

TRANSPORT AND OPTICAL PROPERTIES OF TELLURIUM AND ANTIMONY DOPED CdS THIN FILMS

H. A. Zayed, B.A. Monsour*, H. A. El-Zahed
E. M. Sakr and A. H. Ibrahim

University College for Girls,
Ain Shams University Cairo, Egypt.

* Physics Department, National Research Center
Dokki, Giza, Egypt.

ABSTRACT

Measurements of electrical and optical properties have been made on tellurium and antimony doped CdS thin films of about 280 nm thickness. The structure of the undoped and doped films is studied by X-ray analysis. The structure of Te doped CdS films is found to be crystalline and similar to those for undoped films while the antimony doped CdS films is found to be amorphous. For Tellurium doped CdS films, the dopant was found to act as a deep donor levels in CdS. The conductivity first decreases considerably with Te doping but as we further increase the concentration of the dopant, the conductivity increases. Doping with Sb results in a sharp decrease in the dark conductivity. This behaviour is expected as Sb is a group v element which replaces sulphur in CdS so that it acts as an acceptor. The optical constants (the refractive index n , absorption index k and absorption coefficient α) are measured on Te and Sb doped CdS films. It is observed that the optical energy gap is dependent only on the dopant concentration for Sb doped CdS films.

INTRODUCTION

A detailed knowledge of the electrical, optical and structural changes in CdS films is important in relation to the manufacture of photoresistors and solar cells[1].

The effects of doping CdS crystals with different substances have been studied previously by Bube and his co-workers[2,3]. Gorodetskii et al[4] have studied the photoconductivity and photoluminescence of CdS single crystals doped with different

concentrations of indium. Cadmium sulphide films are more resistive to thermal and mechanical handling than CdS single crystals. Stanley[5] and others[6,7,8] have also studied the resistivities and the mobility in indium doped CdS films. Dresner et al.[9] and Jalar[10] have studied the change in the electrical properties for copper, silver, and aluminium doped CdS films while Ray et al.[11] have studied the effect of doping with bismuth on electrical and photoelectric properties of CdS films. Although a number of studies on some properties of doped CdS thin films have been made,[12,13] the effect of doping on the optical constants (α , k , n) was not thoroughly studied. The photosensitivity, hole mobility and carrier concentration of Te doped CdS crystals and thin films have been studied by Aten et al.[14] and Bnerjee[15].

Tellurium has been chosen as a dopant in order to see the effect of substitution of sulphur anion which is group VI by Te which also belongs to the same group. To see the effect of introducing a group V element as an impurity in CdS, we studied the effect of doping of CdS thin films with antimony on the electrical and optical properties.

EXPERIMENTAL

For doping, spectroscopic standardized CdS powder was mixed with Te or Sb (purity 99.9998) in suitable percentages (0.17, 0.6, 1.0, 1.3, and 2.0 %) and pressed into pellets to avoid splattering. A quartz tube wound with a tungsten heating coil was used as the evaporation source and the substrate holder was placed just above the quartz tube. Thin films of undoped and doped just above the quartz tube. Thin films of undoped and doped CdS were prepared by direct thermal evaporation of pellets under high vacuum (2×10^{-6} torr) using vacuum plant type BAE 121 (BALZERS).

The evaporation source was covered with a shield for one min. after the start of source heating to reach a temperature sufficient for CdS and the source heating to reach a temperature sufficient for CdS and the dopant (Te or Sb) to evaporate. The shield was then removed and depositions were then made onto cleaned glass substrates. The substrate was controlled at desired temperature (200°C) throughout the whole evaporation process.

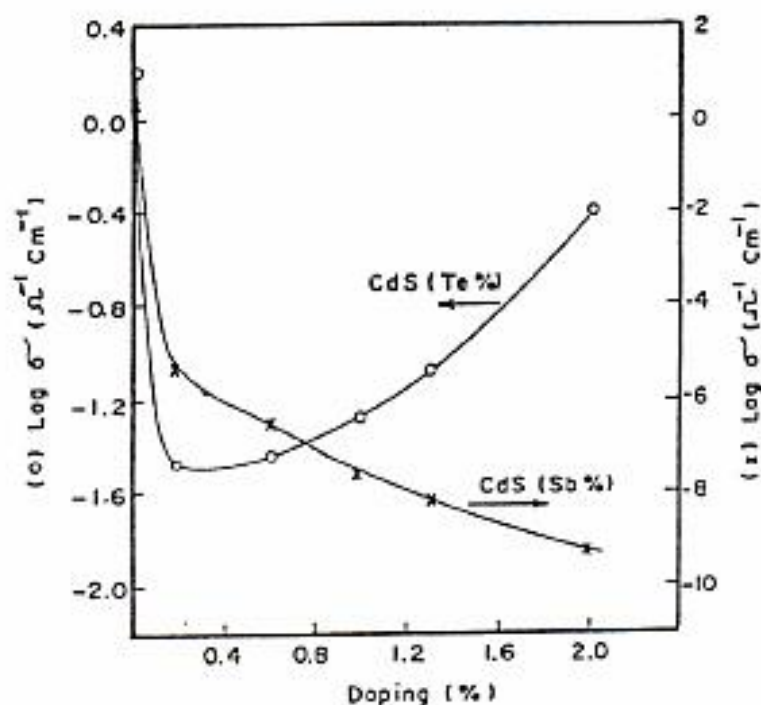


Fig. 1 : Room temperature conductivity of undoped and doped CdS films as a function of doping concentration.

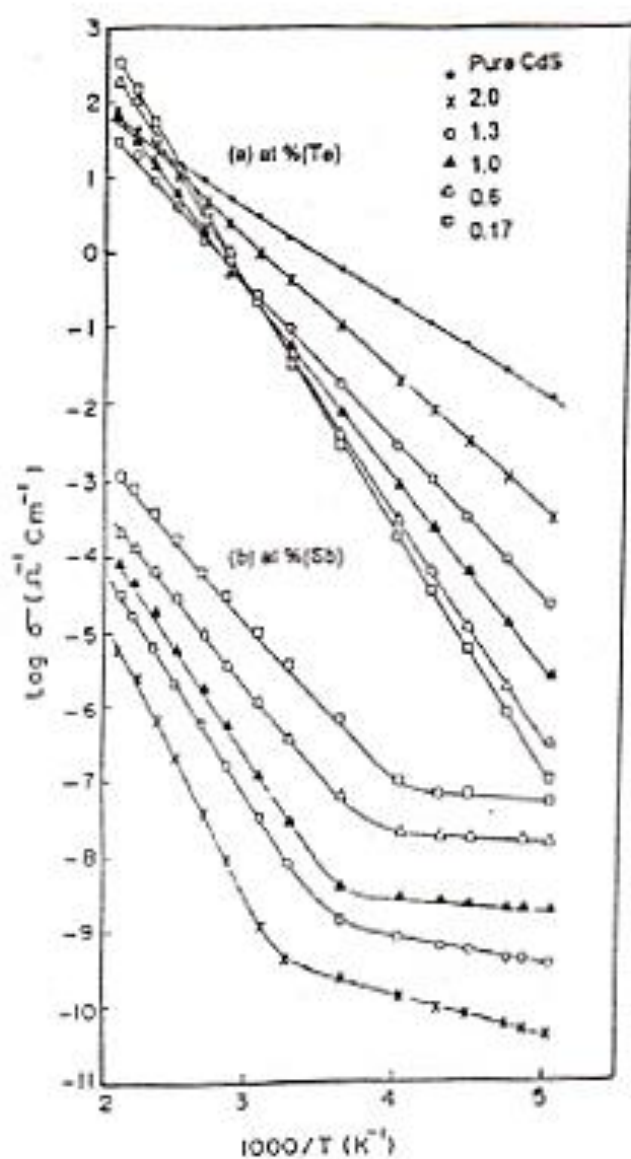


Fig. 2 : Temperature dependence of dark conductivity for pure CdS film and CdS films doped by Te and Sb.

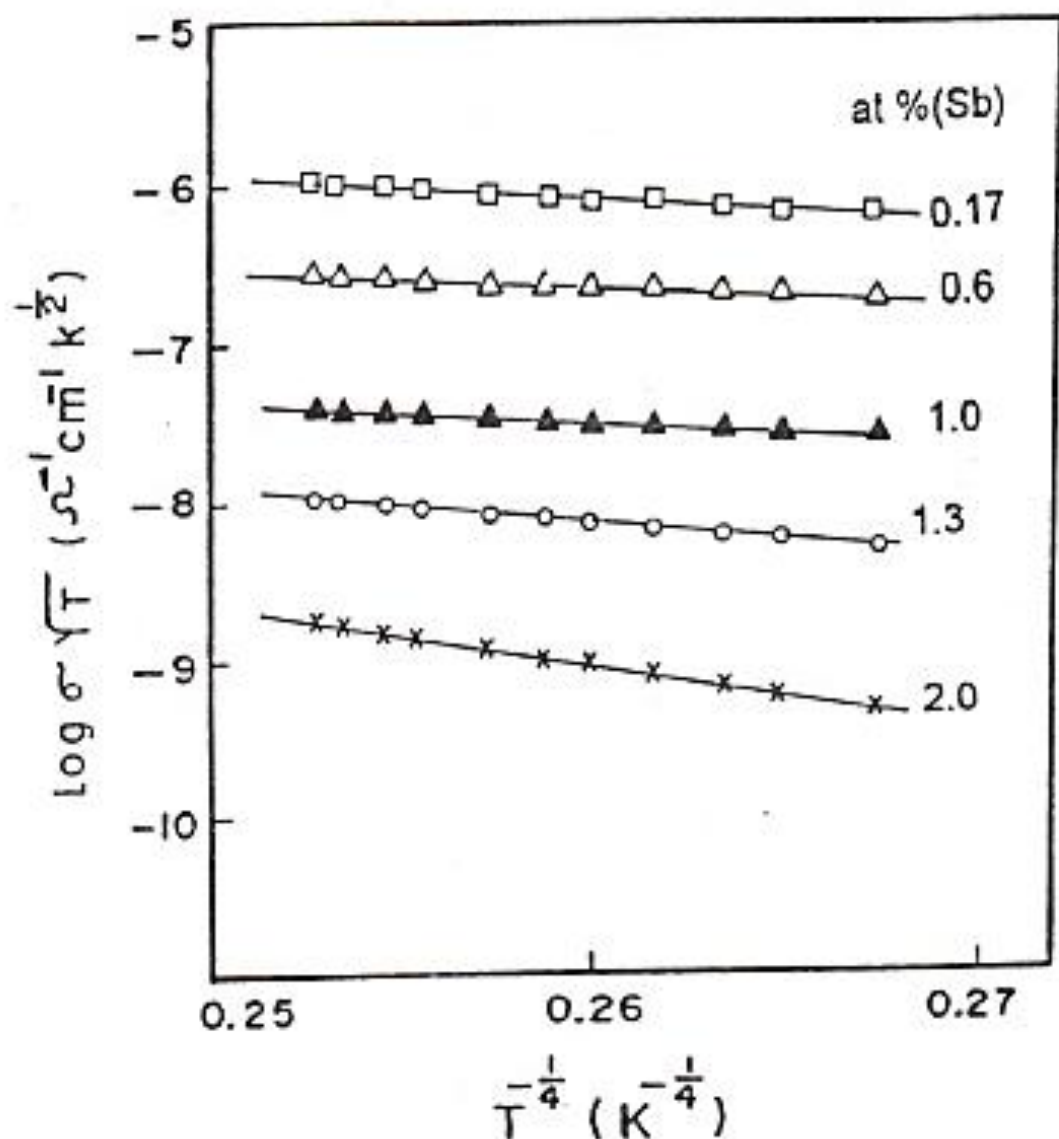


Fig. 3 : $\log \sigma \sqrt{T}$ vs $T^{-1/4}$ for antimony doped CdS films.

The structure of the obtained films was investigated using X-ray diffractometer (Philips PW 1373). Multiple Beam fizeau fringes was used for measuring the film thickness. For the electrical measurements, the films were provided with vacuum evaporated indium for better contact between material and electrodes. Their ohmic behaviour was subsequently tested. The electrical measurements were made by using a keithley 610 digital electrometer.

The transmission T and the reflection R at normal incidence were recorded using a spectrophotometer (Zeiss-PMO*) in the wave length range of 400-1400nm.

RESULTS AND DISCUSSION

Electrical conductivity

The dark electrical conductivity σ of undoped and CdS films doped by different concentrations of Te and Sb at room temperature is shown in Fig. 1. In this figure it is seen that for CdS films doped with Te, the conductivity first decreases with increasing concentration of the dopant but as we further increase the concentration of the dopant, the conductivity increases. According to Hopfield et al[16] Te in CdS acts as a hole traps by introducing deep donor levels near the valence band. This reduces the minority carrier concentration and its contribution to the conductivity. With increasing the concentration of Te, levels may be introduced above these deep donor levels and nearer to the conduction band. These donor levels may contribute some electrons to the conduction band and thus conductivity increases with increasing doping concentration of Te. While in case of antimony-doped CdS films the dark conductivity is less than that of an undoped films and decreases as the dopant concentration increases. This behaviour can be explained as due to the fact that antimony is expected to behave as an acceptor as it is group V element and has one valence electron less than sulphur. It will replace sulphur which is a group VI element in CdS.

Sb concentrations. The activation energies ΔE calculated from these plots (above 250K) according to the relation.

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \quad (1)$$

are given in table 1. For Te doped CdS films when donor levels are introduced near the valence band, the Fermi level is lowered. With increasing concentration of Te, levels are introduced. With increasing concentration of Te, levels are introduced nearer the conduction band and so, the Fermi level is raised. This is supported by the results given in Table (1).

It can be seen that in case of doping with antimony, electrical conduction takes place via two parallel mechanisms

- 1- At high temperature above 250 K the dopant act as an acceptor and by increasing the concentration of Sb, Fermi level is lowered toward the valence band and, hence, the activation energy increases with increasing the percentage of the dopant (Table 1).
- 2- At low temperature (76-250K) conduction takes place by hopping in the localized states near the Fermi level. Replots of the conductivity curves in Fig. 2 lead to Mott's relation for thermally assisted hopping conduction[17].

$$\sigma = (\sigma_0 / T^{1/2}) \exp(-T_0 / T)^{1/2} \quad (2)$$

$$\text{with} \quad T_0 = 16 \alpha_0^3 / k g_f \quad (3)$$

where α_0^{-1} is the special extension of the wavefunction associated with the localized states and g_f is the density of localized states at the Fermi level. The pre-exponential factor σ_0 is given by

$$\sigma_0 = 3e^2 v_{ph} (g_f / 8 \pi \alpha_0 K)^{1/2} \quad (4)$$

where $v_{ph} = 10^{13}$ Hz is the characteristic phonon frequency in most amorphous material. The average hopping distance R and the hopping energy w are given by the expressions

$$R = 9/8 \pi \alpha_0 K T_0 g_f \quad (5)$$

$$\text{and} \quad W = 3/4 \pi R^2 g_f \quad (6)$$

Fig. 3 represents $\log \sigma \sqrt{T}$ versus $T^{1/4}$. We get a linear relation which indicates the occurrence of a variable range hopping conduction mechanism. From Fig. 3, the values of σ_0 and T_0 can be obtained. The calculated values of σ_0 , T_0 , α_0 , g_f , R and W are given in Table 2. The obtained data show that g_f decreases and W increases with increasing the percentage of the dopant (Sb).

Optical properties

To investigate the effect of doping on the optical energy gap E_g , refractive index n and absorption index k of CdS thin films, the transmission (T) and the reflection (R) at normal incidence in the spectral range (400-1500nm) were measured for Te and Sb doped and undoped CdS films of thickness 280 nm with the same concentration of Te and Sb[18].

The optical absorption coefficient (α) for the films was calculated using the following equation :

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{(1-R^2 \exp(-2\alpha t))}$$

where t is the film thickness.

The optical absorption coefficient for these films can, be described by the relation $(\alpha h\nu)$ as a function of $(h\nu - E_g)^{1/2}$ indicating a direct transition. The plots of $(\alpha h\nu)^2$ against photon energy $h\nu$ for Te and Sb doped and undoped CdS films are shown in Figs. 4 and 5 respectively. For all films, the relations are found to be identical in character and indicate tailing of the absorption coefficient towards low photon energies. The exponential form of the tail may be due to the amorphous state of the material. From Fig. 4, for Te doped CdS films, it is evident that the optical energy gap is independent on Te concentration and is equal to 2.4 eV which is similar to that for the undoped CdS films. For antimonydoped CdS films (Fig. 5), the energy gap

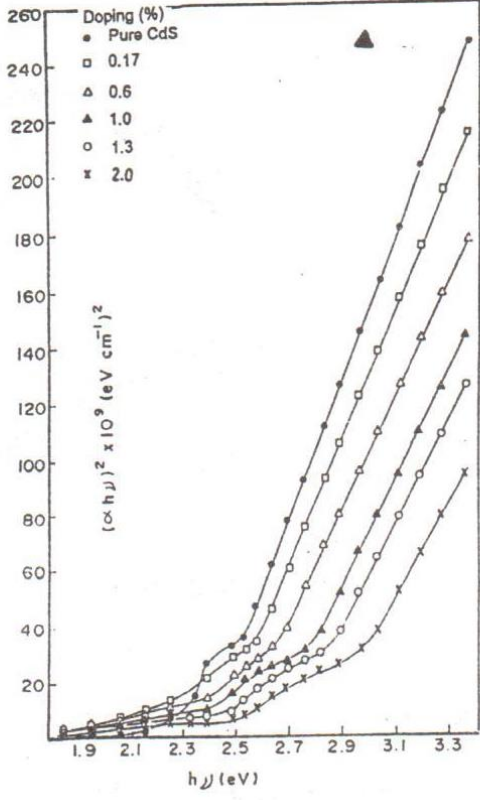
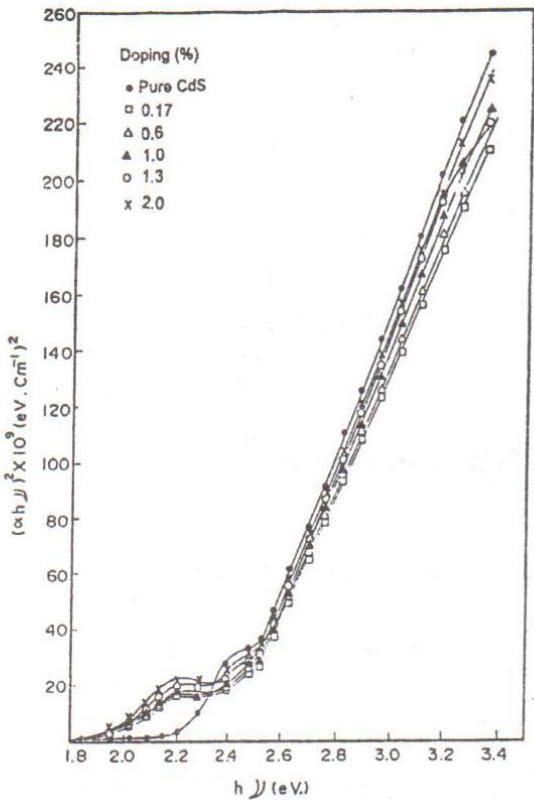


Fig. 4 : Absorption coefficient $(\alpha h\nu)^2$ vs photon energy $h\nu$ for Te doped CdS films.

Fig. 5 : Absorption coefficient $(\alpha h\nu)^2$ vs photon energy $h\nu$ for Sb doped CdS films. ▲

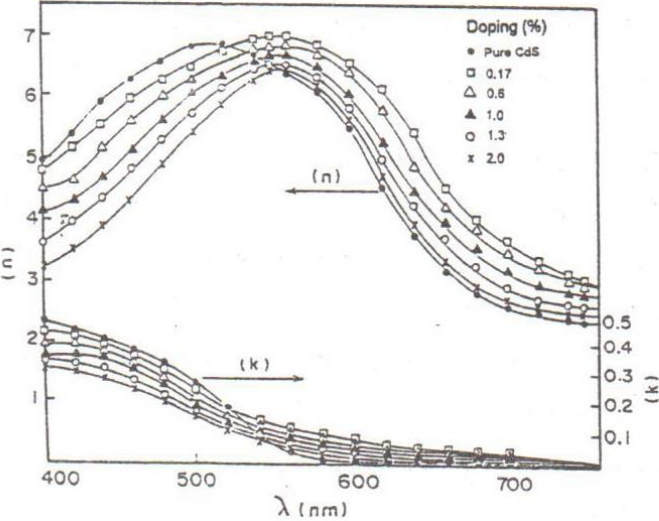


Fig. 6 : Dispersion curves of both n and k for Te doped CdS films.

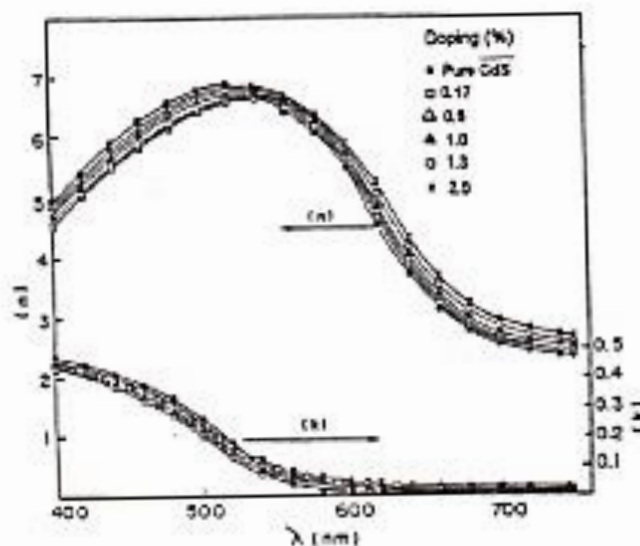


Fig. 7 : Dispersion curves of both n and k for Sb doped CdS films.

increases from 2.45 eV to 2.81 eV with increasing the concentration of Sb from 0.17% to 2.0%.

The dispersion curves of both n and k for CdS films doped by Te and Sb with different concentration are illustrated in Fig. 6 and 7 respectively. It is clear that the general behaviour of these constants are the same, since they have decreased by increasing the wavelength and at low wavelength region n and k decrease with decreasing the dopant concentration at a given wavelength for Te doped CdS films and decrease with increasing the dopant concentration for Sb doped CdS film.

To check the observed results of the optical properties for Te and Sb doped films, we took X-ray diffraction of such films. As an example, an X-ray diffraction of such films. As an example, an X-ray diffraction patterns of CdS films doped with the same concentration (2.0%) of Te and Sb and undoped CdS film prepared under the same conditions are shown in Fig. 8. This figure shows that the antimony-doped CdS film to be amorphous and for tellurium-doped CdS films to be crystalline with hexagonal structure and preferred orientation about the (002) plane and similar to that obtained for undoped CdS film.

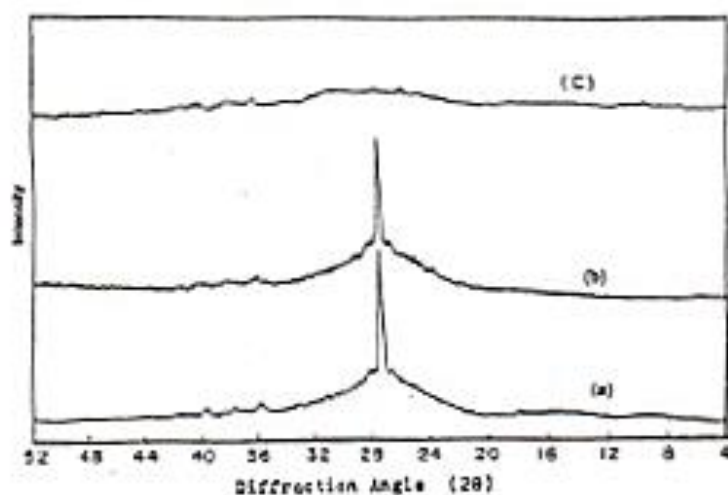


Fig. 8 : X-ray diffraction patterns of :
 a - Pure CdS b - Te doped (2%) CdS c - Sb doped (2%) CdS films

TABLE 1 : ACTIVATION ENERGIES OF UNDOPED AND DOPED CdS Films.

Doping %	Activation energy ΔE	
	To doped CdS films	Sb doped CdS films
0.0	0.25	0.25
0.17	0.66	0.42
0.6	0.602	0.43
1.0	0.57	0.55
1.3	0.48	0.61
2.0	0.33	0.73

TABLE 1: ACTIVATION ENERGIES OF UNDOPED AND DOPED CDS FILMS

Sb %	$T_c \times 10^4$ (K)	σ_o ($\Omega^{-1} \text{cm}^{-1} \text{K}^{1/2}$)	$\alpha_o \times 10^7$ (Cm^{-1})	E_f ($\text{eV}^{-1} \text{cm}^{-3}$)	$R \times 10^{-1}$ (Cm)	ω (eV)
0.17	5.602	2.398×10^{-4}	1.277	6.91×10^{21}	1.119	0.0246
0.6	6.232	2.511×10^{-5}	0.1411	8.38×10^{18}	10.4	0.0253
1.0	18.84	6.309×10^{-7}	0.0062	2.31×10^{14}	314	0.0333
1.3	25.63	4.466×10^{-7}	0.0057	9.55×10^{13}	410.8	0.036
2.0	45.69	3.801×10^{-7}	0.0051	7.86×10^{13}	417.8	0.042

REFERENCES

- 1 - R.G. Seippel, Photovoltaics, Reston Publ. Co., Reston, (1983) 135.
- 2 - R. H. Bube and E.L. Lind, Phys. Rev., 110 (1958) 1046.
- 3 - R. H. Bube, J. Chem. Phys., 23 (1955) 18.
- 4 - Y. Gorodetskii, G. S. Pekar, A.I. Fedrov and M.K. Sheinkman, Sov. Phys. Semicond., 9 (1975) 646.
- 5 - A. G. Stanley, Appl. Solid State Sci., 5 (1975) 273.
- 6 - I. A. Kerpovich and B. N. Zvonkov, Sov. Phys. Solid State, 6 (1965) 2065.
- 7 - A. J. Learn and J. A. Scott. Monck, J. Phys. Chem. Solids, 29 (1968) 2065.
- 8 - N. Romeo, G. Oberveglieri and L. Tarricone, Thin Solid Films, 43 (1977) L 15.
- 9 - J. Dresner and F. V. Shallcross, J. Appl. Phys., 34 (1963) 2390.
- 10 - s. Jalar, A. C. Raslogi and V. G. Bhirole Promana, 10 (1978) 477.
- 11 - S. Ray, R. Banerjee and A. K. Barua, Thin Solid Films, 19 (1981) 155.
- 12 - J. I. B. Wilson and J. Wood, J. Phys. Chem. solids, 34 (1973) 171.
- 13 - A. Yoshikawa, R. Kondo and Y. Sakai, Jpn. J. Appl. Phys., 12 (1973) 1096.
- 14 - A. C. Aten and J. H. Haanstra, Phys. Lett., 11 (1964) 97.
- 15 - R. Banerjee, S. Ray and A. K. Barua, Jpn. J. Appl. Phys., 21 (1982) L 43.
- 16 - J. J. Hopfield, D.H. Thomas and R. T. Lynch, Phys. Rev. Lett., 17 (1966) 312.
- 17 - N. F. Mott and E.A. Davis, "Electronic Processes in Non - crystalline Materials", Clarendon, Oxford, 155 (1971).
- 18 - J. I. Pankove, "Optical Processes in Semiconductors", New York, Dover, (1971).