

OPTICAL ABSORPTION IN ANNEALED TIN SULPHIDE THIN FILMS

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ABSTRACT

Evaporated tin sulphide thin films have been prepared onto glass substrate at room temperature. The films were subjected to long period annealing in running argon gas up to 36 hours. Optical absorption measurements were made on the as prepared and annealed films near the fundamental absorption edge over the visible light regions. Absorption coefficient, α were found to be of the order 10^5 cm^{-1} which suggest the occurrence of indirect optical transition. A further investigation on the $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ plots revealed the existence of indirect allowed and indirect forbidden transitions near the absorption edge, respectively. The resulting optical band gap of the former were found to be 1.33 eV (as prepared) and between 1.59 - 2.01 eV (annealed films) and these values were associated with compositional changes during annealing; the mainly SnS stoichiometric composition of the as prepared films was gradually disproportionated to SnS_2 and completion of the course took place at the end of 20 hours annealing. The optical band gap of 2.01 eV was in a good agreement with those measured earlier on SnS_2 in both thin film and bulk forms.

1-INTRODUCTION

Tin-sulphur compounds comprise mainly of SnS, SnS_2 , Sn_2S_3 and Sn_3S_4 compositions, depending on the formation temperature and percentage of the constituents. SnS and SnS_2 were found to be the most stable compounds with regard to their melting points of $855 \pm 5^\circ\text{C}$ and percentage of the sulphur atoms between 10 - 48% and 68 - 95%, respectively, as indicated in the phase diagram of Sn-S system.^[1] See Figure 1. These, together with their transparent and conducting properties attracted many researchers to study the various aspects of the materials, in particular the thin film form.

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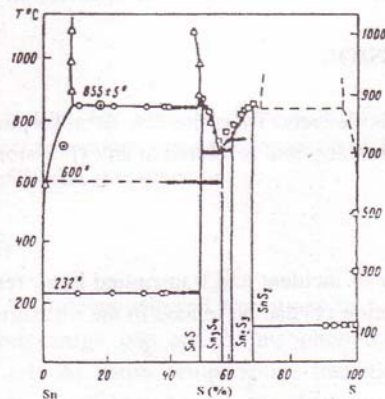


Figure 1. Phase diagram of Sn-S system.^[1]

Tin sulphide (SnS) and tin disulphide (SnS₂) belong to the IV - VI chalcogenide compounds which crystallize in different structures. The unit cell of the former is orthorhombic (D_{2h}¹⁶) with lattice parameter $a = 0.398$ nm, $b = 0.433$ nm and $c = 1.118$ nm.^[2] The latter comprises of tin atoms sandwiched between two close-packed sheets of sulphur atoms which crystallized in hexagonal structure according to CdI₂, C-6 type^[3]. Most of the studies on SnS and SnS₂ thin films were made separately, based on the structural, electrical and optical properties; these were noticeably reported by Deraman *et al.*^[4-6] and Lokhande^[7] and Abbas *et al.*^[8] Earlier studies on the SnS-SnS₂ transformation were due to the work of Grozdanov *et al.*^[9] whom they detected SnS₂ composition in the chemically prepared SnS thin films annealed at 280°C for 24 hours. Recently, Sakrani and Ismail^[10] reported the effects of long period annealing on the structural properties of evaporated SnS thin films. The present work reports the optical absorption of these films subjected to long period of annealing.

2. EXPERIMENTAL

SnS thin films were prepared from granules of 6N purity supplied by High Purity Chemetal, Japan. The material was thermally evaporated onto previously cleaned glass substrates at a pressure of 8×10^{-4} mbar at a deposition rate of 0.2 nms^{-1} and at room temperature. During the deposition, film thickness was carefully monitored using a conventional quartz crystal monitor. After deposition, a measurement using an ellipsometer was made and a further computer calculation (iteration technique) to confirm the accuracy of this film thickness, with all the films fixed at 71 nm.

The transmittance and absorption were measured using a UV Hitachi Spectrophotometer within the wavelength regions of 300 - 900 nm. An uncoated glass substrate was used as a reference during measurements to eliminate any possible influence of the substrate. The procedures were repeated at least on three samples for justification of the results.

3. RESULTS AND DISCUSSION

Absorption coefficient, α was deduced from the law of absorption of light incident at right angle to the transparent surface, and is related to an expression,

$$I = I_0 \exp(-\alpha d) \quad \dots\dots\dots(1)$$

where I and I_0 are the intensity of incident and transmitted light, respectively, and d is the thickness of the sample. Equation (1) can be related to the measured transmittance, T and reflectance, R according to⁽¹¹⁾

$$T = (1 - R)^2 \exp(-\alpha d) \quad \dots\dots\dots(2)$$

with the assumption that $k^2 \ll n^2$ for semiconductors (k and n are the extinction coefficient and refractive index, respectively). The absorption coefficient in equation (2) can be written as,

$$\alpha = \frac{1}{d} \left\{ \ln\left(\frac{1}{T}\right) + \ln(1 - R)^2 \right\} \quad \dots\dots\dots(3)$$

For high absorption material, $R \ll 1$, and therefore the second terms of equation (3) can be neglected. Thus, α is a function of d and T which replaces the ratio I/I_0 in equation (1) as,

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right) \quad \dots\dots\dots(4)$$

Another method of determining α is by measuring the absorption, A ($= \log(I_0/I)$) and substituted into equation (1) as follows:

$$\begin{aligned} \alpha &= \frac{1}{d} \{\ln(I_0/I)\} = \frac{1}{d} \{2.303 \log(I_0/I)\} \\ &= 2.303 \frac{A}{d} \quad \dots\dots\dots(5) \end{aligned}$$

where $0.0000 < A < 9.9999$. Equation (5) assumes double reflection at the film-air and substrate-film interfaces and exponential law for the absorption process. It is to be noted

that calculations using equation (4) and (5) results in α which is comparable and only slightly different at higher wavelength (> 750 nm). The photon energy of the incident light, E is given by

$$E = \frac{hc}{\lambda} = \frac{1.242}{\lambda} \text{ eV} \quad \dots\dots\dots(6)$$

where λ is the wavelength in μm . The intrinsic absorption edge of the film has been examined in terms of indirect transitions using the equation of Bardeen *et al.*^[12], which states that the absorption coefficient, α is given by

$$\alpha h\nu = A (h\nu - E_g \pm E_p)^r \quad \dots\dots\dots(7)$$

where A is a constant, $r = 2$ (indirect allowed transition) or $r = 3$ (indirect forbidden transition), E_g is the indirect energy gap and E_p the phonon energy which is either absorbed (+) or emitted (-). At room temperature, transitions both with phonon absorption and phonon emission will contribute to the absorption. For direct transitions the absorption coefficient, α is given by

$$\alpha h\nu = B (h\nu - E_g)^r \quad \dots\dots\dots(8)$$

where B is a constant, and $r = 1/2$ for direct allowed transition or $r = 3/2$ for direct forbidden transition.

The absorption coefficient, α was calculated using equation (4) for selected wavelength and was checked using equation (5), and the results were plotted against photon energy. As can be seen in Figure 2, α increases rapidly with energy in the visible region ranging between 1.5 - 4.0 eV without indication of exponential reduction as may be observed in some semiconductors like Si, Ge and CdTe.^[13] Such a behaviour may suggest the occurrence of single interband transition process, namely an indirect optical transition. For the as prepared films α varies between $8 - 80 \times 10^4 \text{ cm}^{-1}$, representing the SnS stoichiometric composition. In the case of annealed films, however, these ranges are slightly lowered ($2 - 70 \times 10^4 \text{ cm}^{-1}$) and show a parallel shift to the higher photon energy as SnS₂ formation is accumulated, noticeably after 20 hours annealing. These results are consistent with those reported by Kawano *et al.*^[14] They obtained α in the range $1 - 30 \times 10^4 \text{ cm}^{-1}$ for evaporated SnS₂ maintained at substrate temperatures between 343 - 600°C, and the absorption edge was due to an indirect forbidden transition of energy about 1.93 eV.

The intrinsic absorption edge was examined using equations (7) and (8) by choosing appropriate values of r in order to obtain the suitable transition of electron from the valence to conduction bands, as well as the optical band gap, E_g . Both $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ functions when plotted against photon energy, E gave straight line fit which

correspond to E_g by the extrapolation of this line and intercept at energy axis. All the graphs shown in Figure 3 (as prepared) and Figures 4 to 6 (annealed films) were found to obey both indirect allowed transition ($r = 2$) and indirect forbidden transition ($r = 3$) according to the relationship given in equation (7), with indication of photon band tails caused by the phonon absorption. Attempts using $(\alpha h\nu)^2$ and $(\alpha h\nu)^{2/3}$ functions failed to show such a linearity; suggesting the absence of direct transition leading to the fundamental absorption edge.

Table 1. Optical band gap of the as prepared and annealed SnS thin films

Transition	OPTICAL BAND GAP				
	As prepared (eV)	6 hours (eV)	12 hours (eV)	20 hours (eV) SnS ₂	References (eV) SnS ₂
Indirect allowed $(\alpha h\nu)^{1/2}$	1.33	1.60	1.62	2.01	2.12 ^[15] a 2.07 ^[16] b 2.21 ^[17] b 2.28 ^[8] c
Indirect forbidden $(\alpha h\nu)^{1/3}$	1.62	1.09	1.15	1.50	2.07 ^[15] a 1.93 ^[14] d
Direct allowed $(\alpha h\nu)^2$					2.35 ^[14] d
Direct forbidden $(\alpha h\nu)^{2/3}$					2.88 ^[16] b

a : reactive sputtering **b** : Single crystal
c : Chemical deposition **d** : thermal evaporation

For indirect allowed transition, all the deduced E_g were found to be as follows: $E_g = 1.33$ eV (Figure 3), $E_g = 1.60$ eV (Figure 4), $E_g = 1.62$ eV (Figure 5) and $E_g = 2.01$ eV (Figure 6). Similarly, for indirect forbidden transition, $E_g = 1.62$ eV (Figure 3), $E_g = 1.09$ eV (Figure 4), $E_g = 1.15$ eV (Figure 5) and $E_g = 1.50$ eV (Figure 6). Summary of the results is tabulated in Table 1. The phonon energy, E_p is unable to be determined at this stage of experimental work, but estimated value could be obtained by assuming $E_p \approx kT = 0.026$ eV at room temperature (k and T being the Boltzmann constant and temperature, respectively). It is clear that, from these results, long period annealing causes an increase of optical band gap due to structural changes occurring in the films. Sakrani and Ismail^[10] explained that, evaporated SnS thin films were stoichiometric in nature and temperature dependence; annealing at 310°C for 6, 12 and 20 hours increased the formation of SnS₂

and eventually became the predominant composition. A further longer period of annealing caused an excessive loss of the constituents. The optical band gap of 2.01 eV was found to be within the range 1.93 - 2.28 eV, corresponding to SnS₂ in both thin film and bulk forms. For indirect forbidden transition, the optical band gaps were somewhat beyond the ranges for SnS^[5] and SnS₂^[15-17], and most unlikely to occur in practical application.

4. CONCLUSIONS

Annealed tin sulphide thin films exhibited higher optical absorption within the visible light region. The absorption coefficient at energy range between 1.50 - 4.0 eV were found to be $2 - 80 \times 10^4 \text{ cm}^{-1}$, which were expected for indirect transition. The curves on annealed films showed displacement to the right of photon energy due to changes in composition from SnS to SnS₂. Further investigation on $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ against photon energy plots confirmed the existence of indirect allowed and forbidden transitions, respectively. However, the deduced optical band gaps obtained in the former (1.33 - 2.01 eV) were found to be more acceptable than the latter, and the energy 2.01 eV corresponded to SnS₂ composition. Both absorption coefficient and optical energy gap of the SnS thin films were effected by long period of annealing.

5. ACKNOWLEDGEMENTS

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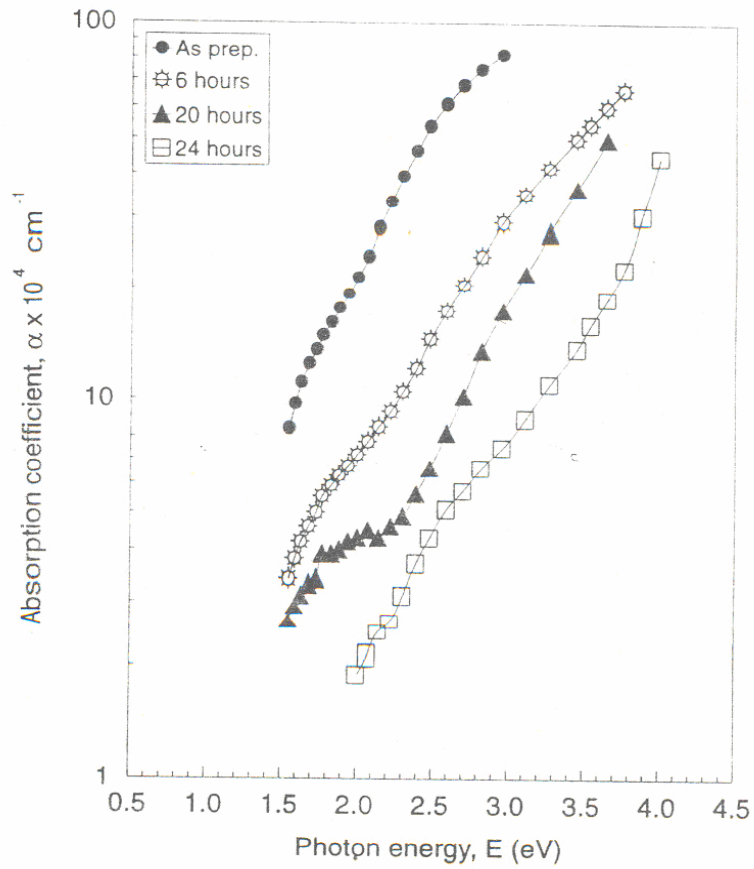


Figure 2. Absorption coefficient, α against photon energy.

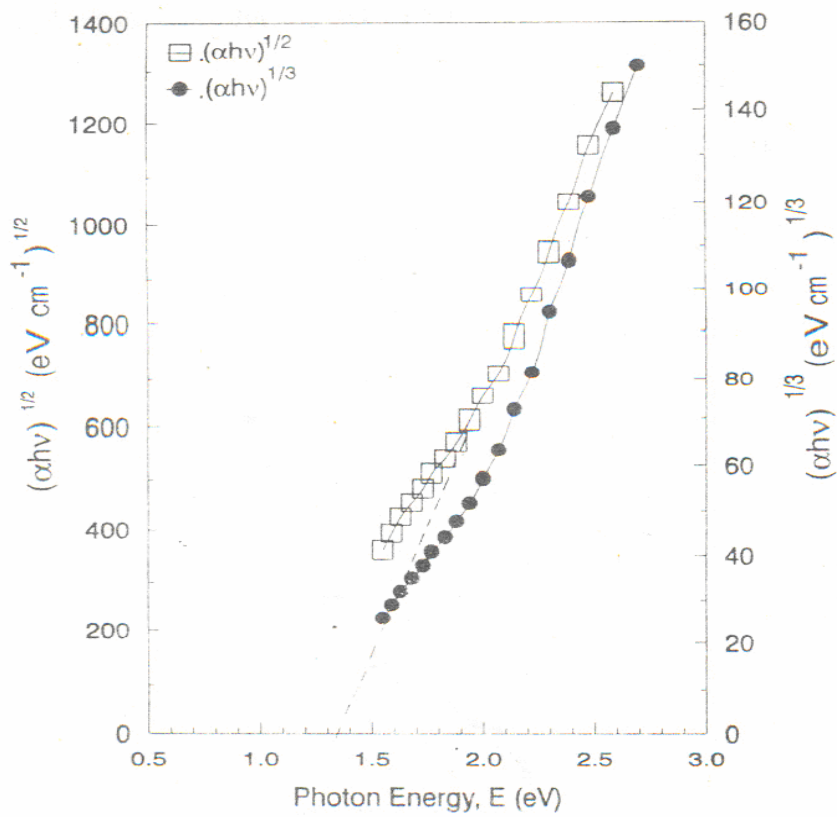


Figure 3. $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ plotted against photon energy for allowed and forbidden indirect transitions, respectively (SnS as prepared)

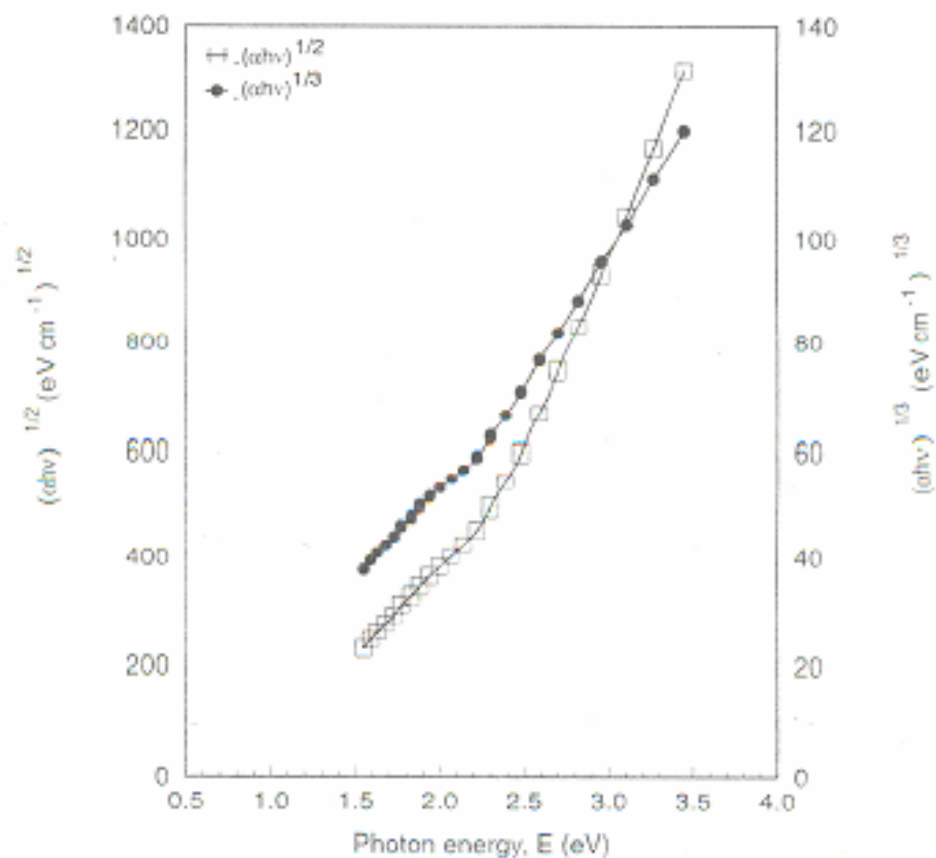


Figure 4. $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ plotted against photon energy for allowed and forbidden indirect transitions, respectively (SnS annealed for 6 hours).

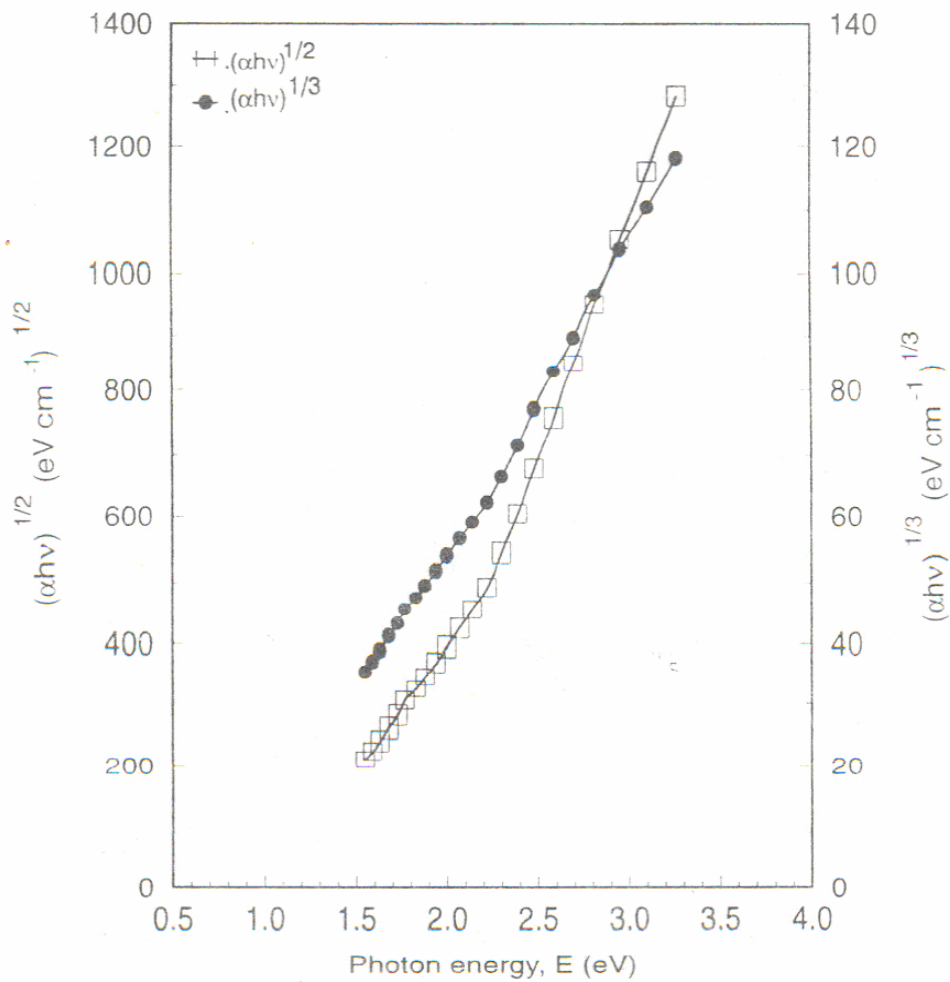


Figure 5. $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ plotted against photon energy for allowed and forbidden indirect transitions, respectively (SnS annealed for 12 hours).

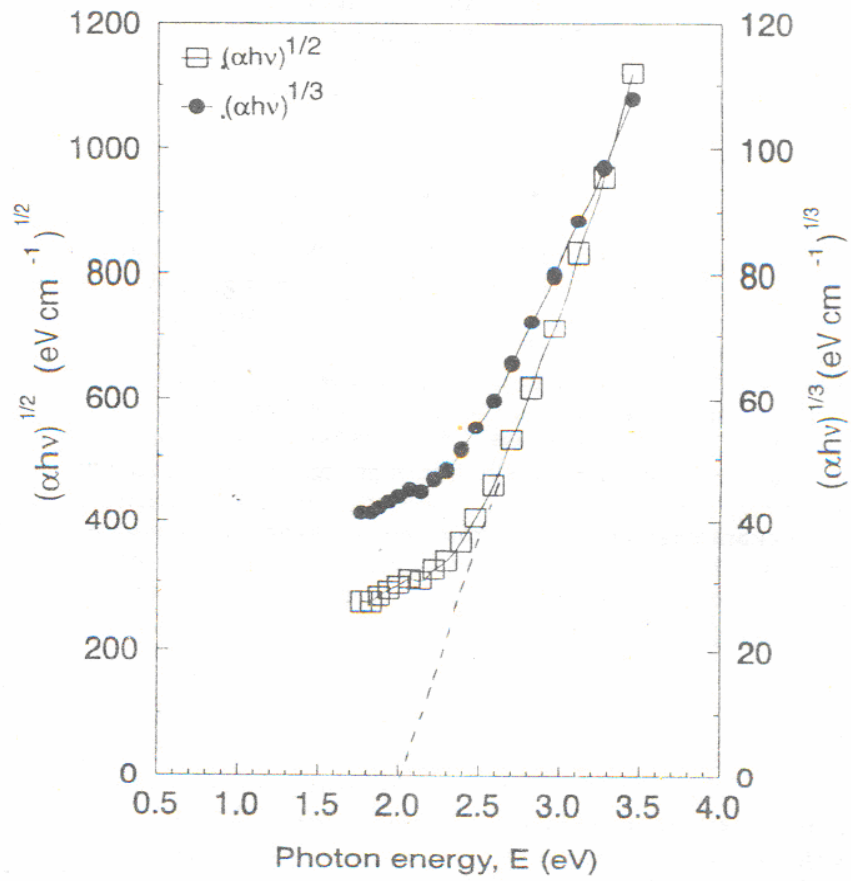


Figure 6. $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ plotted against photon energy for allowed and forbidden indirect transitions, respectively (SnS annealed for 20 hours).