

The electrical and optical properties of semiconductor CdTe films

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반도체 CdTe 박막의 전기 광학적 특성

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Abstract We have investigated the structure and the conductivity of the CdTe films evaporated on the glass substrates by Electron Beam Evaporator (EBE) technique. The structure is observed to be polycrystalline whose phase is mainly hexagonal phase with some cubic phase. Dark electric conductivity is of the order of $10^{-8} \Omega^{-1} \text{cm}^{-1}$ and slightly increased by annealing for an hour at 300°C . Activation energy calculated from the electrical conductivity which varies with increasing temperature is 1.446 eV in the case of room temperature substrates. The values of optical band gap are 1.52 eV in direct transition whereas 1.44 eV in indirect. The photoconductivity of the films is of the order of $10^{-8} \Omega^{-1} \text{cm}^{-1}$ and the peak energy is about 600 nm in the room temperature. The photoconductivity starts to increase at 850 nm, which is close to 1.446 eV, the activation energy of CdTe polycrystal films.

요 약 유리 기판 위에 electron beam으로 증착(EBE)된 CdTe film의 결정구조 및 전기 전도도와 광 전도도를 조사하였다. 그 구조는 거의 hexagonal phase이었으며 cubic phase가 약간 포함된 다결정이었다. 암 전기 전도도(dark electric conductivity)는 $10^{-8} \Omega^{-1} \text{cm}^{-1}$ 정도이고, 300°C 에서 1시간 동안 열처리하여 약간 증가되었다. 온도가 증가됨에 따른 전기 전도도로 부터 계산된 활성화 에너지는 실온에서 증착된 film의 경우 1.446 eV이었다. 흡수계수로 부터 구한 광학적 band gap은 직접 천이(direct transition)인 경우 1.52 eV이었고 간접 천이(indirect transition)인 경우 1.44 eV이었다. Film의 광전도도는 약 $10^{-8} \Omega^{-1} \text{cm}^{-1}$ 정도이고, 실온에서 대략 600 nm일 때 가장 크다. 광 전기 전도도는 850 nm에서 증가하기 시작하며 이는 CdTe 다

결정의 활성화 에너지(activation energy)인 1.446 eV와 근사하다.

1. Introduction

CdTe, a direct gap semiconductor with band gap of 1.45 eV at room temperature has many important applications. Not only is the single crystal CdTe used for the fabrication of γ -ray and X-ray radio sensors, optical and acousto-optic modulators, infrared windows, etc., but it is also used as a substrate for the epitaxial growth of HgCdTe. Thin film CdTe has been shown to be a promising photovoltaic material for energy conversion because it has a high absorption coefficient in the visible range of the solar spectrum and its band gap is close to the optimum value for efficient solar energy conversion. The material can be prepared in n-type and p-type forms so that solar cells can be formed in both homojunction and heterojunction configurations. And CdTe film showed high photoconductivity in 500 nm to 800 nm. The generally used growth methods of CdTe thin film so far are technique of Liquid Phase Epitaxy (LPE), Vapor Phase Epitaxy (VPE), Metal-Organic Chemical Vapor Deposition (MOCVD), and Molecular Beam Epitaxy (MBE), etc.. In our experiment CdTe thin films have been deposited on the glass substrate using EBE technique.

2. Experimental

2.1. Sample preparation

CdTe bulk materials have been synthesized from pure (99.999 %) Cadmium and Tellurium in an evacuated quartz tube. The mixture of Cd and Te in a proper atomic ratio was loaded in a fused quartz tube inside the cylindrical heater. Figure 1 is the time schedule for synthesis of CdTe crystal.

CdTe thin films have been deposited on the glass substrates by EBE (Korea Vacuum Co. KVC-663) in pressure of approximately 1×10^{-6} torr, voltages of 3.7 kV and currents of 3 mA during the evaporation. The deposition rate and the thickness of the films were 2 Å/sec and 5000 Å respectively. The substrates temperature were held at both room temperature and 300°C, and the samples were annealed for 1 hr at 300°C in a vacuum atmosphere. A pair of gold electrodes of 5 mm length at a separation of 1

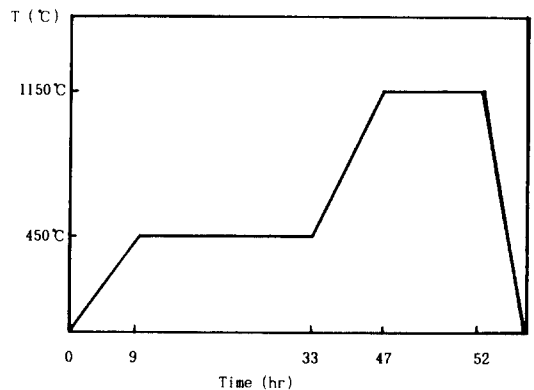


Fig. 1. The schedule for synthesis of CdTe.

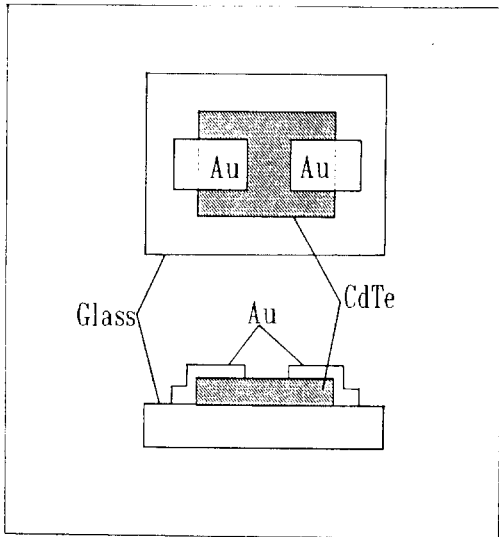


Fig. 2. The schematic structure and dimension of the CdTe film on the glass substrate.

mm has been prepared by thermal evaporation on the surface of the film for electrical measurements. Figure 2 shows a schematic structure and dimension of the thin film on the glass substrates.

2.2. X-ray diffraction experiment

The structure of CdTe film has been studied by X-ray diffraction. The X-ray diffraction patterns of the samples have been obtained using a X-ray diffractometer (Rigaku Geigerflex D/max III a) with Mo-K α ($\lambda=0.711 \text{ \AA}$) radiation with Zr filter. Scattered intensities are measured over 2θ angles from 5° to 60° with step intervals of 0.01° using filtered Mo-K α radiation. The scanning speed is 8° advances in 2θ per minute.

2.3. Characterization of the films

The electrical conductivity as a increasing temperature has measured using the Electrometer (Keithley-617) unit. The rate of increasing temperature is 4°C per minute and the range of temperature is from room temperature to 250°C in Thermostatic Oven (ANDO 9). Optical transmission spectra of the films have been recorded on a UV/VIS Spectrophotometer (Shimadzu 2100S). The photoconductivity was measured under illumination with tungsten light of 150 W. The wavelength range for the photoconductivity measurement was from 300 nm to 900 nm.

3. Results and discussion

3.1. The composition and structure

The surface composition of the as-prepared films (5000 \AA thickness) has been identified by an Energy Dispersive Spectroscopy (EDS). Figure 3 shows EDS spectrum for the measurement of CdTe atomic ratio.

The surface composition of the as-prepared films is slightly different from CdTe source material. Cd losses on the CdTe surface are measured about 4 % of atomic ratio at room temperature substrates and about 8 % at 300°C substrates after the evaporation. It is shown the X-ray diffraction patterns of CdTe powder and as-prepared film in Fig. 4.

The X-ray diffraction patterns obtained at room temperature for CdTe powder show

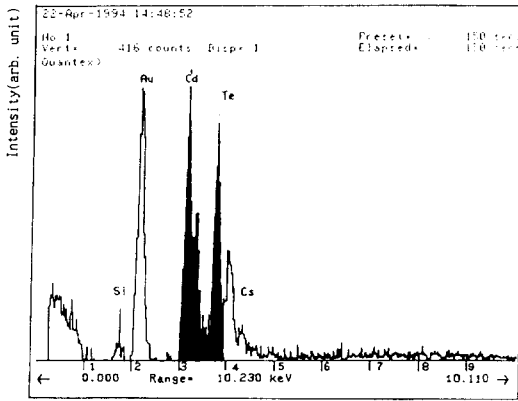


Fig. 3. EDS spectrum for the measurement of CdTe atomic ratio.

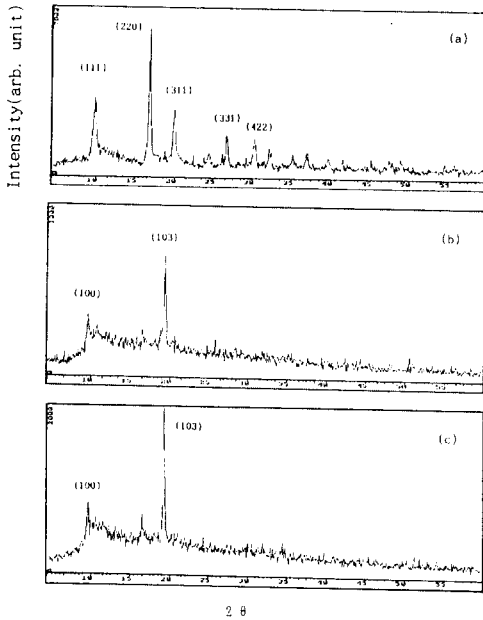
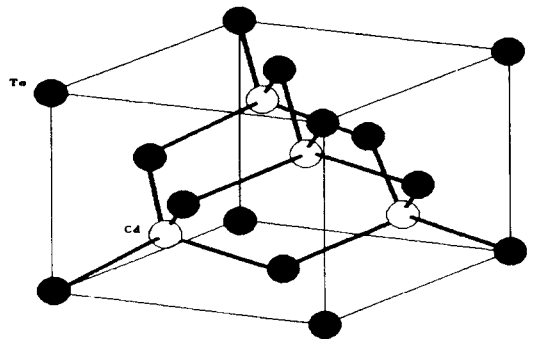


Fig. 4. X-ray diffraction patterns of the representative. (a) CdTe powder, (b) as-prepared film and (c) CdTe film annealed 300°C - 1 hr, using filtered Mo-K α radiation.

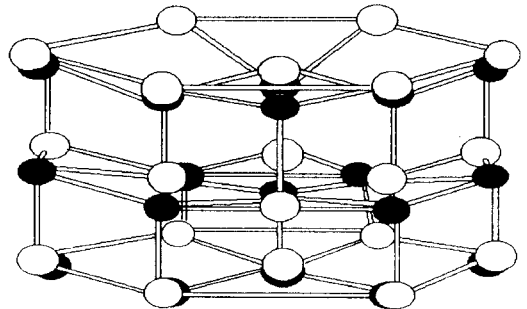
polycrystalline with zinc blende structure. But the relative intensities between (111) peak and (220) peak did not agree with

those of the standard CdTe cubic powder pattern. In fact it has observed that the structure of the films have two phase; the cubic and hexagonal phase. Figure 5 is the structural models of zinc blende and wurtzite. Figure 6 is the diffraction patterns calculated from each phase of CdTe crystal.

We can see in Fig. 4 that the peaks at 2θ values corresponding to CdTe hexagonal plane (100) and (103) have been developed. Lattice parameters of the wurtzite structure have been reported [1] as $a_0 = 4.56 \text{ \AA}$, $c_0 = 7.46 \text{ \AA}$, which correspond to a nearly ideal hcp phase. However, it has been found the new (200) peak of the zinc blende in the dif-



(a) Zincblende 구조



(b) Wurtzite 구조

Fig. 5. The models of zinc blende and wurtzite.

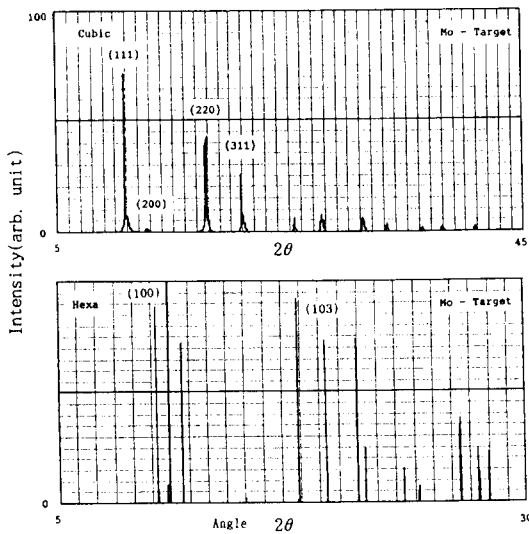


Fig. 6. The diffraction patterns calculated from the models of each phase.

fraction pattern. We do not rule out the possibility that the (002) peak intensity may arise from the simultaneous presence of some extent of cubic phase CdTe.

3.2. Electrical conductivity

Figure 7 and 8 show the dependence of the electrical conductivity on temperature for films deposited at room temperature and 300 °C of substrates. Dark conductivity of the films is of the order of $10^{-8} \Omega^{-1} \text{cm}^{-1}$. Electrical conductivity has increased as increasing temperature and slightly increased in the films annealed for 1 hr at 300 °C as compared to as-prepared.

The temperature dependence of the conductivity in the intrinsic region is dominated by exponential dependence $\exp[-E_g/2k_B T]$ of the carrier concentration [2]

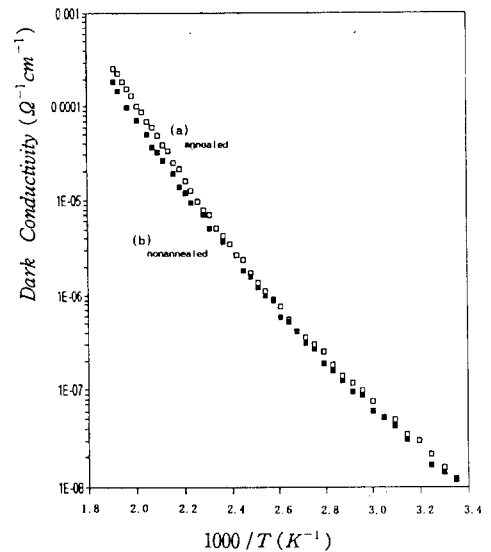


Fig. 7. The dependence of the electrical conductivity on the temperature for films evaporated at room temperature substrate. (a) annealed at 300 °C - 1 hr and (b) nonannealed.

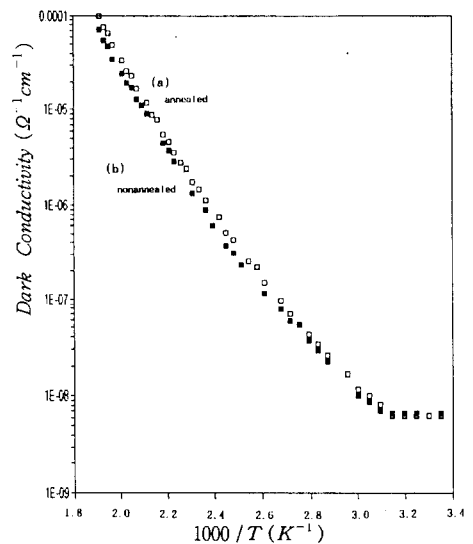


Fig. 8. The dependence of the electrical conductivity on the temperature for films evaporated at 300 °C substrate. (a) annealed at 300 °C - 1 hr and (b) nonannealed.

$$\sigma(T) = n(T) \propto \exp[-E_g/2k_B T], \quad (1)$$

where $n(T)$ is carrier concentration, k_B is Boltzmann constant, and E_g is activation energy. The activation energy at room temperature is 1.446 eV.

3.3. Optical absorption

Near the absorption edge an exponential variation in transmission (T) with absorption coefficient is most probable so α may be determined from

$$T = T_0 \exp(-\alpha d), \quad (2)$$

where T_0 is found to be nearly equal to unity at the absorption edge and d is the thickness of the film. Figure 9 shows the optical absorption at each CdTe thickness. We can see the absorption edge of CdTe films above 3000 Å thickness. Figure 10 shows the optical absorption as increasing the incident photon energies at each substrate temperature. The absorption coefficient is slightly increased at room temperature substrate in comparison with 300 °C substrate.

The structure of films is mainly hexagonal phase with some cubic phase. It has been known the results of optical absorption do not distinguish the cubic phase films from those of hexagonal phase; both types of films yield the same results [3]. Following Birman's Double-Zone Scheme, it becomes apparent that a cubic to hexagonal transformation should have little effect on the original γ state of zinc blende. The absorption co-

efficient α may, in general, be written as a function of the incident photon energy (eV) so that [4]

$$\alpha = A_0(h\nu - E_g)^m, \quad (3)$$

where A_0 is a constant given by

$$A_0 = \frac{e^2}{nch^2 m_e^*} (2m_r)^{3/2}, \quad (4)$$

where m_e^* and m_r being the effective and reduced mass of charge carriers respectively. E_g is the optical band gap at which an optical transition occurs, the nature of which is determined by the value of m in Eq. (3). The band gaps E_g corresponding to these m val-

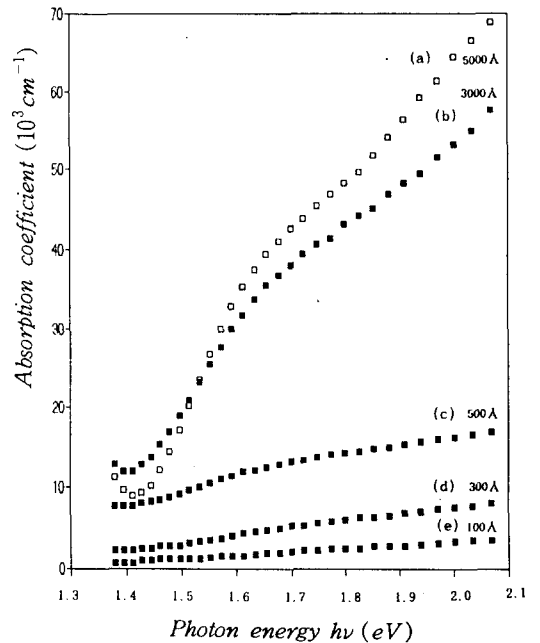


Fig. 9. The optical absorption at each CdTe thickness. (a) 5000 Å, (b) 3000 Å, (c) 500 Å, (d) 300 Å and (e) 100 Å.

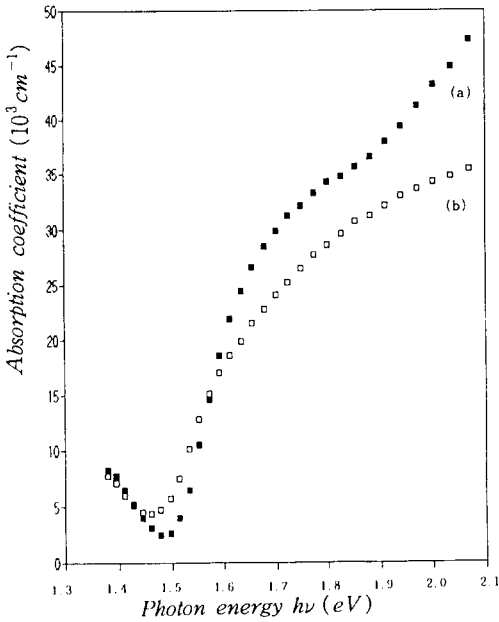


Fig. 10. The optical absorption of the CdTe film at (a) room temperature substrate and (b) 300°C.

ues were obtained by extrapolating the linear portion of the above plots to $\alpha^{1/m} = 0$. Now m 's in Eq. (3) have values of 1/2 for allowed direct transitions and 2 for indirect transitions. Figure 11 shows that allowed direct and indirect transitions occur in our films at optical band gap of 1.52 eV in direct transition whereas 1.44 eV in indirect for the substrate of room temperature. In Figure 12 the optical band gap is 1.48 eV in direct and 1.38 eV in indirect at substrate 300°C. Regarding the indirect transitions occurring in CdTe films Tahutupalli and Tomlin [4] El-Shazly et al. [5], Davis and Shilliday [6], S. Chaudhuri [7] and reported the values of band gap of 1.82 eV, 1.47 eV, 1.44 eV and 1.3 eV, respectively whereas the values of the band gap obtained from our experiment

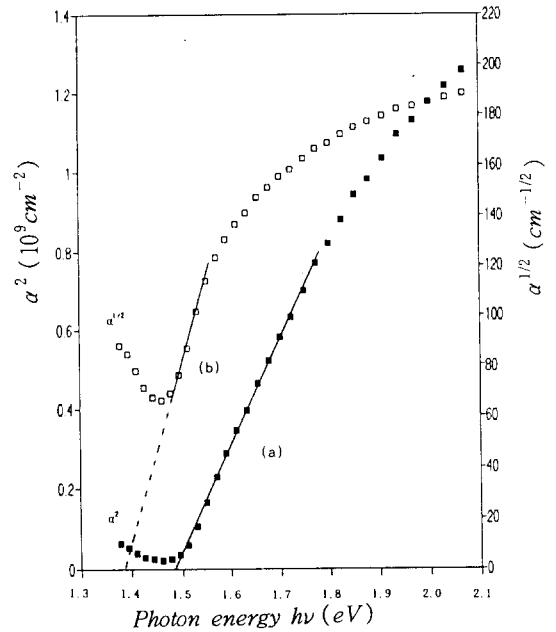


Fig. 11. The optical band gap for allowed (a) direct and (b) indirect transition in room temperature substrate.

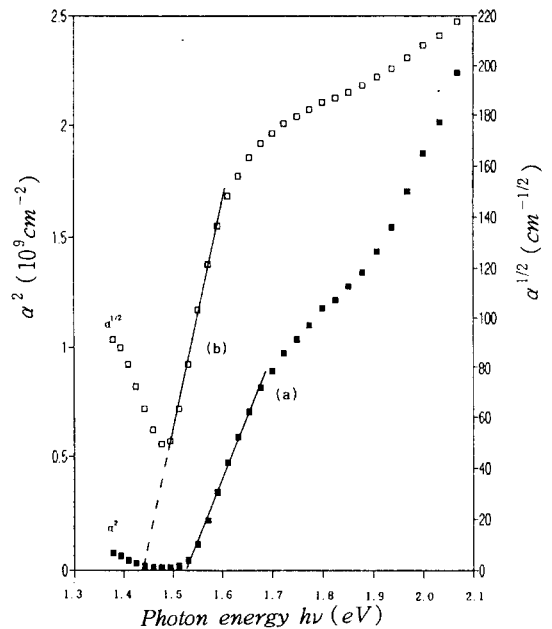


Fig. 12. The optical band gap for allowed (a) direct and (b) indirect transition in 300°C.

for indirect transition are 1.44 eV and 1.38 eV, which is consistent with the above reported values.

3.4. Spectral dependence of the photoconductivity

Figure 13 shows the spectral dependence of the photoconductivity of the evaporated films. The photoconductivity of the films is of the order of $10^{-8} \Omega^{-1} \text{cm}^{-1}$ at room temperature. The photoconductivity starts to increase at 850 nm, which is close to 1.446 eV, the activation energy of CdTe polycrystal. It

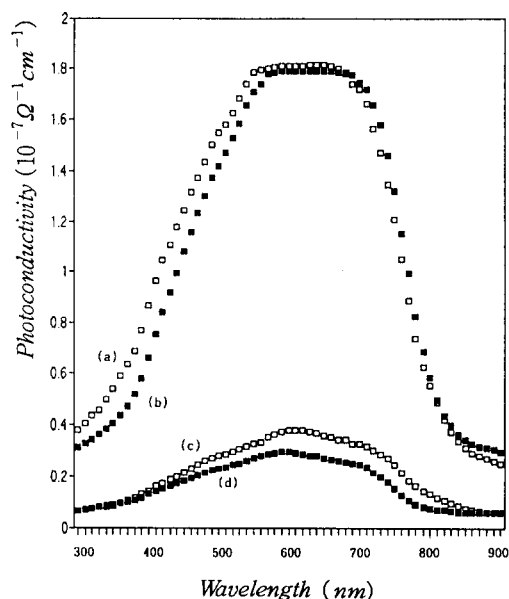


Fig. 13. The spectral dependence of the photoconductivity of the films evaporated (a) substrate room temperature, annealed $300^\circ\text{C} \cdot 1 \text{ hr}$, (b) substrate room temperature, non-annealed, (c) substrate 300°C , annealed $300^\circ\text{C} \cdot 1 \text{ hr}$ and (d) substrate 300°C , non-annealed.

is also slightly increased after the annealing in vacuum for an hour at 300°C . The peak energy of the curve is about 600 nm.

4. Conclusions

CdTe films have been evaporated by EBE and their structure has been investigated by X-ray powder method. The optical properties of the films has been also studied in terms of the optical absorption and photoconductivity. The points in this paper are following :

- 1) The structure of CdTe evaporated on the glass substrate is observed to be polycrystalline whose phase is mainly hexagonal with some cubic phase.
- 2) Dark electric conductivity is of the order of $10^{-8} \Omega^{-1} \text{cm}^{-1}$. It is shown that electric conductivity is slightly increased by annealing for an hour at 300°C .
- 3) Activation energy in the substrate room temperature is 1.446 eV.
- 4) The values of optical band gap is 1.52 eV in direct transition whereas 1.44 eV in indirect at room temperature substrates.
- 5) Photoconductivity of the films is of the order of $10^{-8} \Omega^{-1} \text{cm}^{-1}$ and the peak energy is about 600 nm. The photoconductivity starts to increase at 850 nm, which is close to 1.446 eV, the activation energy of CdTe polycrystal films.

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