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Abstract. Stabilization of the electrical resistivity of CdSe thin films has been studied by air oxidation at room temperature (300 K). Depending on the film thickness, the dark- and photoconductance of the films stabilize over 12 to 25 days of air exposure. The variation of photosensitivity of the films has been explained on the basis of inherent slow recombination states (k centres) and oxygen-assisted conversion of selenium vacancy, cadmium vacancy, cadmium interstitial (V_{Se}–V_{Cd}–Cd_i) to cadmium vacancy–cadmium interstitial (V_{Cd}–Cd_i) complexes. The variation of oxygen adsorption with film thickness is studied. The temperature variation of dark- and photoconductance measurements in these films reveals a thermal quenching of photoconductivity at about 265 K. The k centres are located at about 0.23 eV above the top of the valance band. A selenium vacancy-related level is revealed at about 0.12 eV below E_c. This level disappears as a result of long time exposure of the films to atmospheric oxygen. An oxygen-assisted excitonic transition is revealed along with the band edge transition in the spectral distribution of photocurrent of oxygen-adsorbed stabilized films.

1. Introduction

Cadmium selenide is well known as a very good photoconducting material. It has been investigated for many years for its potential applications in electrography, photoconducting and photovoltaic cells, thin film transistors and lasers [1]. The use of CdSe in photoconductivity results in detectors with a faster response than CdTe photodetectors. Polycrystalline CdSe films have been used to fabricate photoelectrochemical cells and an efficiency of about 5% has been achieved [2]. A significant increase of conversion efficiency by annealing the films in a 2% oxygen atmosphere has been reported by Szabo and Cocivera [3].

CdSe thin films have been prepared by different workers [4, 5] using different techniques. The photoconductive gain of the detectors depends on the method of preparation [6, 7] and sensitization [8–10]. Freshly prepared CdSe films are generally very sensitive to atmospheric oxygen and the dark- and photoconductivity depend strongly on the level of oxygen adsorption in them. After adsorption, the film behaviour depends mainly on its initial conductivity and on the characteristics of the adsorbate–adsorbent binding. Several workers [11, 12] have studied the oxygen adsorption rate and desorption energies in CdSe thin films. The effect of oxygen on the photosensitivity of the films has been studied for sprayed and vacuum evaporated films by Raturi *et al* [5] and Sakai *et al* [13] and also for single crystals by Bube and Burton [14]. An increase of photosensitivity due to chemisorption of oxygen has also been reported by Kanthala [15] for chemically deposited films. Though the explanations of different workers for the increase in dark- and photoresistance of CdSe films are more or less same, in most of the works the films were annealed in air. During annealing in air at elevated temperatures, there are possibilities such as variation of grain size and stoichiometry of the films along with the possibility of oxygen absorption by the films. Therefore, the correlation of dark- and photoconductivity with oxygen adsorption in the films has not accounted for the effect of grain size or stoichiometry variation in most of the previous works.

In the present work, we have studied the effect of isothermal air oxidation at room temperature (300 K) on the stabilization of electrical properties of the vacuum evaporated CdSe films. In the case of CdSe films, their exposures to atmospheric oxygen for different durations produce different $\ln G$ versus $1/kT$ characteristics. However, exposure of the films to atmospheric oxygen for longer periods causes a stabilization of dark- and photoresistance. It has been observed that the dark- and photoresistance stabilizes within 12 to 25 days depending

on the thickness of the films and the initial stoichiometry of the surfaces. The spectral response and temperature variation of dark- and photoconductance are measured on the air-exposed films to study their stability and the mechanism of variation of photosensitivity of the samples.

2. Experiments

CdSe thin films of different thicknesses (0.27–1.70 μm) were deposited by thermal evaporation on thoroughly cleaned glass substrates at room temperature (300 K). The rate of deposition was kept constant (120 nm min^{-1}). Details of the film deposition technique has been described elsewhere [16]. The composition of the films was estimated by energy dispersive x-ray (EDX) analysis (Camscan series 2DV with link system). The composition of the films varied with film thickness [17]. The composition deviates from the stoichiometric value with increase in film thickness. However, in all the films the Cd/Se atomic ratio was > 1.0. The thickness of the films was measured by a Taylor Hobson form talysurf. It can be seen from the x-ray diffraction (XRD) results that all the films are in hexagonal phase [16].

The dark- and photoconductance of the films were measured by a Keithley electrometer amplifier (610C). A tungsten–halogen lamp fed by a stabilized power supply was used for illuminating the samples. The intensity of illumination (1400 W m^{-2}) was measured by an Eppley calibrated thermopile. Colloidal graphite (aquadag) was used for ohmic contacts in the films. As the film resistance was high enough (10^4–10^7 Ω) graphite contacts showed linear I–V characteristics for the applied voltage range (0–30 V). In order to observe the effect of air oxidation, the films were exposed to air after taking the films out of the deposition chamber. The dark- and photoresistance of the films were measured at different intervals of time. The time of exposure to air was measured from the moment of taking the samples out of the deposition chamber.

The conductivity of the films exposed to air for different periods of time was measured in the temperature range 160–305 K by a cryostat having a quartz window. A detailed description of the apparatus has been given elsewhere [18]. To study the dispersion of the conductance characteristics (G versus T) of the stabilized films (exposed to air for a long time) the dark- and photoconductivity of some of the films were measured repeatedly. The spectral response of the photocurrent of the stabilized films of different thicknesses was measured at room temperature using an Oriel (7240) monochromator. Photodecay was recorded by an Omniscribe strip chart recorder (model no 5000). The type of majority carriers and the carrier concentration of the samples were determined from thermoelectric power (TEP) measurements. For calculation of the carrier concentration from the TEP, it is assumed that the scattering factor $r = 0$ and $m_e^* = 0.13 m_0$ [19].

3. Results and discussion

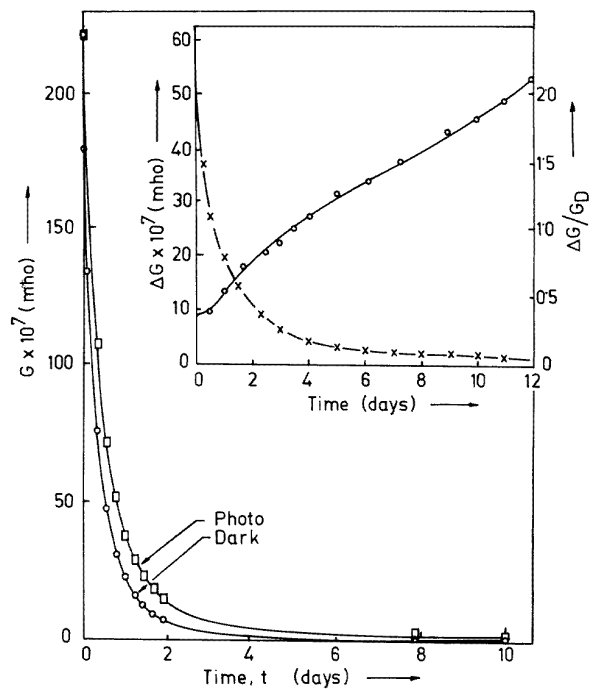Thermoelectric power measurements on the films reveal that all the as-grown and air-exposed films are n-type

Figure 1. Variations of dark- and photoconductance (G) of a 0.46 μm thick CdSe film with air exposure time. The inset shows the variation of excess conductance ΔG ($\times$) and photosensitivity ($\Delta G / G_D$) ($\bigcirc$) of the film.

having a carrier concentrations $\approx 10^{17}$ cm^{-3} at room temperature. When the samples are exposed to air their resistance changes with duration of exposure to air and after a long time resistance becomes stabilized. The nature of variation is same for all the films. The variation of dark- and photoconductance with duration of air exposure is shown for a typical film in figure 1. The exposure time required for the stabilization of the films depends on the film thickness. The change of resistance in air may be due to oxygen adsorption by the films. In case of CdSe, the inherent defects are selenium and cadmium vacancies and also interstitial atoms of the two elements [20]. A change in concentration of these defects can produce a change in the adsorption power of the semiconductor surface. Since acceptor-type adsorbed molecules localize near the conduction electrons, the adsorption power (the sensitivity of the semiconductor to a given type of gas) can be determined as the ratio $\beta = (G_0 - G_a)/G_a$, where G_0 is the conductance before chemisorption of the gas and G_a is the conductance after complete chemisorption. If one takes into account the fact that the chemisorbed molecules or atoms can be sensitive to the type of adsorption centre, values of β provide an experimental basis for studying the properties of the semiconductor surface. In the present investigation, the β value reduces from 307 to 19 with increase in film thickness. The variation of β with thickness, composition and particle size of the films is listed in table 1. Since the Cd/Se atomic ratio for all the films is > 1.0 and the conductance changes with the exposure of the films to air, we can consider the selenium vacancy to be the basic centre for the chemisorption of oxygen in the films. Since particle size increases with the film thickness and the probability of

Table 1. Variations of air adsorption power (β), dark- and photoconductance with particle size and composition for films of different thicknesses.

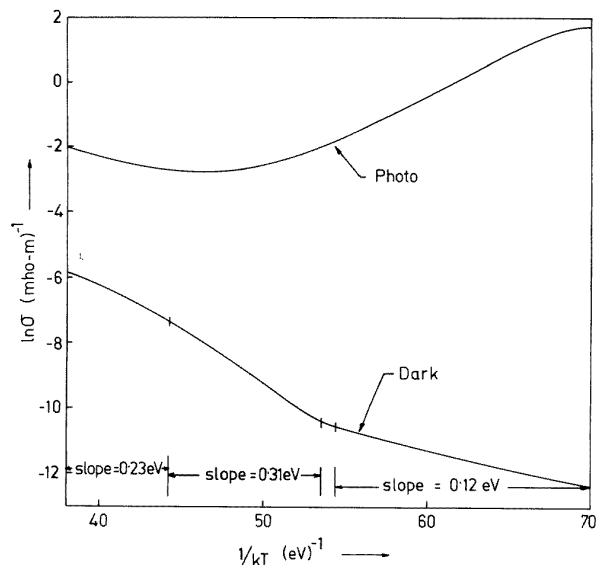| Film thickness (μm)	Cd/Se (atomic ratio)	Particle size (nm)	Values of β obtained from	
			Dark conductance	Photoconductance
0.34	1.026	48.7	307	133
0.46	1.082	60.9	65	48
1.01	1.222	91.8	19	20
1.70	1.300	94.8	45	16

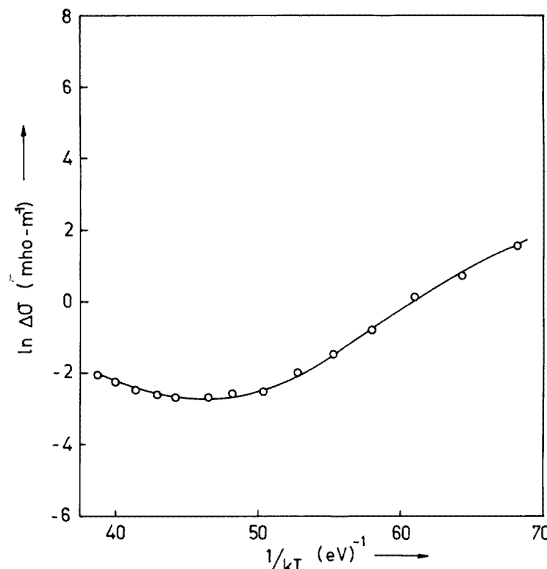**Figure 2.** Temperature variations of dark- and photoconductivity of a 0.46 μm thick CdSe film.

Figure 3. Temperature variation of excess conductivity ($\Delta\sigma$) of a 0.46 μm thick CdSe film.

oxygen adsorption is greater on the grain boundaries, the lower particle size (higher effective grain boundary area) of the thinner films must make some contribution to the higher oxygen adsorption power of these films.

The variations with duration of exposure of excess conductance ($\Delta G = G_{ph} - G_D$) due to illumination and photosensitivity ($\Delta G/G_D$) are shown in the inset of figure 1. It is observed that photosensitivity increases with the exposure of the film to air. The decrease of the dark- and photoconductance of the films in air is due to a reduction of the density of free electrons in the grains and the increase in the grain boundary barrier as a result of diffusion of oxygen [21]. Oxygen atoms penetrate into the bulk of a thin film along the grain boundaries [22].

The temperature variation of dark- and photoconductivity of a typical CdSe film is shown in figure 2. The temperature variation of excess conductivity ($\Delta\sigma = \sigma_{ph} - \sigma_d$) is shown in figure 3. Values of the photorelaxation time constant (τ_{r0}) for the films have been obtained from the slopes of the $\ln(\Delta\sigma)_t$ versus t plots. Here $(\Delta\sigma)_t$ is the excess conductivity after cessation of illumination (weak illumination, 1400 W m^{-2}). Details of the theory of photorelaxation have been described elsewhere [23]. Figure 4 shows $\ln(\Delta\sigma)_t$ versus t plots at different temperatures for a typical film. The photorelaxation time constant (τ_{r0}) is found to be nearly 276 s at 300 K and nearly 265 s at
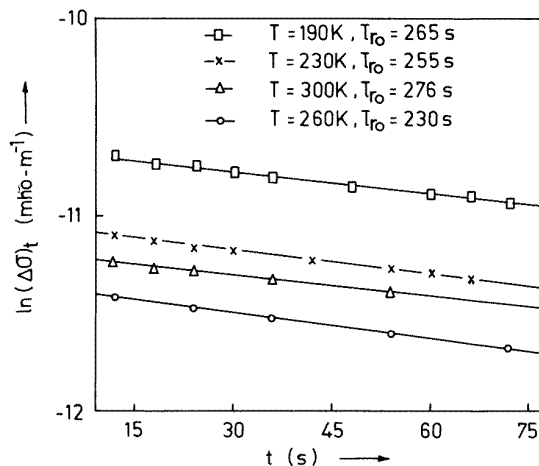

Figure 4. Decay of excess photoconductivity $(\Delta\sigma)_t$ of a CdSe film of thickness 1.70 μm at different temperatures after cessation of illumination.

190 K. The photorelaxation time constant is found to be a minimum (≈ 230 s) near 260 K. The behaviour of the dark- and photoconductivity can be explained by considering different slow recombination centres in the CdSe film. The presence of the k centres in CdSe crystals has been
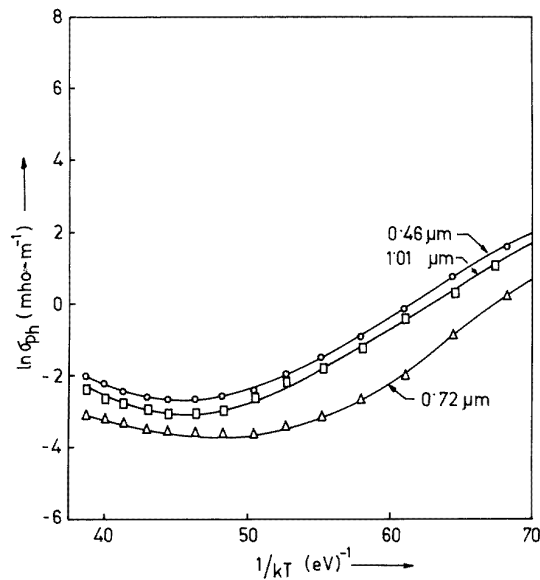
Figure 5. Temperature variations of photoconductivity (σ_{ph}) of CdSe films of different thicknesses.

Figure 6. Variation photocurrent with wavelength of incident light for CdSe films of different thicknesses.

attributed to vacancy-type intrinsic defects [24] or to the formation of V_{cd}–Cd_i complexes, responsible for a 'diffusion level' located at 0.35 eV below the bottom of conduction band and at a level 0.26 eV (k centres) above the top of the valance band [25]. The nature of the k centres in CdSe films has been investigated [21]. Exposure to air produces slow recombination centres in CdSe films which enhances the electron lifetime and hence the photosensitivity. The energy separation between the levels of slow recombination centres responsible for thermal quenching of photoconductivity (see figure 5) has been found to be 0.23 ± 0.02 eV [21 and references therein]. The formation of slow recombination centres, acting as acceptors in the absence of illumination, and the diffusion of oxygen reduce the value of ΔG (figure 1). The slow recombination centres with an activation energy 0.23–0.25 eV were the k centres formed in undoped CdSe films irrespective of the oxidation or other conditions and were regarded as intrinsic lattice defects [21].

Since the slope of $\ln \sigma$ versus $1/kT$ plot for an n-type material gives the activation energy of donors then, in the present study, the values of the slopes of $\ln \sigma$ versus $1/kT$ plots for the dark conductivity of CdSe films (figure 2) 0.12 and 0.31 eV appear to be the activation energies of donors. The value 0.12 eV for the shallow donor level is consistent with the trap depth of a single crystal described by Bube and Barton [14] who pointed out that such shallow traps are responsible for the high conductivity of CdSe crystals. Since in the present investiagtion CdSe films are n-type and Se vacancies are the main donors, it can be predicted that this shallow donor level is formed due to Se vacancies and 0.12 eV is activation energy for V_{Se} [20, 21]. Smyntyna [21] has already reported that the initial value of G_D is governed by the concentration of the main donors (selenium vacancies), and the derease of G_D observed as a result of long-time air oxidation is accompanied by a change in the main donor state from V_{Se} to Cd_i; thus the deep donor
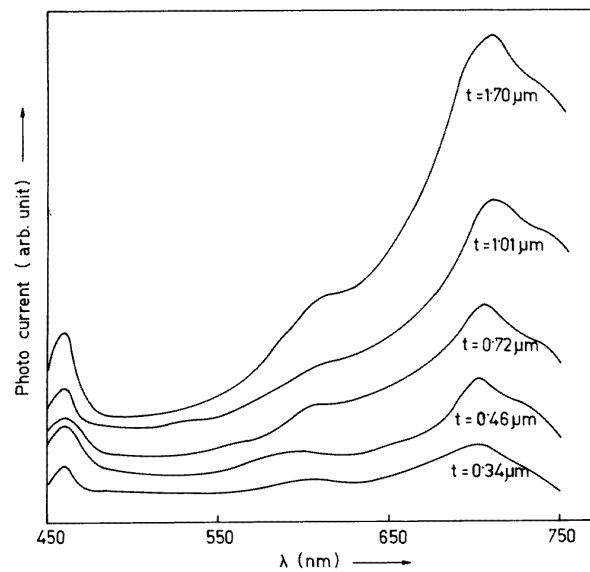
level may be due to Cd_i and the activation energy for Cd_i is found to be 0.31 eV. These values agree more or less with the reported values of shallow and deep donor levels [20, 21, 26]. The other slope (≈ 0.23 eV) of the $\ln \sigma$ versus $1/kT$ plot for dark conductivity represents the presence of a k centre which is formed during air oxidation only and reduces the concentration of selenium vacancies because of the diffusion of these vacancies to the surface of the crystallites which acts as a sink. The subsequent self-compensation process displaces interstitial cadmium atoms to the regular lattice sites. This reduces the concentrations of both donors and cadmium vacancies. A similar effect has also been observed earlier [21, 27, 28] in the case of photoconductivity of air-annealed CdSe films. However, the quenching temperature reported by different workers differs significantly. We have observed a quenching at about 265 K which agrees well with the observation of Robinson and Bube [28]. It is interesting to note that the photorelaxation time constant has a minimum value near this temperature. Lyubchenko *et al* [27] have observed a multiple quenching phenomenon at different temperatures depending on the variation of carrier concentration of the sample with temperature. They studied the dependence of the thermal quenching temperature on carrier concentration. Thermal quenching of conductivity at about 273 K and 247 K has also been observed in compressed CdSe powder by Sato *et al* [29]. The increase of photoconductivity with increase in temperature beyond the quenching temperature may be due to annihilation of the trapping centres with the increase of temperature.

The spectral response of the photocurrent was studied in the range 450–750 nm. The results for films of different thicknesses are presented in figure 6. In all the films a peak appears at about 710 nm that is near the band edge of CdSe films [17]. The slight shift of the peak towards higher wavelengths may be due to release of strain or to a small variation of composition with film

Table 2. A comparative presentation of microstrain, composition, optical bandgap and band-to-band and excitonic peak positions in the spectral distribution of photocurrent of CdSe films of different thicknesses.

Film thickness (μm)	Cd/Se (atomic ratio)	rms strain $\langle e^2 \rangle^{1/2}$ ($\times 10^{-4}$)	Bandgap (eV)	Peak positions in photocurrent	
				For band edge formation (eV)	For exciton transition (eV)
0.27	1.019	48.21	1.90	1.77	1.71
0.34	1.026	38.84	1.85	1.77	1.70
0.46	1.082	32.46	1.62	1.76	1.69
0.72	1.191	28.72	1.69	1.75	1.68
1.01	1.222	35.68	1.70	1.75	1.67

thickness. Two peaks appear near 460 nm and 600 nm. These are due to transitions between higher-order bandgaps of CdSe crystallites [30]. Transitions near the same wavelength have also been observed by Szabo and Cocivera [3] in the absorption and reflection spectra of CdSe films deposited on ITO substrates. The appearance of a hump above the bandgap wavelength of the films (shown in figure 6) is probably due to creation of free carriers by excitons. As the whole spectrum is of broad absorption without fine structure, the appearance of this band (as a hump) suggests the influence of oygen absorption on the formation of free carriers by excitons [31]. The shift of this peak towards a higher wavelength with increase in film thickness is due to a decrease of average stress in the film [16]. A comparative study of the variation of microstrain, composition, optical bandgap and the positions of the band-to-band transition and excitonic transitions obtained from the spectral response of photocurrent in the films is presented in table 2.

The variation of electrical properties of CdSe films of different thicknesses with chemisorption of oxygen was also studied in the present investigation. As it is not possible to detect the chemisorbed oxygen in the films by conventional EDX/AES techniques (a higher oxygen concentration in air-annealed films was detected by Szabo and Cocivera [3] using the SIMS technique), we could not make a quantitative estimation of oxygen content in the films. However, as there is a possibility of absorption of water vapour from the atmosphere during atmospheric exposure of the films, we performed repeated measurements of dark conductivity of the films from low temperature (160 K) to room temperature (300 K) keeping the sample in a vacuum (10^{-2} Pa). As the temperature of measurement was not increased beyond room temperature, there was no possibility of desorption of oxygen from the film surface. As we know that oxygen chemisorption in the films is an irreversible process [3], we can conclude that if the change in electrical properties of a film is due to oxygen absorption by the film then there should not be any significant dispersion in the $\ln \sigma$ versus $1/kT$ characteristics on successive cycles of measurement on a stabilized film. As a matter of fact, repeated measurements on a stabilized film in the present investigation show that the $\ln \sigma$ versus $1/kT$ characteristic is reproducible within the experimental error limit. This justifies the assumption of oxygen chemisorption by the sample during its exposure to

air. As oxygen has no effect on the modification of particle size or stoichiometry [3] and our films were not annealed at high temperature, the change of electrical parameters in this case is controlled by the oxygen incorporated into the films.

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