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Electrical studies on trap levels present in n- and p-type spray pyrolysed CdS thin films

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Abstract. Trap levels in n- and p-type spray pyrolysed CdS thin films were analysed using thermally stimulated current (TSC) and dark-conductivity measurements. TSC measurements of the n-type sample revealed the presence of only one peak under light excitation for a short period due to mobility of sulphur vacancies, but longer excitation could give evidence of one more level which was due to a complex of cadmium and sulphur vacancies. TSC spectra of the p-type sample indicated the presence of two levels of comparable cross section irrespective of light excitation time, which correspond to mobility of the sulphur vacancy and copper impurity. TSC measurements on air annealed n-type samples indicated the presence of a level due to the sulphur vacancies and another level may be due to chemisorbed oxygen. However vacuum annealed samples (10^{-2} Torr) showed results similar to those of as-prepared n-type samples. The dark-conductivity measurements of these samples were found to be in good agreement with the TSC measurement results.

1. Introduction

CdS polycrystalline thin films have received great attention in the last two decades because of their potential uses in the fabrication of semiconductor devices, as the material forms heterojunctions with a number of materials such as Cu_xS [1], CdTe [2] and CuInSe_2 [3]. Elaborate studies were carried out on CdS films prepared using various methods such as vacuum deposition, sintering, chemical deposition and sputtering [4–7]. Chamberlin and Sakarman [8] developed the method of spray pyrolysis for preparing large-area thin films of CdS. Several papers were published on different properties of the sample prepared using this technique [9–12].

Normally the as-prepared CdS films are n-type [13] and the conductivity is controlled by deviation from the stoichiometry resulting from S vacancies or Cd excess, but Kashiwaba *et al* [14] reported p-type characteristics of Cu doped CdS thin films prepared using vacuum evaporation. Later Sunny Mathew *et al* [15] reported the conversion of spray pyrolysed CdS films into p-type by Cu doping. Another recent publication [16] gave a detailed account of the fabrication and characterization of the homojunction prepared on spray pyrolysed CdS thin films. Fabrication of homojunction in a CdS layer has great practical application, especially in the case of solar cells with CdS forming the top layer. Here one can have a tandem cell structure with the fabrication of a homojunction in the top CdS layer. This homojunction can absorb photons of higher energy, while photons of lower energy can be absorbed by the lower junction.

One of the factors affecting the efficiency of thin-film solar cells is the electrical properties of the film, which in turn depend mainly on the presence of different trap levels,

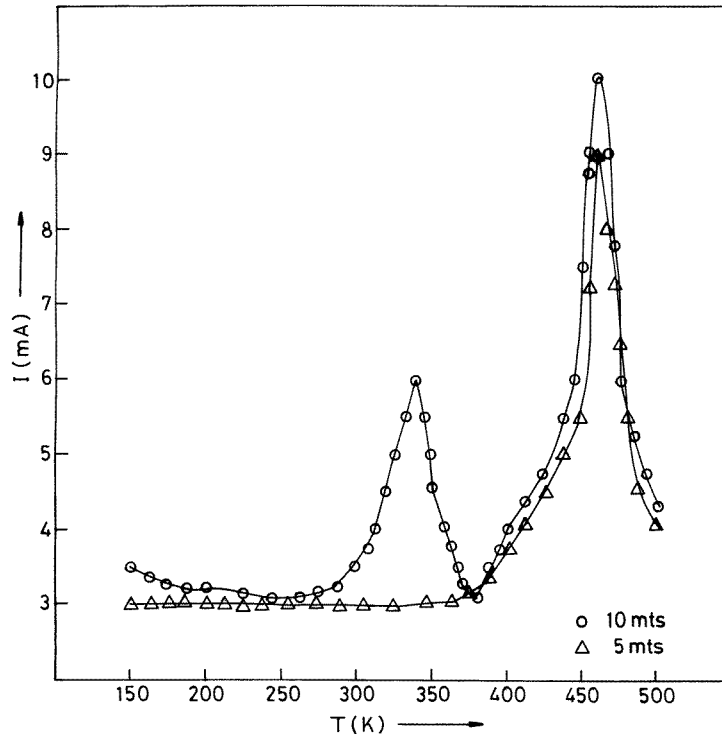


Figure 1. TSC spectra of n-type CdS thin-film samples for different light excitation times.

so a study was conducted to clearly understand the activation energies of trap levels in n- and p-type CdS thin films using the TSC technique. This is a well known non-isothermal technique for the investigation of trap levels in semiconducting materials [17–19]. This permits a survey of the gap states and also the determination of the capture cross section of each trap level. The samples were also analysed using dark-conductivity measurements in order to obtain more details about the existing trap levels. These two studies could give a picture of different trap levels present in n- and p-type CdS and the present paper gives a detailed account of the results obtained from these.

2. Theory

The TSC (I) due to a single trap of depth E (activation energy) with negligible retrapping and monomolecular kinetics is given by [17, 18]

$$I = I_0 \exp \left[-E/kT - \nu/\beta \int_{T_0}^T \exp(-E/kT') dT' \right]$$

where T_0 is the initial temperature, β the warm-up rate and ν is the attempt-to-escape frequency. If more than one type of trap is present, curves obtained by thermal stimulation may be expected to show several maxima depending upon the activation energies of the traps. If carriers are trapped at a single energy level, TSC spectra will show only one peak.

The activation energy can be calculated as $E = 2kT_m^2/(T_2 - T_1)$ where $(T_2 - T_1)$ is the width of the peak at the points where the current has half of its maximum value and T_m is the temperature of the peak maximum.

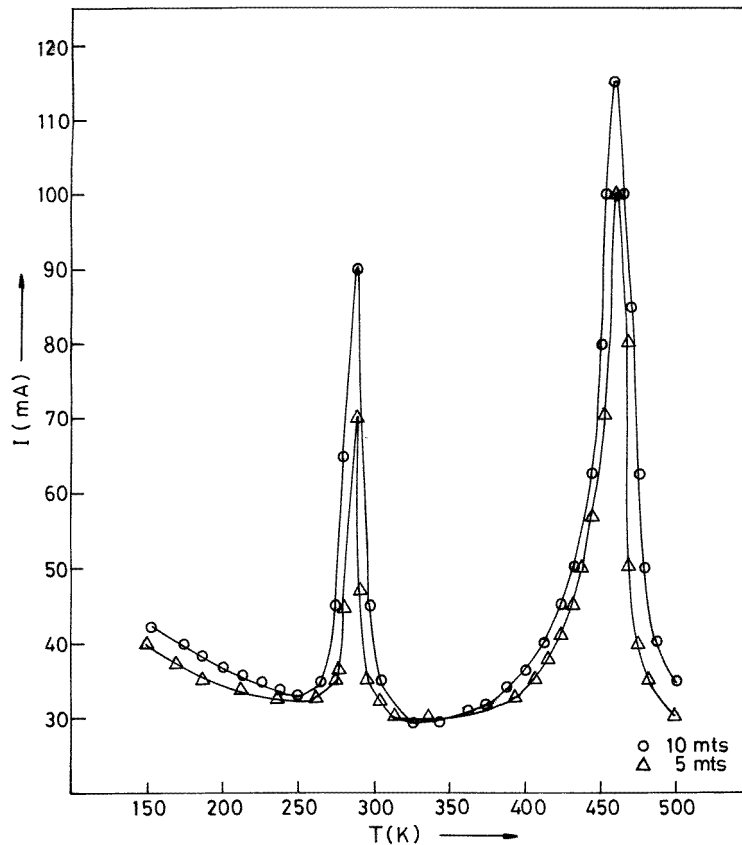


Figure 2. TSC spectra of p-type CdS thin-film samples for different light excitation times.

Mott and Gurney [20] suggested that the capture cross section a of the traps may also be calculated from TSC spectra as $a = a_0 \nu$ where $a_0 = 10^{-26} \text{ cm}^2 \text{ s}$ and $\nu = \beta / T_m (\alpha \exp \alpha)$ and α is defined as E / kT_m .

The variation of dark conductivity (σ) with temperature (T) for an extrinsic semiconductor can be expressed as $\sigma = \sigma_0 \exp(-E/kT)$ where E is the activation energy and it can be calculated from the slope of a plot of $\log \sigma$ versus $10^3/T$.

Table 1. The values of activation energies and capture cross sections of n- and p-type CdS samples obtained from TSC measurements.

Sample type	Activation energy (eV) for different light excitation times		Capture cross section (cm^2) for different light excitation times	
	5 min	10 min	5 min	10 min
n-type CdS	(1) 1.21 ± 0.01 (2) 0.40 ± 0.01	(1) 1.21 ± 0.01 (2) 0.40 ± 0.01	(1) 5.2×10^{-16} (2) 1.04×10^{-23}	(1) 5.2×10^{-16} (2) 1.04×10^{-23}
p-type CdS	(1) 1.21 ± 0.01 (2) 0.73 ± 0.01	(1) 1.22 (2) 0.74	(1) 5.2×10^{-16} (2) 6.9×10^{-16}	(1) 7.1×10^{-16} (2) 1.9×10^{-16}

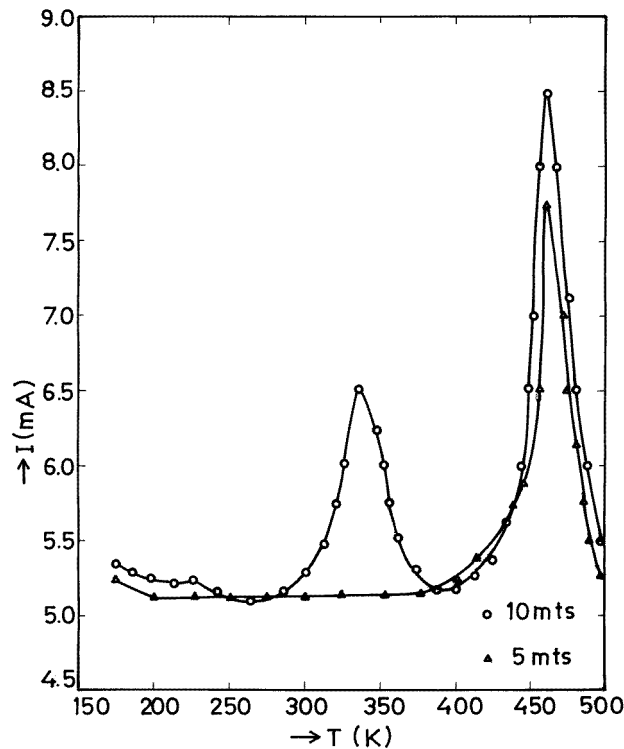


Figure 3. TSC spectra of n-type CdS thin-film samples vacuum annealed at 100 °C for different light excitation times.

Table 2. The values of activation energies and capture cross sections of vacuum annealed n-type CdS films obtained from TSC measurements.

n-type CdS films vacuum annealed at different temperatures	Activation energy (eV) for different light excitation times		Capture cross section (cm ²) for different light excitation times	
	5 min	10 min	5 min	10 min
100 °C	(1) 1.21 ± 0.01	(1) 1.21 ± 0.01 (2) 0.41	(1) 3.48 × 10 ⁻¹⁶	(1) 3.48 × 10 ⁻¹⁶ (2) 2.51 × 10 ⁻²³
200 °C	(1) 1.24 ± 0.01	(1) 1.24 ± 0.01 (2) 0.41	(1) 10.0 × 10 ⁻¹⁶	(1) 10.0 × 10 ⁻¹⁶ (2) 2.5 × 10 ⁻²³
300 °C	(1) 1.23 ± 0.01	(1) 1.23 ± 0.01 (2) 0.41	(1) 9.8 × 10 ⁻¹⁶	(1) 9.8 × 10 ⁻¹⁶ (2) 2.5 × 10 ⁻²³

3. Experiment

CdS thin films were prepared using the spray pyrolysis technique as reported earlier [10–12]. The thickness of the films were measured using the gravimetric method and they were found to be 1 μm, having n-type conductivity. A Cu layer of thickness 40 nm was deposited on this n-CdS by vacuum evaporation and was then annealed for 45 min in vacuum (10⁻⁴ Torr) at 300 °C in order to obtain p-type CdS. This was first confirmed using the hot-probe method. We conducted TSC measurements on both n- and p-type samples. The n-type samples were

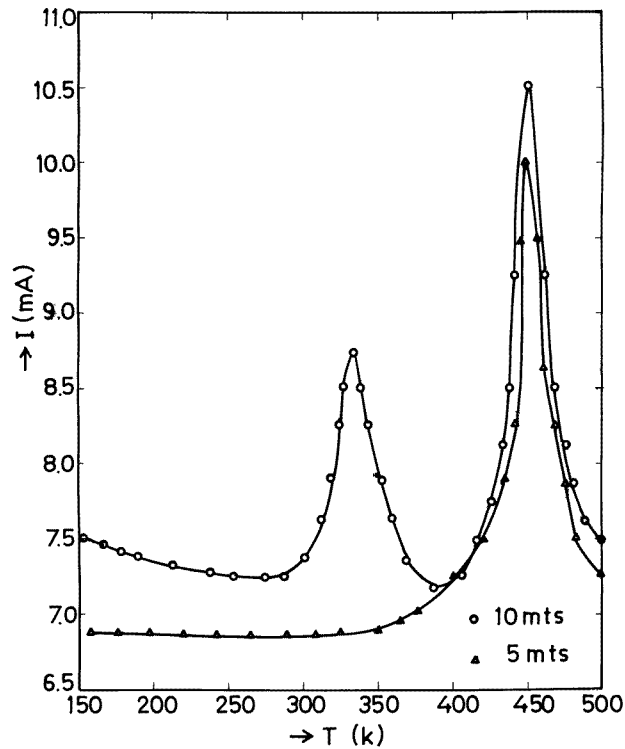


Figure 4. TSC spectra of n-type CdS thin-film samples vacuum annealed at 200 °C for different light excitation times.

Table 3. The values of activation energies and capture cross sections of air annealed n-type CdS films obtained from TSC measurements.

n-type CdS films air annealed at different temperatures	Activation energy (eV) for different light excitation times		Capture cross section (cm ²) for different light excitation times	
	5 min	10 min	5 min	10 min
100 °C	(1) 1.27	(1) 1.27 (2) 0.90	(1) 78×10^{-16}	(1) 78×10^{-16} (2) 2.64×10^{-18}
200 °C	(1) 1.27	(1) 1.27 (2) 0.91	(1) 78×10^{-16}	(1) 78×10^{-16} (2) 7.28×10^{-18}
300 °C	(1) 1.27	(1) 1.27 (2) 0.92	(1) 78×10^{-16}	(1) 78×10^{-16} (2) 21.1×10^{-18}

annealed in air and vacuum from 100 to 300 °C and TSC studies were performed in order to understand the effect of annealing on these samples. We also conducted dark-conductivity measurements on these two types of sample annealed at 300 °C. We selected the n-type sample annealed at 300 °C because the p-type CdS could be prepared only after annealing Cu doped n-CdS at 300 °C.

Vacuum evaporated indium contacts were made on the sample and then the sample was mounted in a metallic vacuum cell at a pressure of 10^{-2} Torr for TSC and dark-conductivity measurements. The sample was first frozen to 100 K (T_0), which is low enough to make

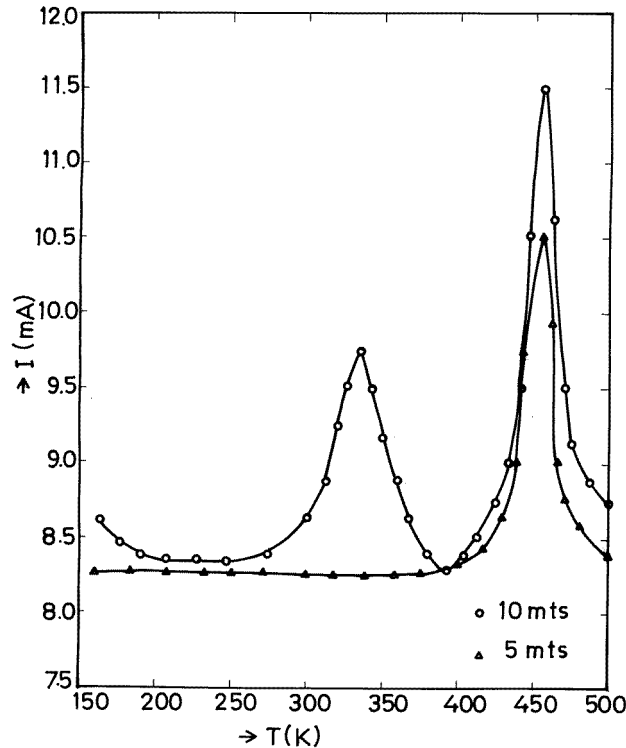


Figure 5. TSC spectra of n-type CdS thin-film samples vacuum annealed at 300 °C for different light excitation times.

the probability of thermal release of carriers negligible. It was then exposed to an optical excitation for a fixed time (5 and 10 min) so that carriers were photoexcited and trapped in the gap states. In the present work, the source of excitation was a tungsten halogen lamp (25 W, Oriel-6394) in order to fill the electronic or ionic traps. After the excitation was stopped, the sample was heated at a linear rate (β) of 0.05 K s⁻¹ always. Current was measured using an electrometer (ECIL-EA815) varying the sample temperature from 100 to 500 K, along the film plane under a dc field of 6 V cm⁻¹.

For dark-conductivity measurements the thickness of the sample was measured using the gravimetric method. Vacuum evaporated indium contacts were made on the sample. It was then mounted in a metallic vacuum cell at a pressure of 10⁻² Torr. Measurements were carried out by applying a steady voltage of 6 V across the sample. In this case also the resulting current was measured using the electrometer when temperature was varied from 100 to 500 K. The conductivity of the sample was calculated for different temperatures and a plot of $\log \sigma$ versus $10^3/T$ led to an Arrhenius plot.

4. Results and discussion

TSC spectra of as-prepared n-type CdS are shown in figure 1. Under 5 min light excitation the spectra depicted only one peak ($T_m = 460$ K) whose activation energy was calculated to be 1.2 eV (table 1). TSC spectra of the same type of sample gave one more peak

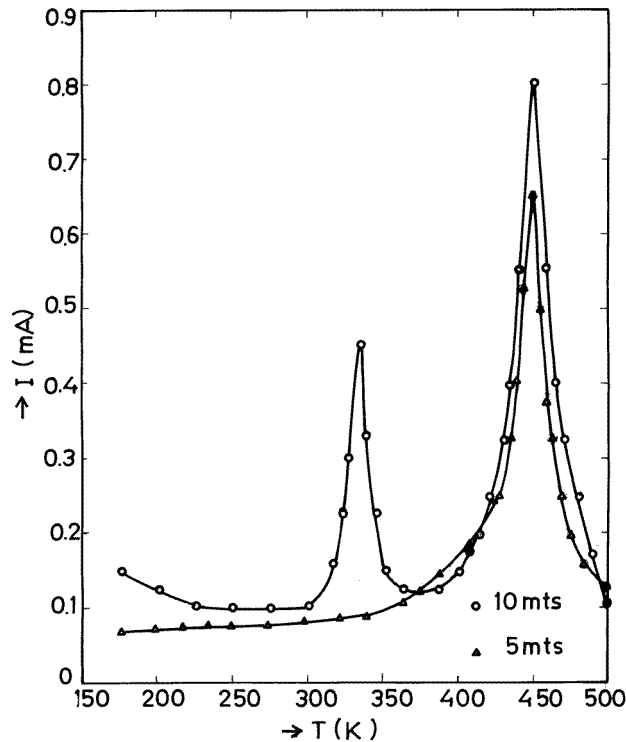


Figure 6. TSC spectra of n-type CdS thin-film samples air annealed at 100 °C for different light excitation times.

($T_m = 340$ K) of activation energy 0.4 eV under light excitation for 10 min. It was reported earlier that the 1.2 eV level is due to mobility of sulphur vacancies [21, 22]. The value of activation energy 0.4 eV obtained under 10 min light excitation corresponds to the activation energy of charge carriers released from the complex of cadmium and sulphur vacancies localized in nearest-neighbouring sites. These traps are reported to be present in the CdS crystal also [23]. From the value of capture cross section calculated for the above two trap levels, it is clear that the 0.4 eV level has a smaller capture cross section than the 1.2 eV trap level. It may be for this reason that the 0.4 eV trap level is not detectable under the light excitation time of 5 min.

TSC spectra of p-type CdS are shown in figure 2. Interestingly two peaks ($T_m = 460$ and 290 K) are observed in this case irrespective of the duration of light excitation. The capture cross section of these two peaks are of the same order (table 1). We have obtained only one peak under 5 min light excitation in the case of n-type samples. The activation energies of the two peaks in the p-type sample were calculated to be 1.2 eV (sulphur vacancy) and 0.72–0.75 eV. Since the p-type sample is Cu doped, we expect a trap level of Cu impurity in this sample and we found that 0.77 eV is an acceptor level of Cu [14]. It was reported [14] earlier that resistivity of Cu doped CdS samples first increases with increasing Cu concentration and shows an unmeasurably high value at about 0.5 at.% Cu. However, it shows a drastic decrease with further increase of Cu content up to about 25 at.% Cu. It was also reported that Cu atoms substituted at Cd sites act as acceptors and, according to Kashiwaba *et al*, the increase of electrical resistivity to the unmeasurably high value on Cu

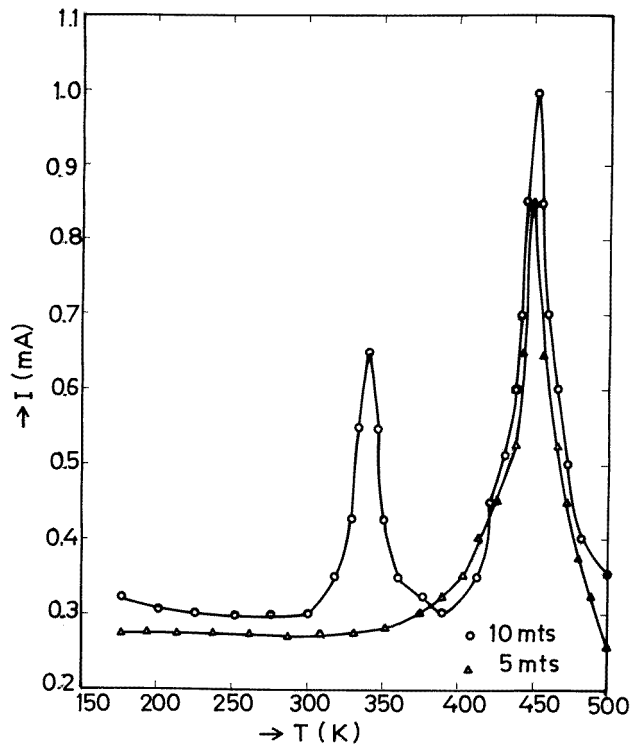


Figure 7. TSC spectra of n-type CdS thin-film samples air annealed at 200 °C for different light excitation times.

doping is due to the compensation of donors which are probably due to sulphur vacancies [14]. They also suggest that the remarkable decrease of electrical resistivity above 0.5 at.% of Cu is due to the increase of active Cu atoms substituted for Cd sites and this gives rise to a p-type conductivity in the sample. In the present work, we could detect a Cu impurity in the p-type sample and there is no trace of complexes of Cd and S vacancies even under 10 min light excitation. We therefore conclude that it may be the Cu impurity on Cd sites that gives the p-type conductivity to spray pyrolysed CdS samples.

It was also reported [14, 15] that as a result of Cu doping no other compound such as Cu_xS is formed and Cu diffuses completely into the CdS. In that work [15], the sample was analysed using XRD, XPS and VASE and it was found that Cu was completely diffused into the CdS layer without the formation of any chemical compound. Our result is also in good agreement with this, since we do not obtain any other peak except the Cu impurity and S vacancy in p-type CdS.

TSC spectra of vacuum annealed n-CdS at 100–300 °C are shown in figures 3–5 and calculated values of activation energy and capture cross section are shown in table 2. Under 5 min light excitation, irrespective of annealing temperature, these samples show one peak ($T_m = 450\text{--}460\text{ K}$) of activation energy 1.2 eV, which again indicates a sulphur vacancy. Under 10 min light excitation, all these samples give one more peak ($T_m = 335\text{ K}$) of small capture cross section and corresponding activation energy was calculated to be $\sim 0.4\text{ eV}$. This shows the presence of complexes of sulphur and cadmium vacancies in the

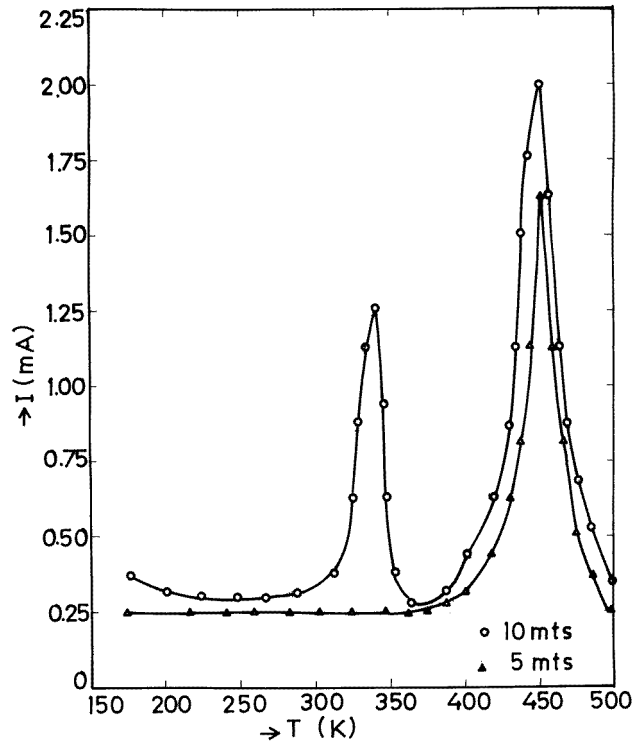


Figure 8. TSC spectra of n-type CdS thin-film samples air annealed at 300 °C for different light excitation times.

neighbour sites. Thus TSC measurements indicate that on vacuum annealing in the range of 100–300 °C, nothing has happened to the defect levels present in as-prepared n-CdS.

TSC spectra of air annealed (100–300 °C) n-CdS are shown in figures 6–8 and calculated values of activation energies and capture cross sections are shown in table 3. Here also under 5 min light excitation we could detect ($T_m = 450$ K) a trap level of activation energy 1.2 eV (sulphur vacancy) in all samples irrespective of annealing temperatures, but an additional peak ($T_m = 335$ K) obtained under 10 min light excitation gave an activation energy ~ 0.9 eV. It was reported earlier that 0.9 eV is due to chemisorbed oxygen [24] and this effect was also reported by Mark in CdS crystals [25]. In these samples, since there is no trap level of complexes of cadmium and sulphur vacancies, we conclude that the 0.9 eV energy in our sample may be due to the chemisorption of oxygen at these vacancy states.

Arrhenius plots of vacuum annealed (300 °C) n-CdS and p-type CdS are shown in figures 9 and 10 respectively. The plot of vacuum annealed n-CdS showed only one peak which corresponds to an activation energy of 1.2 eV and this indicates the presence of a sulphur vacancy in this sample as obtained from TSC measurement. Here we did not observe the presence of a trap level corresponding to a complex of cadmium and sulphur vacancies. This may be because of its small value of capture cross section and this was obtained in TSC measurement only under 10 min light excitation. Interestingly, an Arrhenius plot of p-CdS gives two slopes and activation energies are calculated to be 1.2 and 0.75 eV, indicating the presence of a sulphur vacancy and copper impurity. Thus we see that dark-conductivity measurements are in good agreement with TSC measurements.

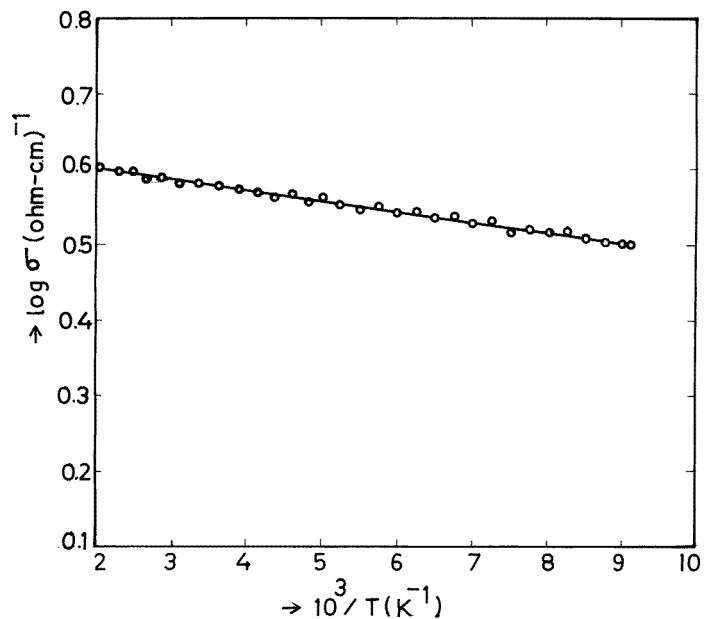


Figure 9. An Arrhenius plot of an n-type CdS thin-film sample vacuum annealed at 300°C.

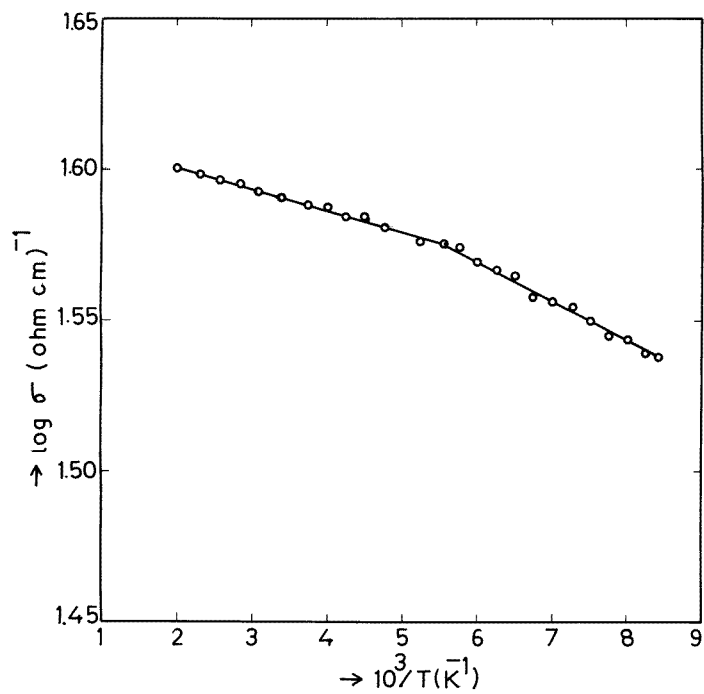


Figure 10. An Arrhenius plot of a p-type CdS thin-film sample.

5. Conclusion

As a part of an improvement of the efficiency of a spray pyrolysed CdS homojunction solar cell, we conducted a study on activation energies of trap levels in n- and p-type spray pyrolysed CdS thin films by the TSC technique, especially for the p-type films for the first time. From TSC measurements we found the sulphur vacancy to be a prominent trap in as-prepared and in annealed (both in air and vacuum) n-type CdS samples, but, in addition to the sulphur vacancy, as-prepared and vacuum annealed n-CdS samples show an additional level of complexes of cadmium and sulphur vacancies of small capture cross section, which we could detect only under an excitation time of 10 min. In the case of air annealed n-CdS samples, even with 10 min light excitation, we did not observe the presence of complexes of cadmium and sulphur vacancies. Instead of this we obtained a trap level of chemisorbed oxygen. TSC measurements of p-type CdS give two distinct trap levels—namely sulphur vacancy and copper impurity—in the case of both 5 and 10 min light excitation time. A possible explanation for this also is discussed in this paper. We have also made a study of existing trap levels by dark-conductivity measurements in n- and p-type CdS samples. These results are found to be in good support of results obtained from TSC measurements.

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