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Optical Properties of Amorphous and Polycrystalline Stibnite (Sb$_2$S$_3$) Films

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Abstract. — A systematic optical absorption study near the fundamental absorption edge was carried out on both amorphous and polycrystalline films of Stibnite in the temperature range 90-320 K. Films were grown using naturally occurring single crystals of Stibnite. The optical band gap of thermally evaporated films which have the stoichiometry Sb$_4$S$_{57}$ was determined to be direct and temperature dependant. The band gap of amorphous phase at any temperature is considerably less than that of crystalline ones. The temperature dependence of band gap in both the cases agrees well with Varshni formula. The optical gap at 0 K for amorphous and crystalline films were determined by fitting experimental data to Varshni formula to be 1.95 eV and 2.13 eV with the temperature coefficient of band gap $-8.72 \times 10^{-4}$ eV/K and $-7 \times 10^{-4}$ eV/K respectively. We strongly believe that the band gap value depends on the sulphur content in the films. The films of thickness greater than 2000 Å show interference pattern in the transmission spectra. The optical constants $n$ and $k$ were determined using the interference fringes in the wavelength range 600 – 900 nm for film thickness 2000 – 8000 Å. In both cases $n$ and $k$ show thickness dependence.

1. Introduction

The binary chalcogenide compounds have received considerable attention in recent times mostly for their optical and photoinduced properties [1]. Since 1970, the optical properties are being studied on these compounds in amorphous as well as crystalline phases. They can be easily prepared in amorphous form by a number of processes like chemical precipitation, thermal evaporation, chemical bath etc. Among all, the Arsenic sulphides, selenides and tellurides are the most studied while Antimony compounds are the least studied. There are few attempts to study the optical properties of Sb$_2$S$_3$. In particular, the results concerning the fundamental absorption edge in bulk [2-6] and in thin film form [7-9]. However, the results show much disparity in the values of energy gap. Also, some of the earlier reports indicate that the band gap of Sb$_2$S$_3$ is of direct type [2-5] while a recent report claim it to be of indirect type [6]. Moreover, there is no any attempt to correlate the band gap with the stoichiometric compositions. These compounds can widely vary stoichiometrically with the formula of the type A$_x$B$_{1-x}$. Therefore, we thought it is worthwhile to investigate the optical properties on well characterised thin film samples of Sb$_2$S$_3$ as a function of temperature.
2. Experimental

The Stibnite bulk samples used in the present work were taken from Geological Museum, V.S.R. College, Tenali (A.P.), India (exact source not known). The grayish black samples were in the form of single crystal which had needle like structure along c-axis typical of layered compounds. They had high resistivity of $10^8 - 10^9\Omega\cdot cm$, characteristic of Sb$_2$S$_3$. The Stibnite was evaporated using a molybdenum boat at a pressure lower than $6 \times 10^{-6}$ Torr onto a very thin glass/quartz substrate held at room temperature or higher temperature. The substrates were thoroughly cleaned first in dilute chromic acid followed by ultrasonic agitation and ion bombardment prior to the film growth. The thickness of the film was monitored by a quartz crystal thickness monitor and was cross checked by a Dektek surface profiler. Films were quite uniform and smooth over the area of 3 cm $\times$ 3 cm. The films grown on the substrates at room temperature were amorphous in nature in confirmation with an earlier report [7]. In order to get a crystalline film, we kept the substrate at 230 $^\circ$C during evaporation and annealed subsequently over 3-4 hours. The crystalline nature of the film was confirmed by X-ray diffraction (using Philips model 1840) as depicted in Figure 1. The analysis of the diffraction pattern indicates the structure as orthorhombic with cell dimensions $a = 9$ Å, $b = 9.8$ Å and $c = 7.2$ Å. However, we have observed a broad hump between 5° and 22° in the X-ray diffractogram of amorphous films (which is also seen in Fig. 1 as background) which may indicate that there can be clusters of medium range ordering. The SEM analysis showed that the grain size in the polycrystalline film was about 6-8 $\mu$m and was fairly uniform throughout the film.

The chemical composition of both bulk and films was determined using a standard colorimetric analyses. Many samples were analysed to confirm the uniformity and reproducibility of the results. It was found that the bulk itself was having a slight sulphur deficiency with a composition Sb$_{41}$S$_{59}$ eventhough it is in single crystal form. The stoichiometry of the films was determined to be Sb$_{43}$S$_{57}$. The composition was determined with an error less than 2%. This was further tested using the ESCA analysis by recording Antimony 3d$_{5/2}$ (533 eV) and 3d$_{3/2}$ (542 eV) peaks and Sulphur 2p (164 eV) peak. The energy shown in bracket for each transition indicates the binding energy of the corresponding electrons for a free or elemental
antimony or sulphur. If these elements are chemically bound then the peaks will be slightly shifted (chemical shift). Antimony peaks show a chemical shift of about 2 eV and the sulphur peak shows a chemical shift of about 3 eV. This indicates the chemically bound nature of both sulphur and antimony. The composition of the film was found to be Sb$_{42}$S$_{58}$ as calculated by the area under the Curve along with their scattering cross sections. The existence of such partially stoichiometric antimony-sulphur compounds is reported in reference [8]. The composition along the thickness was also confirmed by depth profile. ESCA result is more reliable as it is quite accurate and sensitive. It can be noted that on evaporation, there is a slight decrease in the sulphur content in the films. However, in the earlier report [7] which used the evaporation method, there was no attempt to determine the composition of the film. They have assumed the nominal composition Sb$_2$S$_3$. Surprisingly, the composition determined by EPMA of films grown using Sb$_2$S$_3$ shows sulphur deficiency in the films while the composition of the films grown using Sb$_2$S$_3$ was the same as that of the bulk [8]. Therefore, we did a careful and thorough analyses to confirm the composition of the films. We could not get films having the same composition as that of the bulk in case of Sb$_2$S$_3$ despite many attempts by evaporation. Films were always having a small sulphur deficiency. The Atomic absorption analyses showed that there were impurities like Mg (7ppm), Fe (12ppm), Al (10ppm) and Ca (9ppm) in negligible quantities in the bulk samples. However, we do not expect these impurities to perturb the fundamental absorption edge.

Thin films of various thicknesses between 250 Å and 8 000 Å were grown both in crystalline and amorphous form. From our earlier studies [10] on lower thickness films of stibnite, we have observed that the energy gap shows quantum size effect below 150 Å and beyond that it is no more thickness dependent. In the present study we chose to use the films of 250-350 Å thickness for determining the absorption edge and its temperature dependence. The films in the thickness range 2 000-8 000 Å show interference pattern in the transmission spectra and

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Fig. 2. — Recorded optical absorption spectra of amorphous Stibnite films. Only few well separated spectra are shown for the purpose of clarity.
are used to determine the optical constants $n$ and $k$. The optical absorption/transmission studies at various temperatures between 90 K and 320 K have been made using a cold finger type cryostat with a temperature controller placed in the spectrophotometer (Hitachi model 150-20).

3. Results and Discussion

The radiation intensity transmitted by a plane parallel plate of thickness $t$ and of absorption coefficient $K$ for not too small a spectral width and optical thickness is given by [11]

$$I_T/I_0 = \frac{(1 - R)^2 \exp (-Kt)}{[1 - R^2 \exp (-2Kt)]}$$

where $R$ is the surface reflectivity of the sample, $I_T$ and $I_0$ are transmitted and incident intensities respectively. Equation (1) takes into account the multiple reflections in the specimen. To evaluate $K$ from equation (1), $R$ must be known in general. However, in the region of strong absorption, that is near fundamental absorption edge $R$ will be very small and $K$ is very large so that one can make the reasonable approximation that $R^2 \exp (-2Kt) \ll 1$. Then one gets the optical density $D = \log \left( I_0/I_T \right)$ and the absorption coefficient $K$ given by

$$K = 2.303D/t + 2.303 \log (1 - R)^2/t$$

Fig. 3. — Plot of $(Kh\nu)^{1/2}$ versus $h\nu$ for amorphous films of Stibnite.
As $R$ is small in the region of strong absorption, the second term of equation (2) can be neglected. Thus, the absorption coefficient $K$ was calculated as a function of incident energy using the absorption spectra recorded at various temperatures which are shown in Figure 2 for amorphous films.

In case of amorphous materials the relation between the absorption coefficient $K$ and the photon energy $h\nu$ near the band edge is given by [12,13]

$$K h\nu \simeq (h\nu - E_0)^2$$

where $E_0$ is the energy gap of the material. This kind of behaviour has been experimentally verified in most amorphous semiconductors, particularly in binary chalcogenide compounds [12,13]. The energy gap $E_0$ at different temperatures is determined by the extrapolation of the linear portion in the $(K h\nu)^{1/2}$ versus $h\nu$ plot as shown in Figure 3. Similarly, in case of polycrystalline films a general relation of the type [14,15]

$$K h\nu \simeq (h\nu - E_g)^n,$$

was fitted to the experimental data. The best fit was obtained for $n = 1/2$ indicating the direct allowed type of transition. $E_g$ at various temperatures was determined by plotting $(K h\nu)^2$ as a function of $h\nu$ which are not shown for the purpose of brevity. Our room temperature values of energy gap are slightly higher compared to those of reference [7] while comparable with
reference [8]. The room temperature values of band gap for the films in the thickness range 300-6 000 Å are not much different and are in good agreement with the results of Shapiro [2]. In Table I, we have compared the absorption edge determined by various workers using different techniques. It can be noted that only in one report [9] the band gap of crystalline film is less than that of amorphous one which is quite surprising. We have also tried to determine the band gap of sulphur deficient films. The bulk sample was heated in vacuum to various temperatures between 150 °C and 300 °C for an hour or so to get sulphur deficient samples. These samples were used for evaporation to get the films. The sulphur content in the film was further reduced slightly on evaporation. We have observed an increase in the band gap initially and a monotonous decrease with increasing sulphur deficiency. The detailed study will be published elsewhere.

The temperature dependence of energy gap in both amorphous and crystalline 300 Å thick film is shown in Figure 4. The error bar shown on the experimental data indicates the possible error in the extrapolated value of the band gap and the temperature of the film which were correct up to ±0.007 eV and ±2 K. Due to our experimental limitations, we could not make measurements below 90 K. However, we do not expect any drastic change in the behaviour at low temperatures. It can clearly be seen that energy gap decreases nonlinearly at low temperatures and more or less linearly above 200 K.

Fig. 5. — Interference pattern observed in amorphous Stibnite films for three different thicknesses at room temperature. Similar structures were observed in crystalline films also.
Table I. — The room temperature values of the energy gap of Sb$_2$S$_3$ determined by various workers using different techniques.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>$E_g$ (eV)</th>
<th>$dE_g/dT$ (eV/K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Single Crystal</td>
<td>Photoconductivity</td>
<td>1.64</td>
<td>$-5.7 \times 10^{-4}$</td>
<td>[2]</td>
</tr>
<tr>
<td>2. Pure Powder</td>
<td>Diffuse Reflectance</td>
<td>2.20</td>
<td>---</td>
<td>[3]</td>
</tr>
<tr>
<td>5. Single Crystal</td>
<td>Optical Absorption</td>
<td>1.75</td>
<td>---</td>
<td>[6]</td>
</tr>
<tr>
<td>6. Thin Film Transmission</td>
<td>1.88 (Crystalline)</td>
<td>---</td>
<td>[7]</td>
<td></td>
</tr>
<tr>
<td>7. Thin Film Reflectance</td>
<td>1.97 (Crystalline)</td>
<td>---</td>
<td>[8]</td>
<td></td>
</tr>
<tr>
<td>8. Thin Film Optical Absorption</td>
<td>1.74 (Crystalline)</td>
<td>---</td>
<td>[9]</td>
<td></td>
</tr>
<tr>
<td>9. Thin Film Optical Absorption</td>
<td>2.03 (Crystalline)</td>
<td>$-7 \times 10^{-4}$</td>
<td>Present work</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.83</td>
<td>$-8.7 \times 10^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>

Treating $E_g$ as a thermodynamical variable its dependence on temperature can be written as in reference [12]

$$
(\partial E_g/\partial T)_P = (\partial E_g/\partial T)_V - (\alpha_v/K_s)(\partial E_g/\partial P)_T
$$

(5)
Fig. 6.— Construction of $T_{\text{max}}$ and $T_{\text{min}}$ which were used to determine the optical constants $n$ and $k$ as described in reference [20].

where $\alpha_v$ is the volume expansivity $(\text{d}V/\text{d}T)_P/V$ and $K_s$ is the compressibility $-(\text{d}V/\text{d}P)_T/V$. The first term $(\partial E_g/\partial T)_V$ is usually interpreted as due to electron-phonon interaction, whereas the second term on the right hand side represents the effect of lattice dilation. If $(\partial E_g/\partial P)_T$ is negative, then the lattice dilation term is expected to make a positive contribution to $(\partial E_g/\partial T)_P$. But this implies that $(\partial E_g/\partial T)_V$ must be negative and considerably larger to explain the observed results. The data on pressure coefficient $(\partial E_g/\partial P)_T$ for Sb$_2$S$_3$ is not available in the literature. However, a large negative contribution from $(\partial E_g/\partial T)_V$ is observed in case of a large number of semiconductors [16,17]. As summarised by Varshni [18] a linear dependence is expected from the lattice dilation term except at low temperatures. The term $(\partial E_g/\partial T)_V$ is expected to contribute as $T^2$ for $T < \theta_D$ (Debye temperature) and as $T$ for $T > \theta_D$. Combining these results Varshni suggested a relation of the form:

$$E_g(T) = E_g(0) - \alpha T^2/(T + \beta)$$  \hspace{1cm} (6)

where $\alpha$ and $\beta$ are parameters. Normally, $\beta$ correlates with $\theta_D$. We have fitted our experimental data for both amorphous & crystalline films to equation (6) assuming the validity of the equation for the case of amorphous materials also. The best fit was obtained with $\beta = 350$ K, $\alpha = 7.06 \times 10^{-4}$ eV/K, $E_g(0) = 2.132$ eV for crystalline films and $\beta = 350$ K, $\alpha = 8.72 \times 10^{-4}$ eV/K, $E_g(0) = 1.951$ eV for amorphous films. The order of $\alpha$ for these films is in line with those of other semiconductors [18]. If $\alpha$ can be treated as the temperature coefficient of band gap $(\text{d}E_g(T)/\text{d}T)$ then our observed value compares rather well with the only report of Yurkov [2] as shown in Table I. However, it should be noted that this value of Yurkov has been determined assuming a linear dependence of band gap in the temperature range 90-300 K from photoconductivity measurements. It can also be noted that the value of $\beta = 350$ K used for the best fit correlates well with the Debye temperature $\theta_D$ (310 K) of stibnite [19]. It may look quite surprising to see that the temperature dependence of energy gap of amorphous films can also be explained by Varshni formula which makes use of electron phonon and lattice dilation concepts. This may be due to the presence of medium range ordering as evidenced by the
observation of a broad hump in the X-ray diffractogram of amorphous films. However, this formal agreement of temperature dependence of optical gap of amorphous films with a quite general temperature dependence shape need not be taken too seriously as it does not imply any definite physical process.

The films of thickness greater than 2 000 Å showed interference fringes in the transmission spectra. The number of maxima or minima in the interference pattern increases with thickness as depicted in Figure 5. There is a clear thickness dependence observable. These interference fringes are utilised to determine the optical constants, film thickness, absorption coefficient etc. as described in reference [20]. The whole idea is to construct two envelopes $T_M$ (touching maxima) and $T_m$ (touching minima) as a continuous function of wavelength $\lambda$ as illustrated in Figure 6. Then all the above said quantities can be determined as a function of $\lambda$ using only $T_M$ and $T_m$. The refractive index was calculated as a function of $\lambda$ for various thicknesses using the following equation.

$$n = \left[ N + (N^2 - s^2)^{1/2} \right]^{1/2}$$  \hspace{1cm} (7)

where

$$N = 2s\left[ (T_M - T_m) / T_MT_m \right] + (s^2 + 1) / 2$$

and $s =$ refractive index of the substrate = 1.52 for the glass substrates we have used. If $n_1$ and $n_2$ are the refractive indices at two adjacent maxima (or minima) at $\lambda_1$ and $\lambda_2$ the film thickness can be calculated from

$$d = \lambda_1 \lambda_2 / 2 (\lambda_1 n_2 - \lambda_2 n_1)$$  \hspace{1cm} (8)
The thicknesses calculated using the above equation agree very well with the measured ones with an error less than 1%. The absorption coefficient $K$ can be calculated by

$$x = \exp (-Kd)$$

and

$$x = \frac{E_M - \left[E_M^2 - (n^2 - 1)^3 (n^2 - s^4)\right]^{1/2}}{(n-1)^3 (n-s^2)}$$

$$E_M = 8n^2 s/T_M + (n^2 - 1) (n^2 - s^2)$$

The absorption index, $k$, can be calculated using the values of $K$ in the relation $k = K\lambda/4\pi$. The optical constants $n$ and $k$ determined (with an error less than 1%) as described above for both the crystalline and amorphous films are displayed as a function of $\lambda$ in Figure 7. Obviously, the refractive index of crystalline films is greater than that of amorphous films. However, these optical constants show a thickness dependence in the thickness range 2 000-6 000 Å as shown in the Figure 8. Above 6 000 Å the optical constants are no longer thickness dependent. Such a behaviour was also observed by Kucirek [21] in Sb$_2$S$_3$ films. We have chosen the values of $n$ and $k$ at a wavelength of about 600 nm only for the purpose of comparison with those of Kucirek and the agreement is good.
4. Summary and Conclusions

The fundamental absorption edge is determined as a function of temperature in both crystalline and amorphous stibnite films. The films grown by the evaporation method always showed sulphur deficiency in the film. The band gap of Sb$_2$S$_3$ films strongly depends on the sulphur content in the film and is sensitive to heat treatment. Therefore, there are scattered values of energy gap of Sb$_2$S$_3$ in the literature. The so called amorphous films contain a sufficiently large cluster of medium range ordering to allow the use of crystalline formalism in interpreting at least the optical absorption. The optical constants show a thickness dependence up to 6 000 Å. However, a detailed calculation of electronic band structure is needed to understand the dependence of band gap on the chemical composition and temperature. We hope to take up the task to have more insight in the understanding of the interesting system like Sb$_2$S$_3$ which is quite promising for application.

References


