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TRANSPORT PROPERTIES OF $(PbTe)_{9.7}Sb_{0.3}$ THIN FILMS

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Thin films of $(PbTe)_{9.7}Sb_{0.3}$ per weight of different thicknesses have been prepared on quartz substrate by vacuum thermal evaporation. Heating–cooling cycles indicate an increase of resistivity with successive cooling cycles. These observations can be explained by considering the desorption of absorbed gas molecules and creation of defects during the heating process. Isothermal annealing effect was studied. Plots of logarithm of resistivity versus temperature were analyzed to derive the activation energy for the defect formation. The apparent value of the energy was 0.18 eV, i.e. about a half of the activation energy for conduction. The activation energy for conduction and resistivity are thickness dependent. The optical spectrum of $(PbTe)_{9.7}Sb_{0.3}$ in the infrared region was measured. From the spectrum, we derived the values of the direct and indirect energy gaps of 0.29 and 0.19 eV, respectively.

1. *Introduction*

Although continuous attention has been given in the last few decades to the growth and properties of polycrystalline lead chalcogenide films, because of their

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use as IR radiation detectors, the present state of understanding of the role of the intercrystallite regions in the properties of the films is still not satisfactory. In the case of PbTe polycrystalline films it is commonly assumed that the intercrystallite regions, or so-called "barrier" regions, contain oxides of Pb, Te or Pb salts and that they are the location of a high density of chemical and structural imperfections: lattice point defects, foreign-impurities, dislocations, inclusions, precipitates, low angle grain boundaries, cracks and voids [1-4].

The small band gap semiconductor PbTe is an appropriate material for the fabrication of infrared optoelectronic devices [5]. The efficiency of such devices is profoundly influenced by deep levels in the forbidden energy gap which may act as trapping or recombination centers [6,7]. However, one of the curious properties of PbTe has been the absence of observable states in the gap. If PbTe is doped with foreign atoms like Bi or Sb, which are believed to form shallow (or resonant) impurity states, no other changes in recombination have been observed than those due to the change in Fermi level position. From small gap semiconductor $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}$ both photodiodes as well as injection lasers for the middle IR have elaborated. As compared with the relatively high technological performance of such devices reported in numerous papers, there is only little knowledge concerning the recombination of non-equilibrium carriers in this material. In a small-gap semiconductor family like $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}_x$ a tendency is observed for strengthening the relative contribution of intrinsic recombination mechanisms if the energy gap is decreased. Studies of electrical conductivity of lead chalcogenides on thin films as well as on bulk materials have been carried out by many workers both in the low and high temperature ranges [8-11].

Zemel et al. [12] reported a time-dependent behaviour of the electrical properties in PbS, PbTe and PbSe films. The energy gap values reported were 0.41, 0.31 and 0.27 eV for PbS, PbTe and PbSe films, respectively. The study of the optical properties in the visible and near infrared regions of spectra can help for a better understanding of the electronic structure in semiconducting films like PbTe. The minimum direct energy gap at room temperature has been quoted as 0.32 eV for PbTe [13]. Scanlon [14] derived the energy gap for indirect transitions from IR absorption spectrum of PbTe and found that it was 0.29 eV at room temperature. Smith [15] discussed the possible reasons for such discrepancies in the energy gap values. He attributed this to the unusual changes in the band structure of the compound with temperature, to vaporisation of tellurium or to the formation of defects at elevated temperatures. Miller et al. [16] reported that the energy gap values obtained from resistivity measurements were considerably greater than those obtained from the optical absorption spectrum. The disparity between the optical and thermal energy gaps was explained on the basis of an additional carrier generation taking place at elevated temperature.

The aim of the present work is to investigate the effect of temperature and thickness on the conductivity of $(\mathrm{PbTe})_{9.7}\mathrm{Sb}_{0.3}$ thin films. A qualitative explanation for the temperature dependence of conductivity has been given. The thickness dependence of conductivity is analysed on the basis of the "effective mean free path model". The mechanism of conduction and defect formation has been studied.

2. *Experimental*

A stoichiometric mixture of Pb and Te of purity 99.999 % was placed in a silica tube which was vacuum sealed in a vacuum of 7×10^{-3} Pa and heated at 1000 °C for 16 hours. Antimony was added to the previously prepared PbTe in different ratios to select the prefered composition which gives the best results in the resistivity and other parameters, relevant for the application of obtained material in the field of electronics. So, the ratio $(\mathrm{PbTe})_{9.7}\mathrm{Sb}_{0.3}$ was found to be the most appropriate for the aim of such a study. The mixture was heated in an evacuated silica tube at 1000 °C for 18 hours, during which the tube was frequently shaken to homogenise the melt. Later the tube was slowly cooled to room temperature. X-ray diffraction photograph of the alloy ingot samples showed that the stoichiometrically homogeneous compound was formed. Typical diffraction patterns of the bulk $(\mathrm{PbTe})_{9.7}\mathrm{Sb}_{0.3}$ alloy ingot is shown on curve (a) in Fig. 1. Curve (b) in Fig. 1 shows a typical X-ray diffraction pattern of the typical film. The films were found to be polycrystalline in nature. Table 1 compares the d-values calculated for the film and the bulk $(\mathrm{PbTe})_{9.7}\mathrm{Sb}_{0.3}$ with the standard d-values of PbTe alloy taken from the ASTM card. It is seen that there is a good agreement of the d-values confirming that the films are of stoichiometric Pb alloy.

TABLE 1.
A comparison between d_{hkl} values of $(\mathrm{PbTe})_{9.7}\mathrm{Sb}_{0.3}$ *bulk and thin film with theoretical values in ASTM of* PbTe.

d_{hkl} ASTM	d-bulk	d-thin film	Reflecting plane
3.740	3.700	–	111
3.230	3.200	3.200	200
2.280	2.270	2.270	220
1.932	1.930	–	311
1.858	1.855	1.855	222
1.609	1.605	–	400
1.442	1.440	1.440	420
1.314	1.312	1.310	422

This means that the addition of antimony has no effect on the structure. Regardless, it has good effect on the physical properties as indicated from the results. This means that the chemical compositions for the bulk and the film were the same as confirmed by X-ray chart for thin film and bulk as shown in Fig. 1.

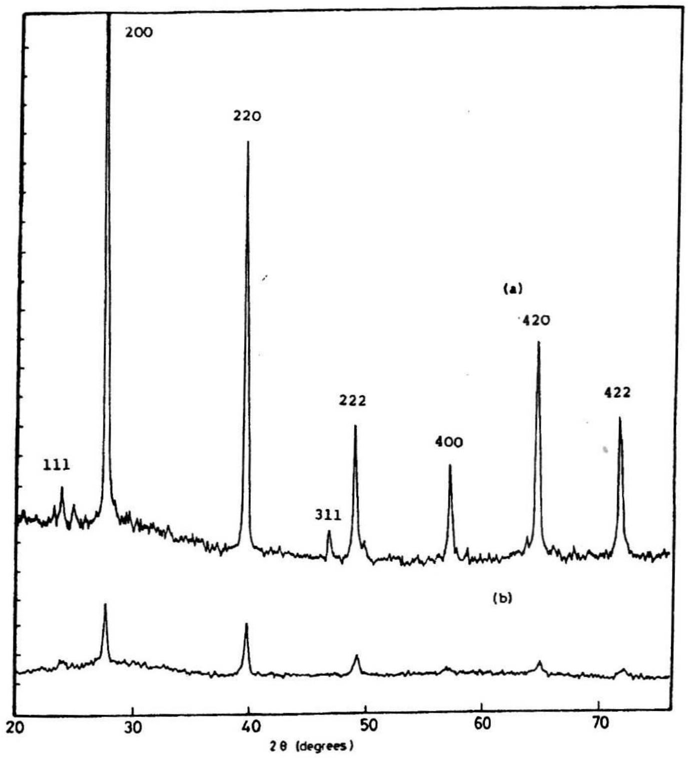

Fig. 1. X-ray diffraction pattern for $(\mathrm{PbTe})_{9.7}\mathrm{Sb}_{0.3}$. *(a) For the powder alloy. (b) For thin film of the alloy.*

Thin films were deposited in a vacuum of 10^{-3} Pa onto quartz substrate by thermal evaporation for both optical and electrical measurements. It is worth noting that each of the prepared films of any thickness is measured three times under the same conditions and the similar results are only taken into account and listed in the text. However, the four prepared films of different thickness listed in Table 2 were choosen from many different prepared films, to be the most appropriate.

TABLE 2.

Values of film thickness and corresponding activation energy deduced from Fig. 3.

Thickness of the film (nm)	Activation energy for conduction (eV)
120.0	0.19
134.3	0.184
161.8	0.17
241.5	0.162

The conductivity which was predominantly due to surface effect was measured by especially designed holder using the four probe method. The four probes were connected to the film and the substrate via silver paste. The $I - V$ characteristics indicate that the assembly was ohmic in contact. The temperature of the substrate and overgrowth were measured and controlled using copper–constantan thermocouple placed very close to the surface of the sample. The precision in measuring the temperature was about ± 1 °C. The samples were measured in the air. For the annealing experiment, the furnace was heated to the annealing temperature, then the sample was placed in the furnace and left to take the furnace temperature. The experiment was carried out both during heating and cooling processes, the rate of temperature change was approximately the same and equal to 2 °C/min to avoid the error in temperature and time reading during heating–cooling cycles. The thickness of the films was measured using a multiple beam interferometer. The optical measurements were made using a computerized infrared spectrophotometer (PU 9712).

3. Results

Figure 2 shows the temperature dependence of the resistivity of Sb doped lead telluride thin films for three cycles of heating and cooling at certian value of thickness ($d = 161.8$ mm). Similar behaviour is observed for films of different thicknesses,

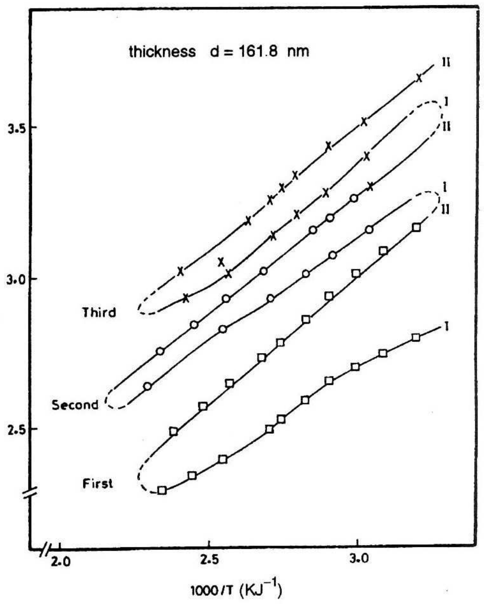

Fig. 2. Plot of logarithm of resistivity versus reciprocal temperature for air–exposed (PbTe)$_{9.7}$Sb$_{0.3}$. *(a) For the powder alloy. (b) For thin film of the alloy.*

the cooling curves being parallel to each other in all the cycles (Fig. 3). During the first cycle, it was found that the resistance decreases with increasing the temperature, $\log \rho$ versus $1/T$ was found to be almost-linear. On cooling, the resistance increases with decreasing temperature and $\log \rho$ versus $1/T$ plot is found to be a straight line, indicating an activated conduction and the semiconducting nature of the film. It was noticed that the cooling plots are always seen to be above the heating plots in all three cycles and the $\log \rho$ versus $1/T$ plots for the three cooling cycles are found to be straight lines parallel to each other. The activation energy calculated from the slopes of the cooling curves for thin films is found to be 0.34 eV. It was noticed from the heating–cooling cycles that the difference in width between the heating and cooling for each cycle decreases successively with increasing number of the cycles, which reflects the tendency to reach saturation state with increasing the number of successive cycles.

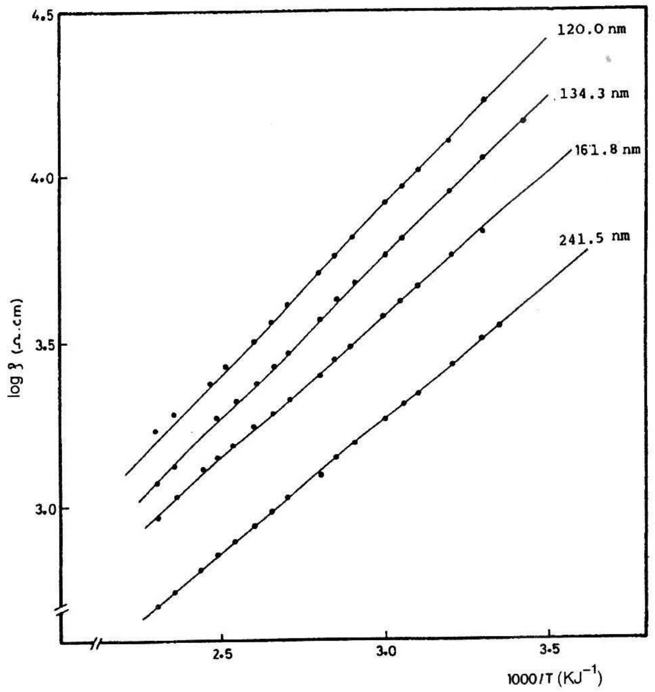

Fig. 3. Plot of logarithm of resistivity versus reciprocal temperature as a function of thickness.

Thin films of different thicknesses were subjected to heating–cooling cycles. The result indicated similar behaviour, i.e. the cooling curves are always above heating curves. Besides a tendency to non–linearity of the heating curves was also observed. The activation energy was derived from slopes of the cooling cycles for different thicknesses of the thin film and was found to be 0.32 and 0.38 eV according to the equation:

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right).$$

The actual values of the activation energies obtained from the optical results were found to be between 0.29 and 0.32 eV [14].

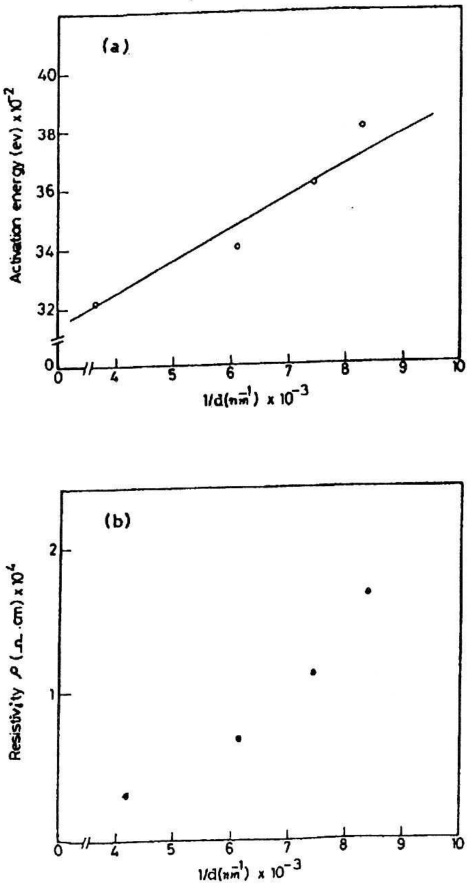

Fig. 4. (a) (○) Plot of the activation energy (E) versus reciprocal film thickness at room temperature $T \simeq 300$ K.
(b) (●) Plot of resistivity versus the reciprocal thickness for $(PbTe)_{9.7}Sb_{0.3}$ *thin films at room temperature* $T \simeq 300$ K.

Figure 4a shows the plot of the values of the calculated activation energies with the reciprocal thickness of the films. It is clear that there is a variation of activation energy with thickness. Figure 4b shows the resistivity versus reciprocal thickness plots at given temperature (room temperature $\simeq 300$ K).

4. *Discussion*

Since it is well known that gas adsorption plays an important role in the electrical properties of Pb chalcogenides, we carried out resistivity studies and heat treatment in air. This was done to understand the temperature behaviour of resistivity of $(PbTe)_{9.7}Sb_{0.3}$ films during heating: (i) intrinsic conduction, (ii) desorption of oxygen and (iii) creation of thermally generated defects, particularly at high temperatures. However, intrinsic conduction at room temperature is debatable since, it depends upon the carrier concentration in the material. We have observed a straight line in the $\log \rho$ versus $1/T$ plot in the temperature range 300–450 K and the activation energy values are comparable with the energy gap of PbTe. Hence, the decrease of resistance during the initial heating may be attributed to the intrinsic conduction taking place in PbTe films, but at higher temperatures the resistance increases relatively steeply. From the isothermal annealing study, it was also observed that the resistance increases with time. This makes us believe that some mechanisms other than intrinsic conduction are responsible for conduction. The desorption of oxygen from the film surface decreases the carrier concentration in a p–type sample and thus increases the resistance of the sample. (Oxygen is a p–type dopand in Pb chalcogenides.) It was argued that in chalcogenides, the defects are created at high temperatures [15]. These defects can act as scattering centers for the carriers, thereby appreciably reducing the mobility of the carriers and causing a sharp increase of resistivity. These defects created during heating cannot be eliminated immediately during cooling, but only after a lap of time. Also, the desorbed gas molecules would be immediately readsorbed. This duration of hysteresis is larger than the time duration of the observations. Hence, the heating and the cooling cycles do not coincide, and the cooling cycles are always above the heating cycles. During cooling only the thermal activation is responsible for the change in the conductivity, and hence, we get linear plot of $\log \rho$ versus $1/T$. It is very interesting to confirm the formation of defects by studying isothermal annealing, since it sheds more light on the energy–activated process of the formation of defects.

Therefore, it will be assumed that the process is controlled by a chemical–rate equation [18]:

$$t \ \exp\left(\frac{-\Delta E_d}{kT}\right) = \text{constant}$$

where k is the Boltzmann's constant, t is the time of change and ΔE_d the energy activating the process. The equivalent times and temperatures prescribing a particular degree of change were measured by the cross–cut method from the regular part of the isothermal annealing curves given in Fig. 5 and Table 3. The activation energy ΔE_d for this process was deduced from Fig. 5 by plotting the logarithm of the time versus the reciprocal of the absolute temperature at certain values of conductivity.

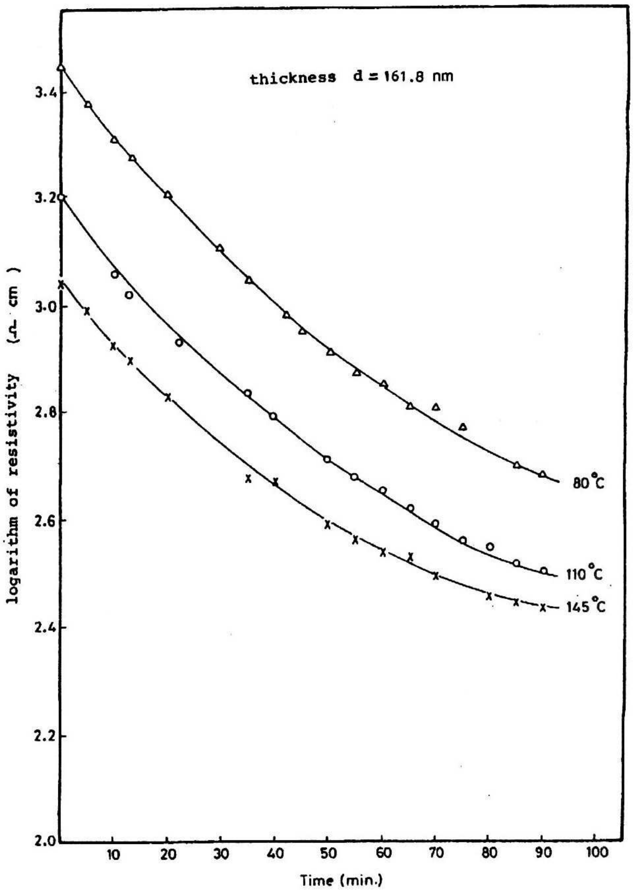

Fig. 5. Isothermal annealing curves at different temperatures (Plot of logarithm of resistivity for thickness 161.8 nm *versus time).*
(a) △ *at temperature 80* °C.
(b) ○ *at temperature 110* °C.
(c) x at temperature 145 °C.

Figure 6 shows a parallel set of straight lines. The slopes of these lines give an average value of ΔE_d to be 0.182 eV. Comparing the value of the energy activating the defects formation process and the energy of the conduction process, it was found that the value of ΔE_d is about half of the value of E_g (E_g = 0.32 eV). Therefore, the defects seem to be easily formed during the conduction process, at high temperature and consequently cause the increase in the resistivity values. However, the isothermal annealing results indicate that the defects may be created not only at high temperature, but also at temperature slightly higher than the room temperature as clearly shown from the decay of the resistivity with time in Fig. 5.

TABLE 3.
Values of resistivities at certain values of temperature and time.

Time (t) min.	$\log \rho$ at 80 °C	$\log \rho$ at 110 °C	$\log \rho$ at 145 °C
10	3.31	3.052	2.943
35	3.04	2.873	2.698
50	2.89	2.701	2.6
60	2.85	2.65	2.54
70	2.77	2.6	2.5
90	2.68	2.51	2.42

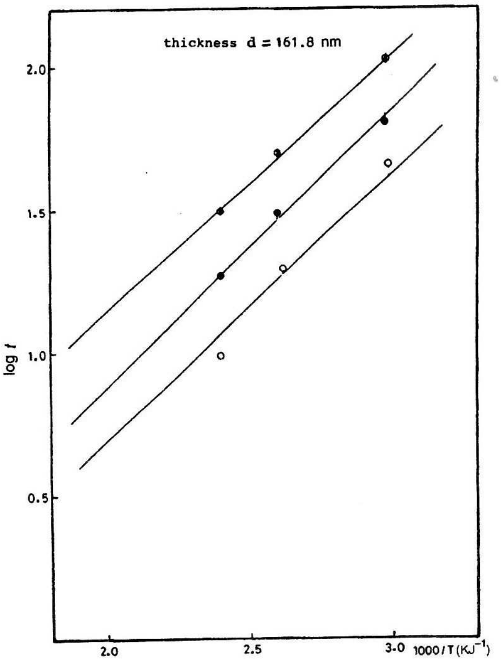

Fig. 6. Relation between $\log t$ *(time) and the reciprocal temperature deduced from Fig. 5 at certain values of conductivity and thickness* 161.8 nm.
⊕ – *For conductivity value of* 841 Ω^{-1}cm^{-1}.
● – *For conductivity value of* 1188 Ω^{-1}cm^{-1}.
○ – *For conductivity value of* 1995 Ω^{-1}cm^{-1}.

The conductivity of air–exposed films did not show any systematic dependence, let alone linear dependence on reciprocal thickness. This is surely because of the fact that the conductivity of the air–exposed films is completely dominated by gas adsorption (oxygen adsorption) effects and hence any size effects dependence is completely masked by the gas adsorption effects.

The lead chalcogenides have an important technological interest as highly sensitive infrared detectors. In an impure semiconductor, it is possible to excite bound electrons by direct absorption of appropriate optical quanta.

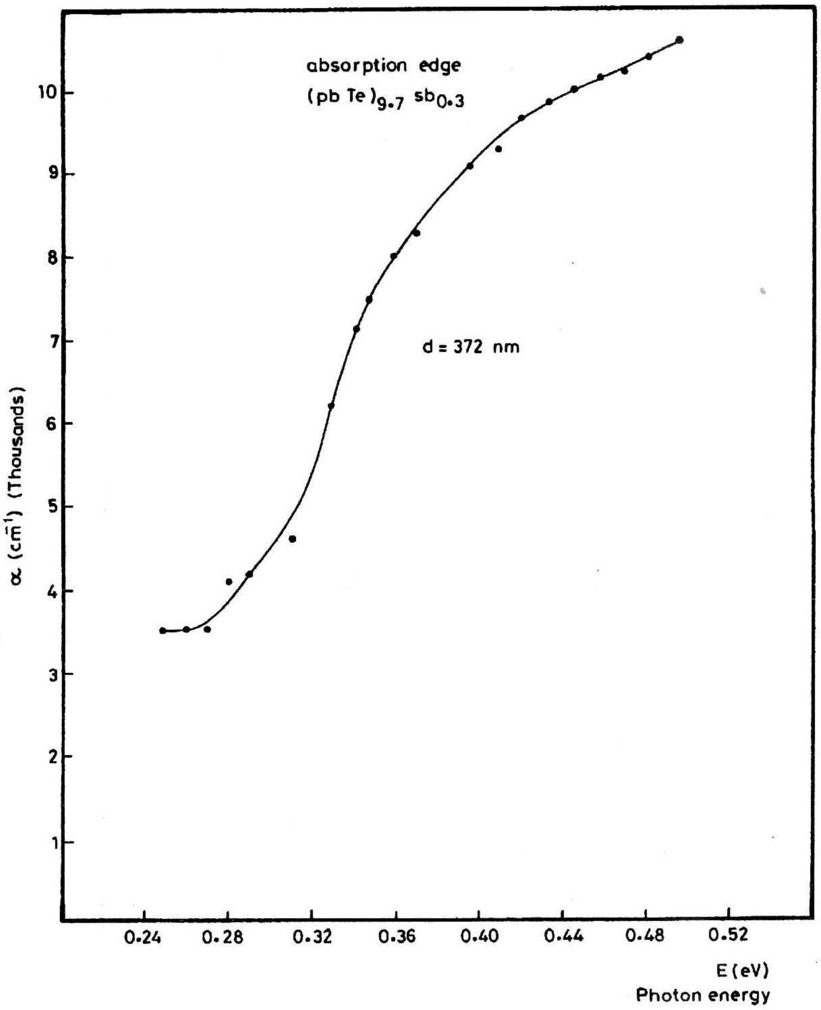

Fig. 7. The optical absorption coefficient for $(\mathrm{PbTe})_{9.7}\mathrm{Sb}_{0.3}$ *as a function of photon energy.*

The absorption would be strong for all $h\nu \gg E_g$ and ceases more or less abruptly at $h\nu = E_g$ [19]. The analysis of absorption spectrum of the alloy indicates the integral data of the absorption edge (the optical absorption coefficient as a function

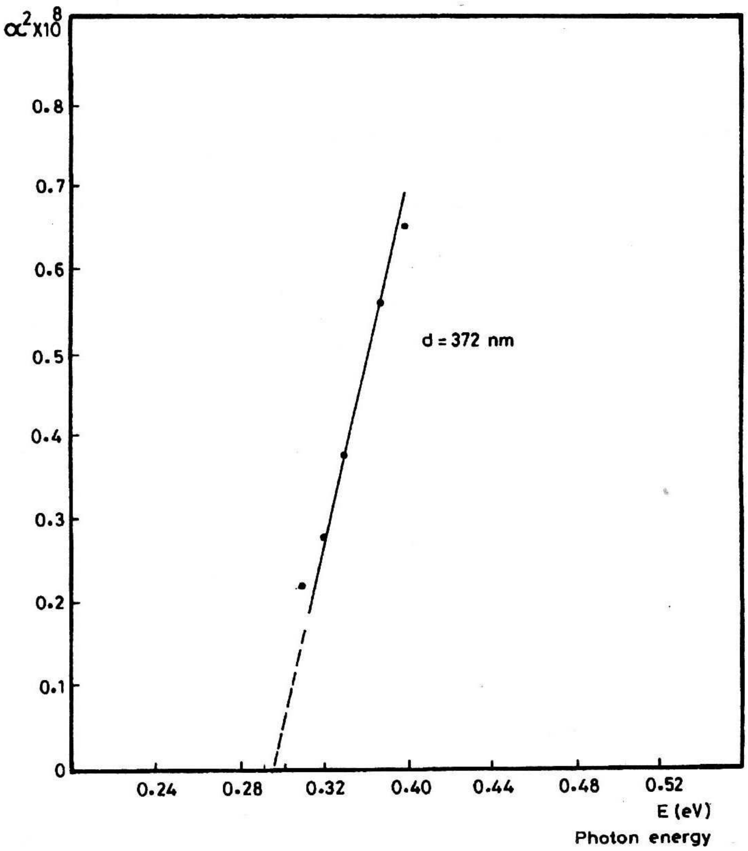

Fig. 8. Relation between the square of the absorption coefficient (α^2) and photon energy.

of photon energy in the whole energy interval). In order to determine the direct and indirect transition, the data were ploted in accordance with the relations:

$$\alpha = \frac{A}{h\nu}\sqrt{h\nu - E_g} \tag{1}$$

and

$$\alpha = \frac{A}{h\nu}\left(h\nu - E_g^{'}\right)^2 \tag{2}$$

where E_g and $E_g^{'}$ are forbidden band widths for direct and indirect transitions. Relations (1) and (2) for $(\mathrm{PbTe})_{9.7}\mathrm{Sb}_{0.3}$ thin films are ploted in Figs. 8 and 9. The intersection of the straight line in the graph in Fig. 8 with energy axis gives direct optical gap transition energy $E_g = 0.295$ eV, while the intersection of the straight line in the graph in Fig. 9 with energy axis gives indirect optical gap transition energy $E_g' = 0.195$ eV which is smaller than the direct transition optical gap E_g. This result may be attributed to the presence of antimony in the sample.

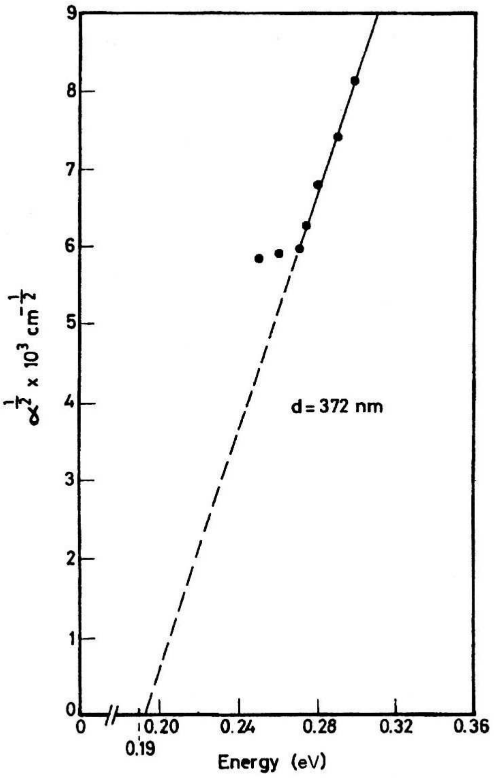

Fig. 9. Relation between the square root of the absorption coefficient ($\alpha^{1/2}$) and photon energy.

5. Conclusions

The following conclusions are obtained:

(i) The initial decrease in resistance of $(PbTe)_{9.7}Sb_{0.3}$ with temperature during heating in each cycle can be attributed to intrinsic conduction in the film. On cooling, the resistance increases with decreasing temperature indicating an activated conduction and the semiconducting nature of the film.

(ii) It was noticed from the heating–cooling cycles that the conductivity increases with each cycle and that the difference in width between the heating and the cooling for each cycle decreases successively with increasing the number of the cycles, which reflects the tendency to reach saturation with increasing the number of successive cycles.

(iii) The activation energy values are found to be different for films of different thickness, so, it appears that the activation energy is dependent on film thickness. On the other hand, the dependence of the conductivity on the thickness of thin films under investigation shows that this dependence occurs only during the cooling cycle. This arises because of the size effects influencing the film conductivity and can be explained by a suitable size–dependent film conduction model like the effective mean free path model.

(iv) The isothermal annealing results indicate that the defects may be created not only at high temperature, but also at temperature slightly higher than the room temperature as clearly shown from the decay of the resistivity with time. These defects created during heating cannot be eliminated immediately during cooling, but only after some time. Also, the desorbed gas molecules would be immediately readsorbed. Hence, the heating and the cooling cycles do not coincide, and the cooling cycles are always above the heating cycles.

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TRANSPORTNA SVOJSTVA TANKIH FILMOVA $(PbTe)_{9.7}Sb_{0.3}$ SLITINA

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Tanki filmovi $(PbTe)_{9.7}Sb_{0.3}$ različitih debljina pripređeni su na kvarcnom substratu isparavanjem u vakuumu. Ciklusi zagrijavanja–hlađenja pokazuju povećanje otpora pri sukcesivnim ciklusima hlađenja. To se može objasniti desorpcijom apsorbiranih molekula plina i pojavljivanjem defekata tijekom zagrijavanja. Proučavan je učinak termičkog otpuštanja. Razmatrajući ovisnost logaritma otpora o temperaturi određena je aktivacijska energija stvaranja defekata. Prividna vrijednost energije je 0.18 eV, što je dvostruko manje od aktivacijske energije vodljivosti. Aktivacijska energija vodljivosti ovisi o debljini uzorka. Mjeren je optički spektar $(PbTe)_{9.7}Sb_{0.3}$ u infracrvenom području. Na temelju mjerenja određene su vrijednosti direktnog i indirektnog energijskog procijepa 0.29 odnosno 0.19 eV.