Conduction Mechanisms in Chemically Deposited CdS Films for Solar Cell Applications

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Abstract: Current-Voltage measurements on CdS films prepared by chemical bath deposition method have been made over a temperature range of 300 to 458K. It has been found that at low biases the current voltage characteristics follow an ohmic behavior whereas at increased biases a high power law is obeyed. This has been interpreted on the basis of a space charge limited conduction mechanism. The density of traps has been calculated as 3.25 X 10^{19} $cm^{-3}eV^{-1}$ on the basis of a uniform distribution of traps.

Key Words: CdS films, CBD CdS films, SCLC.

INTRODUCTION

CdS/CdTe heterojunction solar cells provide an attractive alternative for low cost applications. Solar spectrum peaks at 1.43eV and CdTe with a direct bandgap of 1.45eV is an ideal absorber material for solar cells. CdS, on the other hand, with a wider bandgap of 2.42eV makes for an effective window material. The as fabricated layers of CdS are n-type in character, while the as deposited layers of CdTe are of p-type conductivity. CdS and CdTe layers on top of each other make an ideal pair for the formation of a hetero pn-junction. There remain several issues to be resolved, all leading to a single objective of improving the over all photovoltaic conversion efficiency of the solar cell. One major issue is the resistance of the cell in series with the pn-junction. This result in the power drop across the films of the cell reducing the power delivered to the load. The window material, CdS in this case, has been a focus of attention in this regard. Attempts have been made to reduce the thickness of the films to a minimum [1], anneal it to increase the grain size to enhance its conductivity [2] and on a more fundamental level, to study the various current transport mechanisms operative in these films [3].

Thin films for the solar cell materials, like CdS, have been fabricated by a variety of methods like vapor phase deposition [4], sputtering [5] and close space sublimation [6]. Chemical bath deposition technique (CBD) however, offers the advantage of cost effectiveness, simplicity of the equipment, deposition of films of uniform thickness over large areas and the possibility of adapting the process to mass production. CBD method also produces films in the correct stoichiometeric ratios of the constituent elements. It has remained a popular method of fabricating good quality thin films of CdS ever since it was first demonstrated by Kaur *et al.* in 1980 [7]. Chemical reactions can be manipulated to alter this ratio to produce desired excess of one type of atom to give an enhanced conductivity [8]. Although, several workers have reported results on the current transport in CdS/CdTe structures [9, 10], relatively less attention has been given to the study of temperature dependent current transport behavior of the CdS films. Since the solar cells are subjected to a hotter environment it would be useful to know how the conduction in these films varies with temperature. This study presents results on I-V-T measurements performed on chemically deposited CdS film with a view to ascertain the nature of the mechanism(s) responsible for current transport.

EXPERIMENTAL

Transparent ITO (Indium Tin Oxide) coated substrates were used for the deposition of CdS films by chemical bath deposition. Prior to deposition the substrates were thoroughly washed in distilled water and later degreased ultrasonically in a methanol bath. These were subsequently dried in hot air using a hot air blower.

Actual deposition of CdS films took place in a reaction cell which was a 150 ml beaker.

To deposit thin films of CdS on the ITO coated substrate, 25 ml each of 0.1M solutions of $CdCl_2$ (cadmium chloride), NH_4Cl (ammonium chloride) and NH_4OH (ammonium hydroxide) were placed in the reaction cell. The pH of the solution was kept in the range of 10.5-11.0 by adjusting the ammonium hydroxide solution.

The reaction cell was placed on a hot plate with a magnetic stirrer. The temperature of the reaction cell was kept constant at 85°C. ITO substrates were hung vertically in the reaction cell and the solution was continuously stirred by the magnetic stirrer. After the solution had reached the stable temperature of 85°C, 25ml of 0.1M $CS(NH_2)_2$ (thiourea) was added to the alkaline solution to induce the reaction. Cadmium Sulfide was produced by the following reaction.

$$CS(NH_2)_2 \rightarrow H_2S + N_2CH_2$$

$$H_2S + CdCl_2 \rightarrow CdS + 2HCl$$

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CdS thus produced precipitated on the substrates and on the inside walls of the reaction cell. The substrates were washed by rubbing them gently under running water to remove excess chemicals and smudges. They were then washed in distilled water and finally dried under hot air. By this process clear amber colored films of CdS were obtained. Films of different thickness were obtained by repeating the deposition procedure several times.

Temperature dependent electrical characteristics were determined by making sandwich structures having the geometry glass ITO-CdS film-Al. The top Aluminum electrode was deposited in an Edwards 306 vacuum coating unit which was evacuated to 5 X 10^{-5} torr. Aluminum could not be used as the base electrode because it reacted with the chemicals in the reaction cell. The geometry of the samples is shown schematically in Fig. (**1**).

The thickness of the film "d" was determined by measuring the capacitance "C" of the sandwich structure and using the simple relation;

$$d = (\varepsilon_r \varepsilon_o A)/C.$$

Where; $\varepsilon_r = 8.9$ is the relative dielectric constant of CdS

$\varepsilon_o = 8.85 \text{ X } 10^{-14}$ F/m is the permittivity of free space, and

A is the area of the device/top contact.

Capacitance C was measured using a Fluke 6303 programmable RCL meter.

I-V-T measurements were also performed on this programmable RCL meter. The samples were mounted inside a shielded Edelstahl Memmet Oven whose temperature could be adjusted from room temperature to 325°C. For more accurate measurements of the temperature, a Wavetek 23XT thermocouple was placed directly underneath the sample.

RESULTS AND DISCUSSION

The current-voltage behavior of a typical sample is shown in Fig. (**2a**) for various temperatures in the range 300K to 458K. A non linear behavior is apparent at higher biases. As the temperature is increased to 458K the current becomes considerably larger and a near ohmic region is obtained over the full bias range. This is shown plotted in Fig. (**2b**). The magnitude of the current is much larger at this temperature which is why it is shown plotted on a separate current scale.

To determine the power relationship between current and voltage, log I has been plotted against log V. This is shown in Fig. (**3a**). Two distinct slopes are clearly visible indicating two possible conduction mechanisms. Table **1** summarizes the slopes for the sample at different temperatures. It is seen that the slopes are near unity at lower biases and exhibit a higher power law at higher biases. However, for temperatures in excess of 400K the slope over the entire voltage range approaches unity as can be seen in Fig. (**3b**).

Table 1. Slopes of the logI Vs. logV Plots at Various Temperatures

Temperature	Slope of Region AB	Slope of Region BC
300	1.28	5.9
323	1.16	5.6
368	1.4	7.7
383	0.91	4.6
413	1.26	
458	1.13	

Such a behavior of the I-V characteristics is a clear indication of a Space Charge Limited Conduction mechanism [11]. In such cases the functional relationship between current and voltage is given by a power law of the type;

$$I \ \alpha \ V^n$$

Where n = 1 for ohmic behavior, n = 2 for an insulator without or with shallow traps and n > 2 for traps distributed in energy. The trap distribution for an exponent greater than two is more likely to be the one where the traps density falls

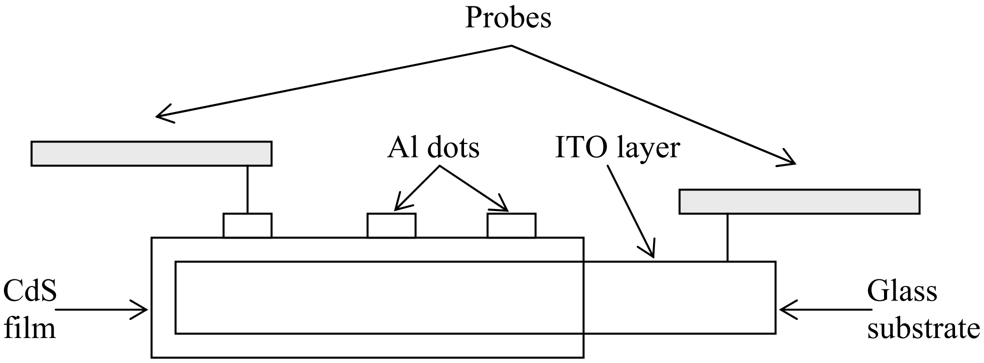

Fig. (1). Geometry of the samples used for I-V-T measurements.

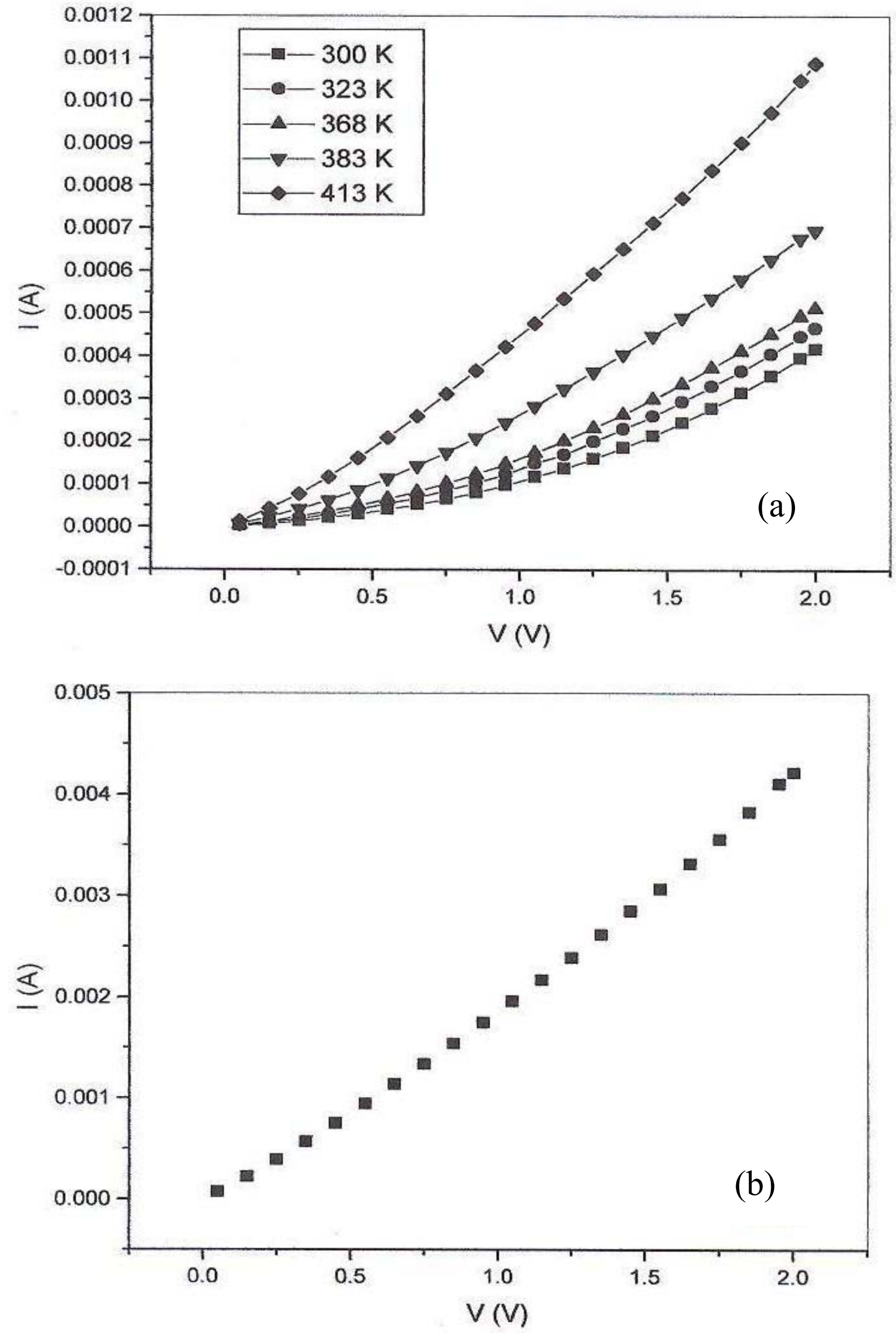

Fig. (2). a). I-V plots as a function of temperature for 250nm thick film. **b).** I-V behavior for the 250nm thick film at 458K. It is plotted separately as the magnitude of current is too large to fit the scale at lower temperatures.

towards the middle of the bandgap with increasing energetic distance from the bottom of the conduction band. Higher values of "n" correspond to a steep variation of the traps density from the edge of the conduction band [11]. This is the classic case of Urbach's rule for amorphous materials and is often used to define a mobility gap rather than the band gap. This is seen to be a consequence of the disorder present in amorphous materials which causes the extension of the band edges into the band gap. The character of electron states changes from "continuous" to "localized" as the energetic distance from band edges increases resulting in the formation of traps. The chemically deposited films studied here were completely amorphous in nature and as such are expected to have a high density of traps and localized levels in the forbidden region.

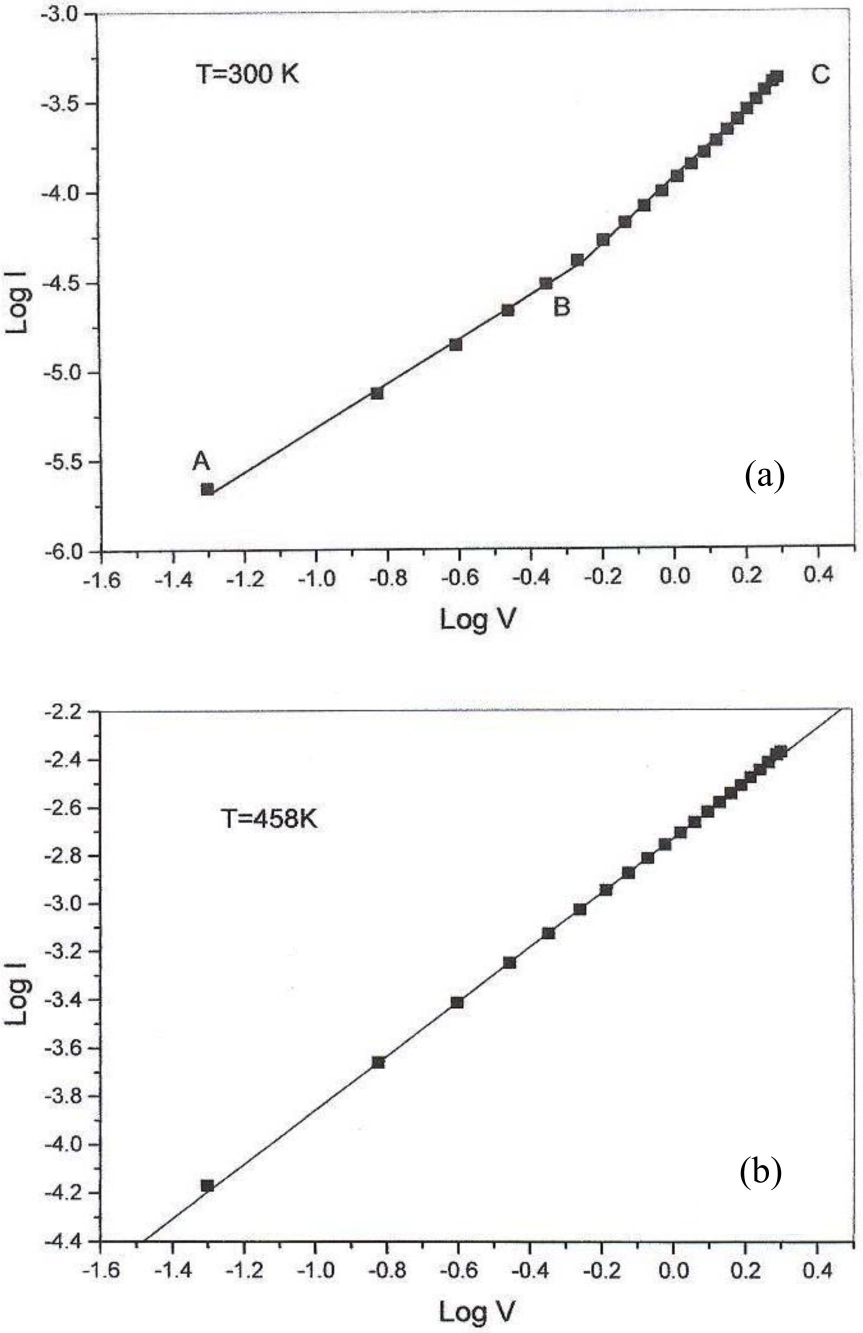

Fig. (3). a). log I Vs. log V for a typical film at 300K.The characteristics exhibit two regions AB and BC with distinct slopes. **b).** log I Vs. log V plot for the film at 458K. At higher temperatures the films exhibit a single slope

The ohmic region observed at low biases (low fields) is seen to be a consequence of the bulk generated free carriers. Much the same way the current is carried in thermistors. For low biases the injected charge from the electrodes is small and does not affect the position of the Fermi level. Consequently, the CdS layer remains relatively free of space charge. In such cases the conductivity is dominated bulk generated carriers. For higher biases on the other hand, the amount of charge injected by the negative electrode is larger than can be drawn from the other electrode resulting in a net built up of charge which fills the trap levels. This results in a movement of the fermi level towards the conduction band edge. The amount of charge trapped will depend upon the nature of the trap distribution in energy. Under such conditions the current is given by the high powered law alluded to earlier.

The two currents, ohmic and space-charge-limited, occur in the same physical volume. The dominant conduction mechanism will be the one which introduces the majority of the free carriers. As the temperature increases there is an increase in carriers due to thermal generation. The bulk generated carriers dominate over the injected carriers which are responsible for space charge limited conduction. Which is why, the slope of the log I - log V curves approach unity for the highest two temperatures. The effect of temperature is to increase the conductivity of the bulk material. Temperature does not affect the trapped charge but releases this charge more easily to the conduction band giving enhanced conductivity.

For the case of uniform distribution of traps "N_t" currents and voltages are related by; [12],

$$I = KV\exp(SV) \quad (1)$$

where K is a constant,

$$\text{and, } S = 2\,\varepsilon_r\varepsilon_o / eN_t d^2 kT \quad (2)$$

Here "k" is the Boltzmann's constant and "T" is the absolute temperature.

Equation (1) can be rewritten as;

$$\ln(I/V) = \ln K + SV \quad (3)$$

If the current-voltage characteristics are manipulated according to equation 3 by plotting ln(I/V) against V it should be possible to obtain the density of traps in the CdS films prepared by chemical bath deposition method. Fig. (**4**) shows such a plot for 300K for a 250nm thick film where ln(I/V)-V plot shows a straight line. The slope of these lines according to equation 3 is equal to "S". The slopes of the plots for the temperature range 300K to 458K are listed in Table **2** and plotted against (1/T) in Fig. (**5**). This according to equation 2 should be a straight line with a slope "S" given by;

$$S = 2\,\varepsilon_r\varepsilon_o / eN_t d^2 k \quad (4)$$

Table 2. Values of Slope "S" for 250nm Thick CdS Film at Different Temperatures

Temperature	Slope of Ln (I/V) Vs V
303	0.7855
323	0.6437
368	0.6050
383	0.5622
413	0.2082
458	0.1457

Since all the parameters are known the value of "N_t" can be calculated. The calculated value is found to be 3.25 X 10^{19} cm^3eV^{-1}. This value has been calculated on the basis of a uniform distribution of traps and agrees reasonably well with the reported value of 1.26 X 10^{19} $cm^{-3}eV^{-1}$ [13]. The assumption appears justified if one considers the fact that these films are n-type and the fermi level is already close to the conduction band. An excess charge in these films is only expected to move the fermi level marginally over which the density of states can be considered constant.

CONCLUSIONS

I-V-T measurements of the Chemical Bath Deposited CdS films indicate that the dominant current transport mechanism is space charge limited. The amorphous nature of

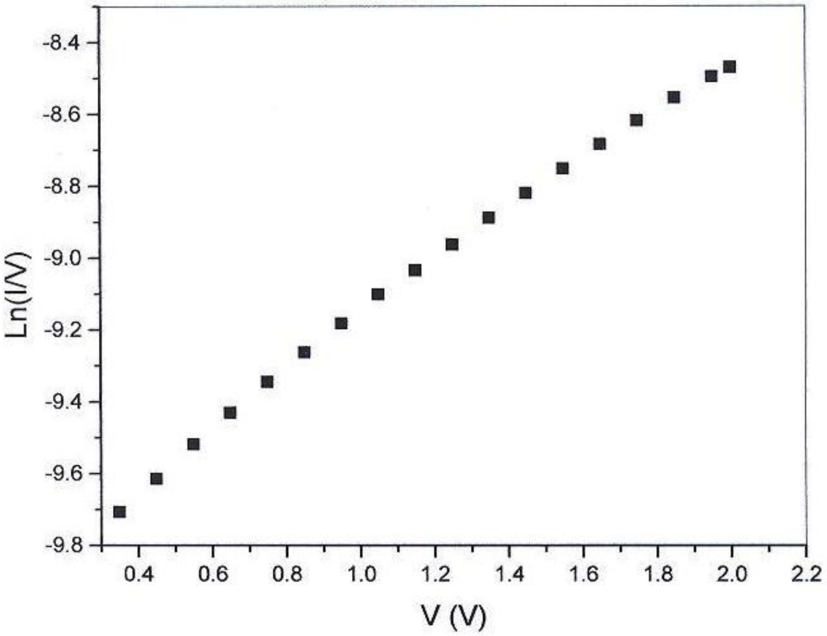

Fig. (4). ln(I/V) Vs. V plot at 300K. A near linear behavior with a slope S is observed.

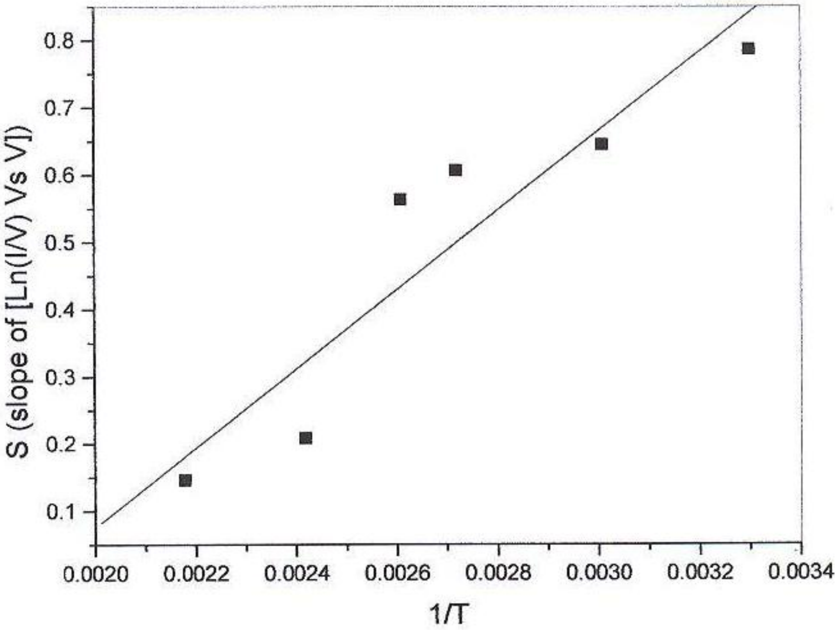

Fig. (5). S [Slope of ln(I/V)] Vs. 1/T .

the films give rise to a large number of defect states in the band gap which could provide sites for the trapping of charge carriers. Interpreting the results on the basis of a uniform distribution of traps, their density is determined as 3.25 X 10^{19} cm^{-3} eV^{-1}.

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