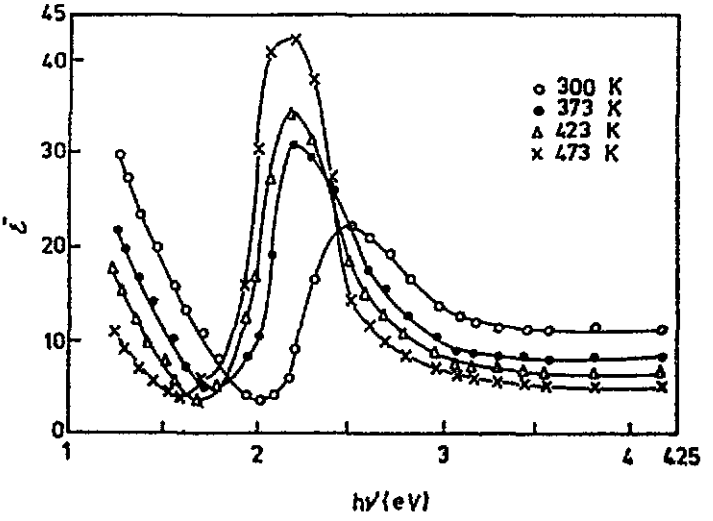

Figure 7. ε' as a function of photon energy ($h\nu$) for $AgSbS_2$ thin films for different annealing temperatures.

The optical absorption coefficient α for the as-deposited and heat-treated films was calculated using the following equation (Pankove 1971):

$$T = (1 - R)^2 e^{-\alpha d} / 1 - R^2 e^{-2\alpha d}$$

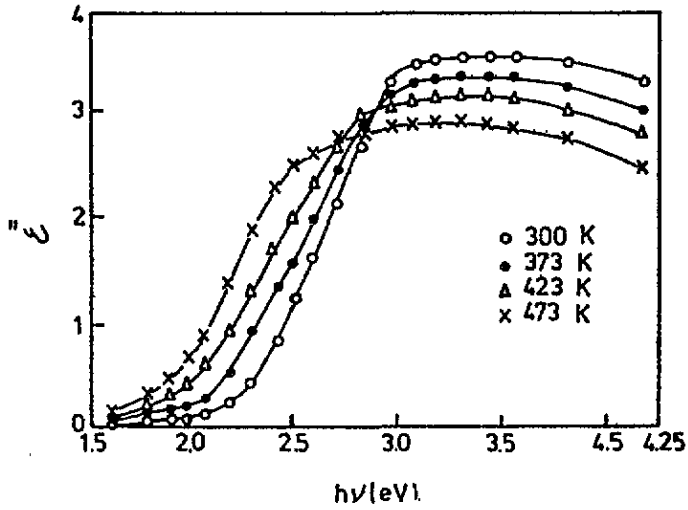

Figure 8. ε'' as a function of photon energy ($h\nu$) for $AgSbS_2$ thin films for different annealing temperatures.

where d is the thickness of the film.

The optical absorption coefficient for these films is illustrated in figure 3 and is found to obey the relation $(\alpha h\nu) = A(h\nu - E_g^{opt})^{1/2}$ for a direct transition (Brook 1955, Bardeen *et al* 1956) in the region of high photon energy.

The plot of $(\alpha h\nu)^2$ against photon energy $h\nu$ for the tested thin films is shown in figure 4. The calculated values of the direct optical energy gaps E_g^d of $AgSbS_2$ films are found to decrease from 2.0 eV to 1.77 eV on increasing the annealing temperature from 300 to 473 K. At low photon energies, the optical absorption coefficients for these films were found to obey the relation $(\alpha h\nu) = A(h\nu - E_g^{opt})^2$ for an indirect transition (Moss 1973). The plot of $(\alpha h\nu)^{1/2}$ against photon energy $h\nu$ for the tested thin films is shown in figure 4. The relations are found to be identical in character and indicate tailing of the absorption coefficient towards low photon energies; this tail may be due to the amorphous state of the material or to the broadening of the impurity band, which extends into the forbidden gap (Moss 1973). The calculated values of the indirect optical energy gaps E_g^i of $AgSbS_2$ films are found to decrease from 1.38 eV to 1.17 eV on increasing the annealing temperature from 300 to 473 K. The decrease of the band gap with temperature may be due to the broadening of electron and hole energy levels, which results from the scattering of electrons and holes. Figure 5 shows the variation of valence band density of states g_i with photon energy $h\nu$ for $AgSbS_2$ films annealed at different temperatures. We see from this figure that all the curves have similar behaviour and g_i increases with increasing annealing temperature. From the reflection R and extinction coefficient, the reflective index can be calculated by using the relation

$$R = [(n-1)^2 + K^2]/[(n+1)^2 + K^2].$$

Figures 6–8 show the dispersion curves of the reflective index n and the dielectric constants $\varepsilon' = n^2 - k^2$ and $\varepsilon'' = 2nk$, respectively, for $AgSbS_2$ thin films annealed in vacuum at different annealing temperatures. It is clear that n, ε' and ε'' at a given photon energy decrease with decreasing annealing temperature; this may be attributed to the effect of the degree of crystallinity.

4. Conclusion

$AgSbS_2$ films have monoclinic structure. The as-deposited thin films of $AgSbS_2$ are amorphous in character, while those heat treated at moderate temperatures are crystalline and at 500 K a new crystalline plane, (200), characteristic of the binary α-AgS_2 appears besides $AgSbS_2$; it can also be concluded that $AgSbS_2$ has two optical transition mechanisms, direct and indirect transitions, and the optical energy gap E_g^d and E_g^i values decrease with increasing annealing temperature.

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