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Abstract
Polycrystalline CdS films have been deposited by ultrasonic spray pyrolysis method. The electrical properties of the sample have been studied by means of an analysis based on the thermally stimulated current (TSC) spectrum at a heating rate of 0.06 K s^{-1} in the temperature range of 40–250 K. In order to evaluate the trap parameters of the sample, we have used curve fitting and initial rise methods. The TSC spectrum indicates that the sample has seven overlapped peaks located at levels in the range of 0.021–0.138 eV below the conduction band. The values of the frequency factor, the capture cross section and the concentration of the traps have been determined from the observed peaks in the TSC spectrum of the sample.

1. Introduction

CdS belonging to the II–VI group is an important semiconductor because of its intermediate band gap, high absorption coefficient, reasonable conversion efficiency, stability and low cost [1, 2]. CdS crystallizes in two forms, cubic and hexagonal phases [3], and it is possible to produce CdS films in both these phases [4]. CdS films are deposited using various methods such as vacuum evaporation [5], RF sputtering [6], chemical vapor deposition [7], ultrasonic spray pyrolysis (USP) [8], molecular beam epitaxy [9], and electrodeposition [10]. Amongst all the deposition methods, the USP is a simple, an economical, and a suitable method for large area deposition of many binary, ternary and quaternary semiconducting films with varying anion and cation concentrations.

Knowledge of the structural, optical, and electrical properties of CdS films is important in many scientific, technological, and industrial applications which find places in the field of optoelectronic devices, particularly solar cells. For the preparation of reproducible and reliable solar cells, it is important to control the electrical properties of CdS layer. The photoconductivity and thermal conductivity of CdS films are related to traps which are an individual impurity or defect in a crystal that affect the carrier transport properties. Therefore, it

is important to get information about the activation energies of the trap levels in CdS films.

Some of the measurement methods widely used for the investigation of charge carrier traps in materials are thermoluminescence (TL) [11], thermally stimulated depolarization conductivity (TSDC) [12], and thermally stimulated current [13]. Among them, the TSC measurement is a well known non-isothermal technique for the investigation of trap levels in semiconducting materials. Many insulating, semi-insulating and semiconductor materials show thermally stimulated effects during heating. The TSC is one of the highly sensitive methods for studying the trapping characteristics in high resistivity materials having trap levels usually below 1.5 eV [13]. In principle, this method consists in filling the traps after cooling down the material to low temperature and then heating the material at a constant rate and observing the thermally stimulated current as the traps are emptied. The energy level within the band gap of a particular trapping center is related to the temperature at which it is emptied, while the number of traps contributing to the observed current peak depends on the amount of trapped charges, which are released [14]. The TSC permits a survey of the gap states and also the determination of the capture cross section of each trap level [15].

The subject of this work is to obtain more information concerning traps in CdS film by means of thermally stimulated

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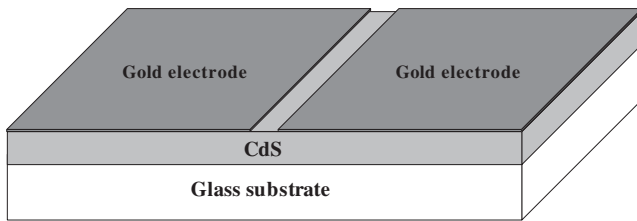
Figure 1. View of the sample in the form of planar structure.

current measurements in the temperature range of 40–250 K. The experimental data have been analyzed by using curve fitting and initial rise methods. The trap energy, the capture cross section, and the concentration of the traps in CdS film are reported.

2. Experimental details

CdS samples were produced on microscope glass substrates by the USP method at 225 °C substrate temperature. The full details of the deposition system used in this work had been given elsewhere [16]. The USP method involves spraying a solution onto the heated substrate. The substrates ($8 \times 8 \times 1$ mm^3) were boiled with detergent, soaked in chromic acid, cleaned in isopropyl alcohol, rinsed in distilled water at each step, and dried. The solution is usually made by dissolving salts of the constituent atoms of desired compound in aqueous medium. Solutions of various concentrations were tried to optimize the right stoichiometry of the films and the solution of concentration 0.1 M was found to give good quality stoichiometry films of CdS. Aqueous 0.1 M CdCl$_2$·H$_2$O dissolved in a mixture of methanol and deionized water (1:1), and 0.1 M (NH$_2$)$_2$CS were used to obtain CdS films. The samples have been produced by spraying the aqueous solution of 0.1 M CdCl$_2$·H$_2$O and 0.1 M (NH$_2$)$_2$CS in a 1:1 (by volume) onto the substrates at 225 °C. For the preparation of good quality films, various parameters such as the substrate temperature, the distance between the substrate and the ultrasonic spray head, solution flow rate and the carrier gas pressure were optimized. The ultrasonic spray head to the substrate distance was approximately 30 cm. The flow rate of the solution and the carrier gas pressure during spraying were adjusted to be 1 ml min^{-1} and 0.2 bar, respectively. Nitrogen was used as the carrier gas. The deposition time was 45 min. After the spraying procedure, the electrical heater was switched off and the samples were left on the copper hot plate and subsequently cooled in air before removal.

The average thickness of the sample was determined by weight difference method assuming the sample is uniform and dense as that of the bulk having density of 4.82 g cm^{-3}. The prepared CdS films were highly adherent to the glass substrate and had no crack or discontinuity or blister on them. For this reason the density of the sample had been taken as the same as that of the bulk CdS. The average thickness of the sample has been determined to be 3.89 μm. The sample was found to be n-type as determined from the hot probe method, and has also been reported by Sahu and Chandra [2].
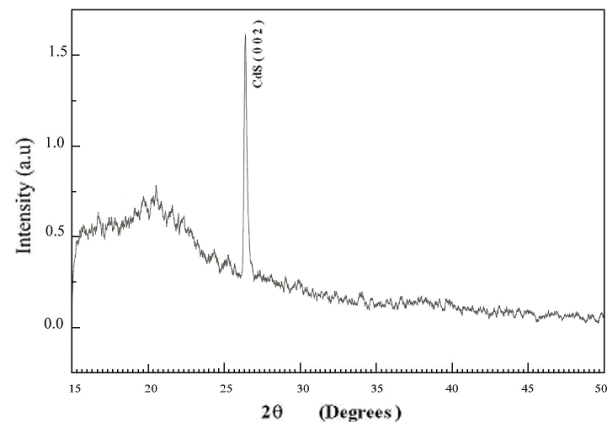
Figure 2. X-ray diffraction spectrum of CdS film deposited by the ultrasonic spray pyrolysis at 225 °C substrate temperature.

The crystal structure of the sample was characterized by Phillips x-ray diffractometer using Cu Kα radiation ($\lambda_{K\alpha} = 1.541$ Å). The scanning angle 2θ was varied between 15° and 50°.

The planar structure of the metal–semiconductor–metal system has been obtained by vacuum deposition of the gold electrodes on the sample by using Leybold Heraus 300 Univex System. The electrodes are placed at two opposite edges of the surface of the sample as shown in figure 1. The space between the electrodes was 0.5 mm and the width of the electrodes was 8 mm. Gold wires were attached to the electrodes by small droplets of silver paste.

The TSC measurement was carried out in an Oxford Instruments 43305 Model Cryostat by using Agilent 34401 Model Digital Multimeter, HP 4140B pA meter/dc voltage source, and VEE One Lab 6.1 Computer Program. The details of TSC measurement system had been given elsewhere [17]. The TSC measurement was performed after introducing the sample into the cryostat. The sample was cooled to an initial temperature of about 40 K and kept it in dark for 30 min before illuminating. The trapping centers were filled at 40 K for 5 min by illuminating with a UV lamp ($\lambda = 254$ nm, 6 W) with the illuminating intensity of 0.36 W m^{-2} over the sample. After the light was turned off, the sample was heated up to the room temperature at a constant heating rate of 0.06 K s^{-1}. The discharge current under a constant bias voltage of 20 V was recorded as a function of temperature.

3. Results and discussion

X-ray diffraction spectrum of the sample prepared at 225 °C is shown in figure 2. It indicates the presence of (002) plane for hexagonal CdS. The information on the grain size (L) of the sample has been calculated from Scherrer relation [18],

$$L = \frac{0.9\lambda}{D \cos \theta} \tag{1}$$

where D is the full width at half maximum (FWHM) of the diffraction peak. The grain size has been determined to be 47 nm.
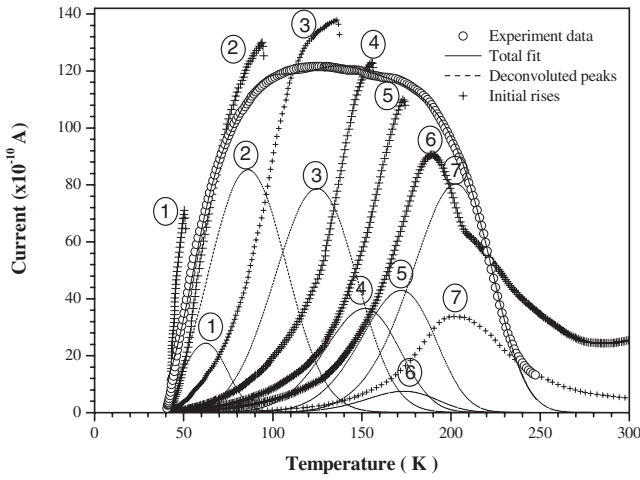
Figure 3. Deconvolution of the TSC curve of the CdS sample into seven separate peaks using the curve fitting method, and initial rises.

The TSC curve clearly shows the existence of crystalline defects and/or impurities that act as electronic trapping sites, each characterized by a different trap energy and frequency factor. There are several methods such as curve fitting, heating rate, initial rise, and peak shape to determine the trap energy from the experimental TSC curve. Many of them are based on the measurement of the maximum and the high and the low half intensity temperatures. However, the applicability of the many methods is restricted for a TSC curve which is complex due to the presence of a number of overlapped peaks. More reliable values can be found in many cases if more data are used [19].

The TSC spectrum which was obtained with the heating rate of 0.06 K s^{-1} and 20 V across the sample is shown in figure 3 and the experimental part of the thermal cleaning is also shown. The peaks with the same number are related to each other for comparisons. The discharging of the traps takes place between 40 and 250 K. A glance at the TSC spectrum of the sample exhibits broad band for the curve. In this work, the experimental TSC curve for the sample has been analyzed by using curve fitting and initial rise methods.

3.1. Curve fitting method

In the curve fitting method for determining the trapping parameters from an experimental curve, different equations are utilized depending on the recombination kinetics. Under monomolecular conditions (i.e. slow retrapping), the TSC curve of a discrete set of traps with a trapping level E_t below the conduction band is described by [20],

$$\sigma(T) = n_t \tau e \mu \nu \exp\left\{ -\frac{E_t}{kT} - \int_{T_0}^{T} \frac{\nu}{\beta} \exp\left(-\frac{E_t}{kT} \right) dT \right\} \quad (2)$$

where σ is the thermally stimulated conductivity, n_t is the initial density of filled traps, τ is the lifetime of the free electron, e is the electronic charge, μ is the electron mobility, ν is the frequency factor of a trapped electron, β is the linear heating rate, k is the Boltzmann constant, T_0 is the initial temperature, and T is the temperature. The frequency factor ν depends on temperature like T^a with $-2 \leqslant a \leqslant 2$ which

is related to the dependence of the effective density of states in the conduction band, N_c, and thermal velocity of free carriers, υ_{th}, on temperature. This is a rather mild dependence on temperature as compared to the exponent $\exp(-E_t/kT)$ in equation (2), and can therefore be neglected as a first approximation [13]. Should it be assumed that ν is independent of T and that over the temperature range of the TSC curve, the variation of μ and τ with T can be ignored. Thus, for slow retrapping, $\sigma(T)$ can be rewritten as [19, 21]

$$\sigma(T) = A \exp\left\{ -\frac{E_t}{kT} - \frac{\nu}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E_t}{kT} \right) dT \right\} \quad (3)$$

where A is a constant, $\nu = SN_c\upsilon_{th}$, S is the capture cross section of the trap, and $N_c = 2(2\pi m_e^* kT/h^2)^{3/2}$. Using the first term of the relevant asymptotic series for evaluating the integral, and putting $B = \nu E_t/\beta k$ and $t = E_t/kT$, equation (3) becomes

$$\sigma(T) = A \exp\{ -t - B \exp(-t)t^{-2} \} \quad (4)$$

where B is a constant and can be approximated by

$$B \cong B' = \exp(t_m) \frac{t_m^3}{t_m + 2} \quad (5)$$

where $t_m = E_t/kT_m$ and T_m is the temperature at maximum conductivity, σ_m. By using B' instead of B, the free parameters become E_t, and T_m which replaces ν. This leads to a convenient method of the curve fitting, with only one variable parameter E_t, since T_m is known experimentally.

In order to analyze all peaks of the TSC spectrum simultaneously, the fitting function consisting of the sum of all features of the TSC spectrum is described by [22]:

$$\sigma(T) = \sum_{i=1}^{n} \sigma_i(T). \quad (6)$$

In this equation, $\sigma_i(T)$ represents the current contribution of each peak, which is calculated from equation (4), and n is the number of peaks involved in the calculation. The overlapping TSC spectrum of the sample is found to be best fitted to seven peaks by using OriginPro 7.5 computer program. The program uses a Marquardt–Levenberg algorithm to minimize the difference between the experimental data and the fitting equation. The deconvoluted peaks and the total fit of the seven peaks together with the experimental data are also shown in figure 3.

Maximum peak temperatures were initially determined from the initial rise method given in the following section. Then these values were used in the curve fitting method as starting values for the program. These starting values have eventually changed into the final values to get the best fit for the curve. Once the curve had been fitted and the final values of the trap energies below the conduction band and T_m for each peak were determined as given in table 1, then equation (5) was used to calculate B and hence the frequency factor ν. Knowing the value of ν, we have calculated the capture cross section S for each trap level. Since this equation contains the effective density of states in the conduction band, the value of

Table 1. The trap energy (E_t), capture cross section (S) and concentration of traps (N_t) for seven TSC peaks of the CdS sample.

Peak number	T_m (K)		E_t (eV)		ν (s^{-1})	S (m^2)	N_t (m^{-3})
	Curve fitting	Initial rise	Curve fitting	Initial rise			
1	62	55	0.021	0.024	0.131	5.26×10^{-30}	2.91×10^{25}
2	86	90	0.022	0.034	0.0243	5.09×10^{-30}	4.93×10^{25}
3	125	135	0.047	0.037	0.119	1.19×10^{-30}	5.37×10^{25}
4	152	160	0.081	0.071	0.943	6.36×10^{-30}	4.98×10^{25}
5	171	178	0.108	0.079	2.938	1.54×10^{-30}	4.95×10^{25}
6	173	189	0.116	0.083	4.797	2.47×10^{-30}	4.90×10^{25}
7	203	201	0.138	0.108	5.056	1.91×10^{-30}	5.44×10^{25}

the electron effective mass is required for CdS. Therefore, we have used the value of $0.2m_0$ for the sample with hexagonal structure [23]. The values of the frequency factor ν and the capture cross section S calculated from the curve fitting results are also given in table 1. It can be noticed that the values of the frequency factors are by far lower than usually expected values of 10^{12} s^{-1} [13]. In the literature, a low frequency factor 10 s^{-1} has been found in a work on TL in polystyrene [24]. The reasonable explanation for low values of the frequency factors is probably related to that the peak we got by the deconvolution is a combination of more peaks. This makes the peak look very broad which, in turn, yields low effective trap energy and therefore, a very low effective frequency factor [13].

After obtaining the total fit and the deconvolution, the density of the traps can be estimated from the area under the deconvoluted peak corresponding to that trap [25]:

$$N_t = \frac{1}{eG^*V} \int J_{TSC} \, dt \qquad (7)$$

where V is the sample volume, G^* is the photoconductive gain, and J_{TSC} is the thermally stimulated current density. A reasonable approximation for G^* can be obtained by measuring the photon flux Φ needed to produce a photocurrent equal to the J_{TSC} at the T_m of TSC maximum [25]:

$$G^* = \frac{J_{max}}{e\Phi} \qquad (8)$$

where J_{max} is the maximum TSC. Hence, knowing the values of the peak area, sample volume, and photoconductive gain, we can calculate the concentration of the traps. The set of resulting parameters are also summarized in table 1.

3.2. Initial rise method

In order to apply the usual analytical methods correctly, it is necessary to isolate the peaks which appear in TSC spectrum. Thermal cleaning procedure [26], which is widely used to isolate the peaks, was applied as follows. After having obtained the whole TSC spectrum between 40 and 250 K with the heating rate of 0.06 K s^{-1}, the sample was recooled to 40 K. Then, the sample was illuminated for 5 min. When the heating was started through the same cycle once more with the same heating rate, the heating was stopped at a temperature of T_1 and the device was kept at this temperature until a reasonable decay in current was observed. In this way, traps related to the first peak in the TSC spectrum were substantially emptied.
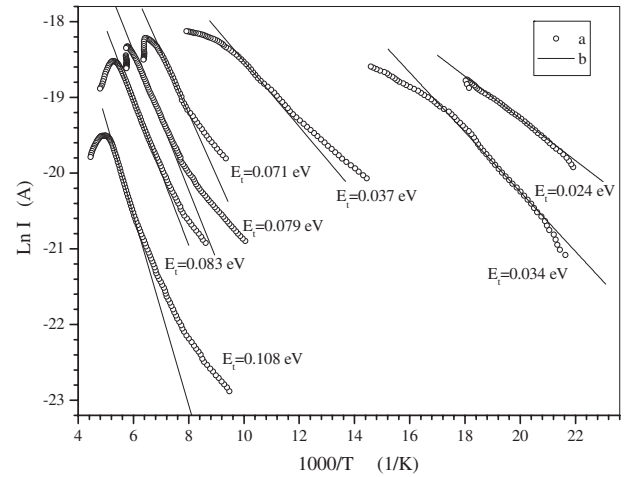
Figure 4. $\ln I$ versus $1000/T$ for all seven peaks in the TSC spectrum of CdS: experimental data (a) and theoretical fits using the initial rise method (b).

The sample was recooled to 40 K and kept for 20 min at this temperature. The sample was reheated with the same heating rate and the new increase in current was determined as carriers released from the traps related to the second peak in the TSC spectrum. This operation gives us the initial risings of the peaks individually. The thermally stimulated currents were produced by activation of the charge carriers from the traps in the band gap to the conduction band. The current passing through the sample was observed as a result of the increasing temperature. Garlick and Gibson [27] showed that when the traps begin to empty as temperature increasing; the TSC can be expressed by

$$I_{TSC} = A \exp(-E_t/kT) \qquad (9)$$

where A is a constant that depends on the concentration of initially full traps and the probabilities of the transitions involved in the TSC processes. Arrhenius plot, i.e. the natural logarithm of the current against $1/T$ should yield a straight line with a slope of $-E_t/k$ in the region of initial rise.

The method of thermal cleaning has been employed in an attempt to isolate seven individual TSC peaks. From the initial rising of each peak the trap energies were calculated from the Arrhenius plots as shown in figure 4. The trap energy values are also given in table 1.

If semiconductor films are deposited under non-epitaxial conditions or on amorphous substrates, then it is most likely

that they will occur in a polycrystalline form. Polycrystalline films are composed of large numbers of grains joined together by grain boundaries [25]. It is also well known that the TSC spectrum of a polycrystalline material is very sensitive to the structural changes of defects, grains or grain boundaries, and the presence of shallow and deep trapping levels. Therefore, the number of trap states and the values of trap energies are strongly affected by the variation of defects, grains or grain boundaries in the lattice. The concentration of atoms at the grain boundaries is higher than the other places in the sample which causes incomplete bonding between atoms and therefore defect levels or trapping levels are formed. They then become chemisorbed having captured a conduction electron which binds them to the surface. The energy level of such a bound electron is sufficiently below the conduction band, which the electrons can easily escape from the trap levels to the conduction band with a very small amount of energy. It is also generally accepted that oxygen plays a crucial role as trapping centers either at the surface or at the grain boundaries where it can easily be adsorbed [28–30].

　　Examining table 1, we see that T_m values for the curve fitting and the initial rise methods are rather close to each other. For E_t values it could be evaluated as E_t (eV) < 0.03 due to the chemisorbed oxygen atoms at the film surface [31], and $0.03 < E_t$ (eV) < 0.1 due to the heavy concentration of carriers and the presence of adsorbed oxygen at the grain boundaries [31–33], and $E_t > 0.1$ due to the defects at localized states [32]. Considering the trap density we see that it is in the order of 10^{25} m^{-3} which seems to be larger. This is not unreasonable regarding the fact that an increase is expected in the grain boundary areas because of the smaller size of the crystallites, since decrease in the size of the crystallites results in the increase of the surface area to volume ratio, and unwitting impurities during the production of the sample. These trap density values are in the reasonable range when compared with the literature values [30, 34–36].

4. Conclusions

CdS films have been deposited onto glass substrates at 225 °C by the USP method. The n-type CdS films have been obtained in polycrystalline form with hexagonal structure. We have studied the thermally stimulated current measurements for the investigation of the trap densities, trap energy levels, frequency factors and capture cross sections in the sample. Using the curve fitting method for slow retrapping conditions and initial rise method, the TSC curve of Au–CdS–Au planar structure revealed that seven overlapped peaks were located at levels in the range of 0.021–0.138 eV below the conduction band. The observed trap energy levels are thought to arise from chemisorbed oxygen atoms at the film surface, the heavy concentration of carriers and the presence of adsorbed oxygen at the grain boundaries, and the defects at localized states. The concentration of traps associated with the individual peak has been calculated between 2.91×10^{25} and 5.44×10^{25} m^{-3}. We could also say that the results of these two different methods are in accord with each other.

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