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THE EFFECT OF FILM THICKNESS ON THE OPTICAL PROPERTIES OF LEAD TELLURIDE

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Thin films of PbTe have been prepared by thermal evaporation under vacuum of $\sim 1.3 \times 10^{-3}$ Pa. The thickness of the films ranged between ~ 200 and ~ 700 nm. X-ray diffraction patterns reveal the formation of polycrystalline films. Optical gap has been estimated and was found that it lies at about 0.3 eV for all films. Ellepsometry shows the presence of two absorption peaks at about 1.45 eV and 2.6 eV. The obtained results are discussed in terms of the band structure of PbTe.

1. INTRODUCTION

THE OPTICAL behaviour of absorbing films is usually described by their optical constants. Optical properties in the visible and near infrared regions are related to electron transitions. The study of optical properties in such spectral regions can help in obtaining a better information of electronic structure of thin semiconducting films.

Lead telluride is a polar semiconductor, which crystallizes in face centred cubic lattice (f.c.c.) of the sodium chloride type. The space group belongs to ^5O_h. PbTe is classified as a member of the lead chalcogenides group, which is characterized by high dielectric susceptibility, high mobility and a narrow band gap ~ 0.2 eV [1]. Theoretical and experimental studies reveal that the top of the valency band, and the bottom of the conduction band lie at the point L ($K = \pi/a$ (1 1 1)) at the surface of the Brillouin zone [2–4]. The relativistic effect and the LS-coupling in such compounds, can cause shift of energy levels, which may exceed the width of the gap. Accordingly, such effects should be taken into consideration.

The aim of this article is to study the dependence of optical absorption and optical gap on the thickness of PbTe thin films.

2. EXPERIMENTAL WORK

Lead telluride of 99.999% purity (Koch-Light Limited, England), was used to prepare the thin films. Films of thicknesses ranging from ~ 200 nm to ~ 700 nm, were prepared by thermal evaporation under vacuum of $\sim 10^{-3}$ Pa. The rate of evaporation was $\sim 0.5\,\mathrm{nm\,s^{-1}}$. Film thicknesses have been determined using multiple-beam Fizeau fringes at reflection [5]. Reflection and transmission measurements were obtained using PMQ11 (Carl Zeiss) spectrophotometer. The error in reflection and transmission measurements do not exceed 0.01 eV. The details of the ellipsometric measurements are given in previous paper [6]. The ellipsometer was calibrated by a single crystal and parallel to (1 1 1) face. The uncertainty in optical constants does not exceed 0.02 eV.

3. RESULTS

X-ray diffraction patterns indicate the formation of PbTe polycrystalline films. It was observed that the number of reflections and their intensities increase by increasing film thickness. This is more likely to be due to the increase of the degree of crystallinity of PbTe films. All the prepared films reveal the presence of traces of free lead. Films containing negligible quantities of free lead were only considered. The intensity of (1 1 1) & (2 0 0) reflections of Pb were used for the rough estimation of lead.

Reflection and transmission spectra for some films are shown in Figs. 1 and 2. Both reflection (R) and transmission (T), show edges at the short wavelength side. The reflectivity is higher than the transmissivity throughout the investigated spectral range. This may be due to the absorbing nature of the films. Similar behaviour was observed in case of lead selenide films [7]. The optical gap was determined by the method described by Demichelis *et al.* [8].

Near the absorption edge, the transmittance is given by;

$$T = (1 - R)\exp(-\alpha t)$$

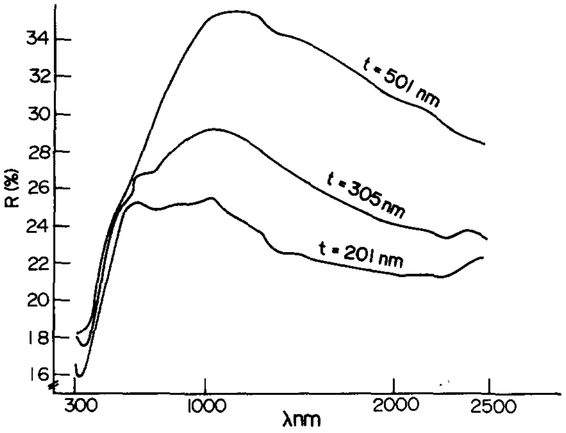

Fig. 1. The relation between the reflectivity percent and wavelength in nm.

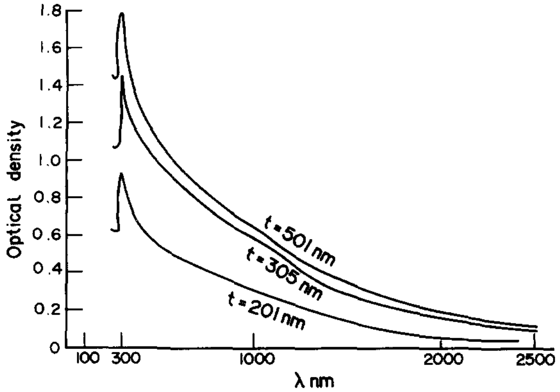

Fig. 2. The relation between the optical density and wavelength in nm (transmission spectra).

α is the absorption coefficient and t being the film thickness, then

$$\alpha = \frac{\ln [(1 - R)/T]}{t} = \omega(R, T).$$

The dependence of the absorption coefficient on the wavelength is complicated. However, consideration of the mechanism of the different possible electronic transitions leads to the following equation [8].

$$\alpha^{\tau} E^{\sigma} = A(E - E_g) = [\omega(R, T)]^{\tau} E^{\sigma} \qquad (1)$$

where E is the photon energy, E_g is the optical gap and τ and σ are parameters depending on both the type of the transition (direct or indirect) and the profile of the electron density in the valency and conduction bands. Here A, is a constant including the thickness t. It is worthy to note that the method eliminates the errors arising from the uncertainty in thickness determination.

The dependence of $[\omega(R, T)]^{\tau} E^{\sigma}$ on the photon energy E was plotted for different values of τ and σ. The best fit was observed for $\tau = \sigma = 1$. Figure 3, illustrates such dependence. Extrapolation gives the values of E_g the estimated values of the optical gap for different thicknesses are listed in Table 1.

Table 1.

t(nm)	$L_1^6(2)$–$L_{3'}^{6'}(1)$ E_g eV	$L_1^6(2)$–$L_{2'}^{6'}(2$ E_1 eV	$L_3^6(1)$–$L_{2'}^{6'}(2)$ E_2 eV
201	0.34	1.44	2.66
305	0.34	1.40	2.62
359	0.32	1.40	2.58
501	0.28	1.46	2.58
601	0.30	1.42	2.44
701	0.28	1.42	2.44
Bulk	$\begin{cases} 0.19^{(11)} \\ 0.19^{(11)} \end{cases}$	$1.30^{(9\,\&\,10)}$ $1.24^{(12)}$	$2.52^{(9\,\&\,10)}$ $2.45^{(12)}$

It is observed that the width of the gap tends to decrease with increasing thickness, and approaching the known value of the bulk PbTe. This behaviour could be accounted for by assuming that at low thickness, the morphological characteristics of the prepared films are different than that of bulk lead telluride. In addition, in bulk the small crystallites are randomly oriented and hence almost all X-ray reflections can be observed. This is in agreement with the obtained X-ray diffraction data where the degree of crystallinity (number and intensity of reflections) increases by increasing film thickness. In other words the films approaches the bulk behaviour as the thickness increases. It is worthy to mention that although films of thickness $t \leqslant 150\,\text{nm}$ exhibit polycrystalline nature, they give no systematic or reproducible results.

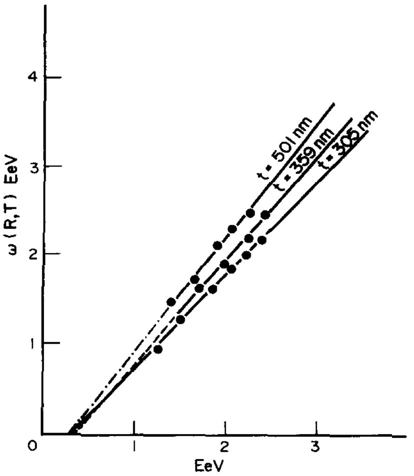

Fig. 3. The dependence of $[\omega(R, T)]\ E$ on the photon energy E.

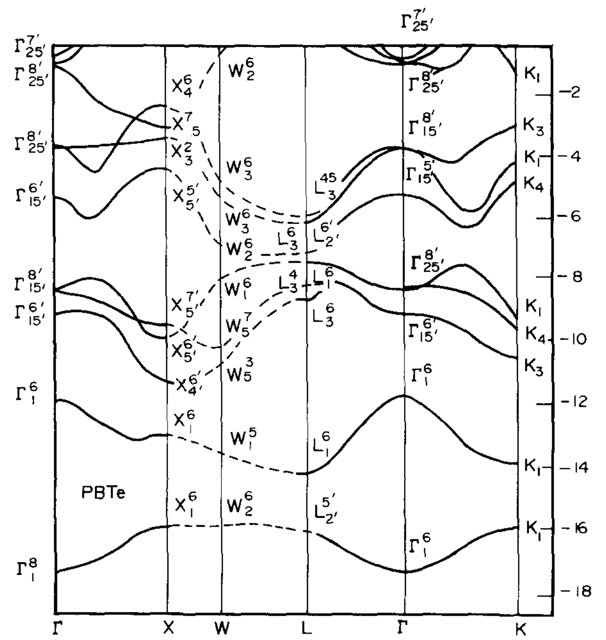

Fig. 4. The band structure of PbTe.

Consideration of the band structure of PbTe (Fig. 4), allows to assume that such gap from the direct transition between levels $L_1^6(2)$–$L_{3'}^{6'}(1)$. Such transition was found both theoretically [9, 10] and experimentally [11] to be 0.19 eV. The different values obtained in the present study may be attributed to the difference between the bulk and film. In the latter case, although the features of the band start to appear, surface effects cannot be neglected.

4. ELLIPSOMETRIC MEASUREMENTS

The dependence of the optical constants n and K of some films on the wavelength is shown in Fig. 5. The calculated absorption coefficient $\alpha = (4\pi K)/\lambda$ as a function of photon energy for some films is illustrated in Fig. (6). The spectra of all films follow a common pattern. Two peaks are observed at about 1.4 and ~ 2.5 eV. The position of bands are listed in Table 1. It could be seen that the obtained values differ from those obtained by other authors [11]. This may be due to the difference between the bulk and the films, as stated in above argument.

5. ANALYSIS OF THE RESULTS

The band structure of PbTe given in Fig. (4), shows that the lowest possible transition lies at the point L [$K = \pi/a$ (1 1 1)], on the surface of the Brillouin. For PbTe, such transition is of energy of 0.19 eV [9–11]. The estimated optical gap is slightly higher than this value, which may be due to the structural differences between bulk and films. The above argument is supported by the fact that the estimated values for higher-thickness films approach that of the bulk.

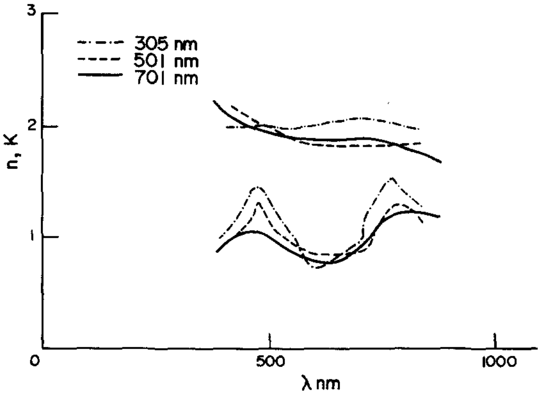

Fig. 5. The dependence of the optical constants (n and k) on wavelength.

For polycrystalline material, direct transition corresponds to $\tau = \sigma = 1$ [9]. This allows to attribute the estimated gap to the direct transition $L_1^6(2)$–$L_{3'}^{6'}(1)$.

The symmetry of the point L is D_{3d} and the total wave function is transformed according to direct product $L_i \times D_{\frac{1}{2}}$ [12].

Resolving into the irreducible components reveals the splitting into six components. The possible transitions along with their energies are listed in Table 1. It is worthy to note that three of such levels belong to the valency band and the others to the conduction band. The symmetry types of wave function involved are S, P and d of Pb and Te as shown in Table 2.

The allowed predicted transitions in the visible region will be $L_1^6(2)$–$L_{2'}^{6'}(2)$ and $L_3^6(1)$–$L_{2'}^{6'}(2)$. Accordingly, it is easy to assign the observed absorption bands. The first band at ~ 1.4 eV, most probably arises from the transition $L_1^6(1)$–$L_{2'}^{6'}$ while the second

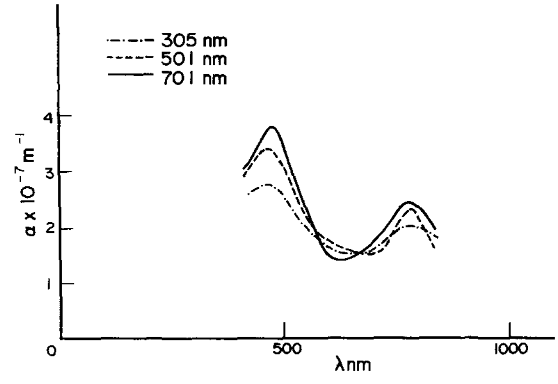

Fig. 6. The relation between the calculated absorption coefficient (α) and photon energy.

Table 2.

State	Anion	Cation
L_1	P	S
$L_{2'}$	S	P
L_3	P	d
$L_{3'}$	d	q

$L_3^6(1)$–$L_2^6(2)$ is responsible for the absorption band at ~2.5 eV. Moreover, in terms of atomic wave function of both Te and Pb and according to Table 2 it is clear that:

(i) The optical gap is due to transitions from $(P_{\mathrm{Te}} + S_{\mathrm{Pb}})$ to $(d_{\mathrm{Te}} + P_{\mathrm{Pb}})$

(ii) The two peaks are due to

$$(S_{\mathrm{Te}} + P_{\mathrm{Pb}}) \rightarrow (P_{\mathrm{Te}} + S_{\mathrm{Pb}})$$

and

$$(P_{\mathrm{Te}} + d_{\mathrm{Pb}}) \rightarrow (P_{\mathrm{Te}} + S_{\mathrm{Pb}}).$$

It is clear that all the levels are mixed, considering the transitions between levels of the same atoms, it could be seen that all the above transitions are dipole transitions, except the last one. The last one is forbidden by selection rules. The observed high absorption corresponding to such transition could be accounted for the the strong overlap between P_{Te} and d_{Pb}; P_{Te} and S_{Pb}.

REFERENCES

1. I.M. Cidelkovskii, *Electrons and Holes in Semiconductors Energetic Spectra and Dynamics*, chap. 4, Nauka, Moscow, 1972 (In Russian).
2. P. Stiles, E. Burstein & D. Longberge, *J. Appl. Phys.* **32,** 2174 (1961).
3. G. Pratt & L. Ferreira, *Proc. Int. Conf. S.C. Physics*, Paris (1964).
4. S. Rabii, *Phys. Rev.* **197,** 801 (1968).
5. S. Tolansky, "*Introduction to Interferometry*", p. 157, Longmans Green, London (1955).
6. M.M. El-Ocker, F.A. Sultan, S.A. Youssef & S.A. El-Sahhar, *Phys. Status Solidi* (*a*) **83,** 263 (1984).
7. M.M. El-Ocker, F. Sharaf, S.M. Youssef, F. Matawe & M. El-Dessouki, Accepted for Publication at *Phys. Status Solidi* (*b*).
8. F. Demichelis, G. Kanidakis, A. Tagliferro & E. Tresso, *Appl. Optics* **9,** 26 1737 (1987).
9. L. Kleinman & P. Lin, *Proc. Inter. Confer. Semicond. Physics*, p. 63, Paris (1966).
10. L. Kleinman & P. Lin, *Phys. Rev.* **142,** 478 (1966).
11. E. Palik, D. Mitchell & J. Zamel, *Phys. Rev.* **135,** A763, (1964); *Proc. Inter. Confer. Semicond. Physics*, p. 325, Paris (1964).
12. M. Cardona & D. Greenway, *Phys. Rev.* **113,** A1685 (1964).