

# Tunneling-Enhanced Recombination in Polycrystalline CdS/CdTe Solar Cells

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## Abstract

The dominant dark current transport mechanism in as-grown and CdCl<sub>2</sub> processed CdS/CdTe heterojunction solar cells for temperatures below 300 K was investigated. The current-voltage properties of these solar cells is explained via tunnelling enhanced bulk and interface recombination models which give a quantitative description of the electronic loss mechanisms in the chalcopyrite-based heterojunction solar cells. The temperature dependence of the saturation current and the diode ideality factors of the as-grown and CdCl<sub>2</sub> processed CdTe solar cells are shown to be well described by this model.

**Key Words:** CdS/CdTe; Solar cell; Tunnelling; Recombination.

## 1. Introduction

Cadmium telluride (CdTe) is a favourable material for photovoltaic solar energy conversion. The calculated theoretical efficiency for CdTe solar cells has been estimated at around 29% but in practicality efficiency has only reached 16.5% [1]. Understanding the diode characteristics and electrical conduction mechanisms in these solar cells are important steps in improving device efficiencies. Regarding the carrier transport mechanisms in the n-CdS/p-CdTe cell, several research groups have reported various conduction models to explain the temperature dependent current-voltage characteristics [2–6]. Nevertheless, above approximately 280 K, there is a consensus on the dominance of interface recombination in as-grown and air annealed devices and depletion region recombination in CdCl<sub>2</sub>-processed devices. Below 280 K, tunneling is identified to be the dominating transport mechanism for both unprocessed and processed devices.

In this study, it is proposed that for temperatures lower than 300 K, the current transport mechanism limiting the photovoltaic performance of CdTe solar cells can be investigated by essentially the same approach developed for Cu(In,Ga)(Se,S)<sub>2</sub> based solar cells [7, 8]. By comparing the theoretical model with experimental data, it was found that tunnelling enhanced recombination plays a significant role for temperatures below ~240 K in both as-grown and CdCl<sub>2</sub> processed CdTe solar cells.

## 2. Experimental

CdTe and CdS films were deposited by thermal evaporation technique in the Department of Physics at Middle East Technical University. A detailed description of the growth conditions and the current-voltage

measurement system has been published elsewhere [2]. Device fabrication consisted of the following steps. (i) Successive layers of indium-doped CdS and antimony-doped CdTe were deposited on tin oxide (TO) coated glass substrates. (ii) The substrates were then divided into two subgroups: half were dipped in a solution of CdCl<sub>2</sub>:CH<sub>3</sub>OH (1:100) for 2–5 s before annealing in air at 300 °C for 5 min; and half were left untreated. (iii) All devices were then etched with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>:H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O solution for 1–2 s. (iv) Ohmic contacts were created on p-CdTe by evaporating 300–400 Å of gold onto the CdTe surface; then followed by annealing at 200 °C in a nitrogen atmosphere for 5 min.

### 3. The Models for Recombination in Heterojunctions

The electronic transport in polycrystalline heterojunction devices [9, 10] is well established. If current transport is dominated by any of the thermally activated mechanisms like injection, interface or depletion region recombination, the current density-forward voltage (J-V) relationships take the general form

$$J = J_0 \exp\left(\frac{qV}{nkT}\right) = J_{00} \exp\left(\frac{-E_a}{nkT}\right) \exp\left(\frac{qV}{nkT}\right) \quad (1)$$

where  $n$  is the diode ideality factor,  $J_o$  is the reverse saturation current density,  $E_a$  is the activation energy,  $k$  is the Boltzmann's constant and  $J_{oo}$  is a prefactor which depends on the transport mechanism (tunnelling or thermal activation) and  $J_{oo}$  is proportional to the density of recombination centres in both cases.

The predominant features of all the relationships valid for thermally activated transport are: i) at a constant temperature, the forward voltage dependence of current is  $\text{Log } I \propto qV/nkT$ , where  $n$  takes values between 1 and 2, depending on the current transport type and the doping concentrations of the n and p-type layers; ii) at constant voltage,  $\ln J_o$  and  $\ln J$  varies linearly with  $T^{-1}$ .

Shockley-Read-Hall (SRH) model [11, 12] assumes that recombination in the space charge region takes place via a single trap level within middle of the gap of low doped side of the junction. This provides that the value of  $n \approx 2$  and independent of temperature. However, for an exponential distribution of trap states [7] in the space charge layer of a typical  $n^+p$  - junction, the value of  $n$  may lie between 1 and 2 [13].  $J_o$  is thermally activated and  $E_a \cong E_g/2$ , where  $E_g$  is the half of band gap energy of the absorber.

Direct recombination through states at the pn junction interface appears to be an important route of transport in many heterojunctions as well as CdS/CdTe [9] because of the large lattice mismatch (9.7% for CdS/CdTe) which leads to the high density of interface states ( $\sim 10^{13}$ – $10^{14}$  cm<sup>-3</sup> [14]). The current density due to interface recombination is determined by the hole and electron densities at the metallurgical junction. For asymmetrically doped heterojunction  $N_D > N_A$ , interface recombination dominated current transport determines that the value of  $n$  lies between  $1 > n > 2$  and depends on the ratio  $[\varepsilon_p N_A / \varepsilon_n N_D]$  where  $N_D$  and  $N_A$  are the donor and acceptor concentrations and  $\varepsilon_n$  and  $\varepsilon_p$  are the dielectric constants of n and p-type regions, respectively.

A relatively new approach explaining the tunnelling enhancement of recombination via deep centres in the space charge region, or at the heterojunction interface, provides analytical expression for the forward current transport in Cu(In,Ga)Se<sub>2</sub> (CIGS)-based solar cells [7, 8]. The basis for the determination of the dominant recombination path in CIGS solar cells is that the diode saturation current density  $J_o$  can also be written according to Eq. (1). The value of the activation energy  $E_a$  can be deduced from experimental data by reorganising equation (1) as

$$n \ln(J_0) = \frac{-E_a}{kT} + n \ln(J_{00}). \quad (2)$$

Thus, the activation energy  $E_a$  of the process can be calculated from the slope of a linear plot of  $n \ln(J_0)$  versus  $1/T$ . According to this model,  $E_a$  represents the interface barrier height,  $\Phi_b^p$ , for holes in the case of

interface recombination and the band gap energy of absorber material  $E_g$  in the case of bulk recombination. The contribution of tunnelling to the recombination is accounted for by the temperature dependence of  $n = n(T)$ . Tunnelling of holes from the absorber bulk into the interface states and subsequent recombination with photo-generated electrons available in the buffer layer yields the temperature dependence of the diode ideality factor [7, 8]:

$$n = \frac{E_{oo}}{kT} \coth \left( \frac{E_{oo}}{kT} \right), \quad (3)$$

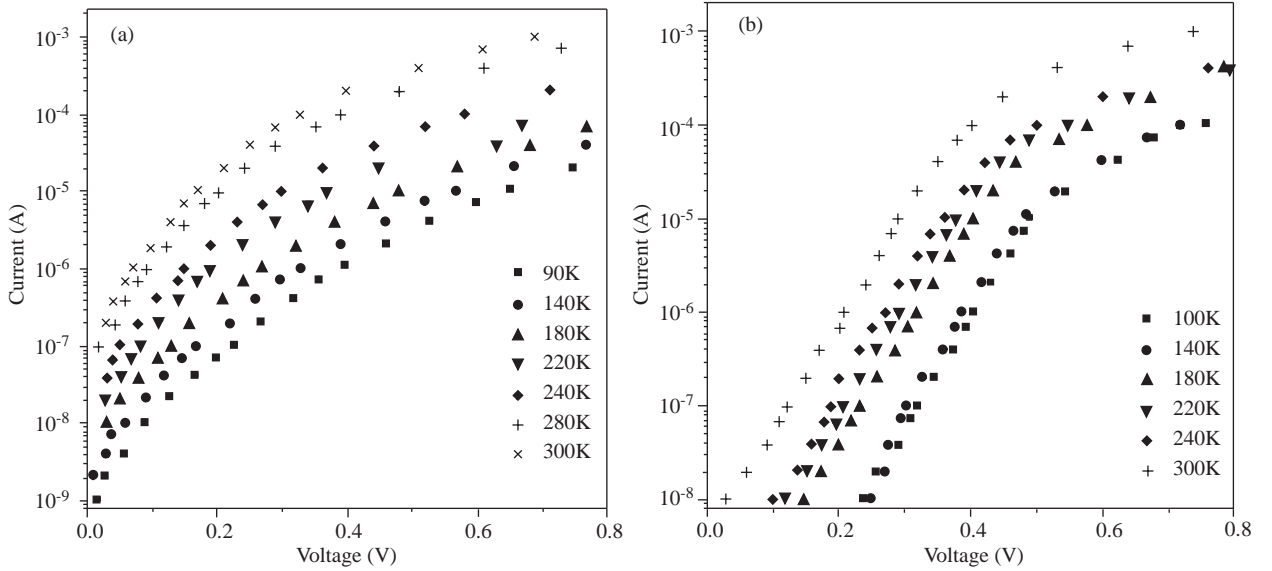
where  $E_{oo}$  is the characteristic tunnelling energy, which measures the contribution of tunnelling to the recombination process. If recombination via trap states in the neutral bulk of the absorber is dominant, the temperature dependence of  $n$  is given as [7, 8]

$$\frac{1}{n} = \frac{1}{2} \left( 1 + \frac{T}{T^*} - \frac{E_{oo}^2}{3k^2 T^2} \right) \quad (4)$$

where  $kT^*$  is the characteristic energy of an exponential distribution of trap states.

## 4. Results and Discussions

In Figures 1(a) and 1(b) one can see the current-voltage response as function of temperature, for both as-deposited and CdCl<sub>2</sub>-processed CdS/CdTe heterojunction solar cells, respectively. The values for  $n$ ,  $J_o$  and the slope of the I-V plot ( $q/nkT$ ) evaluated at different temperatures are given in Table.

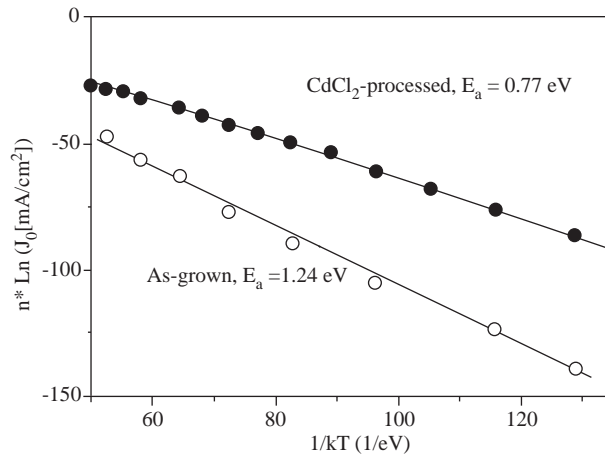


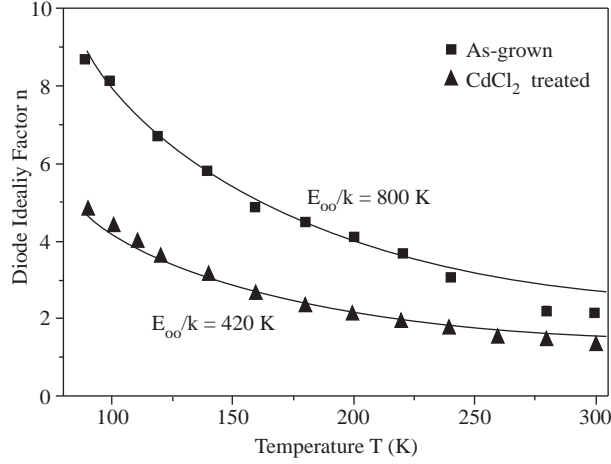
**Figure 1.** The dark I-V characteristics of (a) as-grown and (b) CdCl<sub>2</sub> processed solar cells for temperatures between 90 K and 300 K.

**Table 1.** The  $I_o$ ,  $q/nkT$  and  $n$  values for the typical as-grown and CdCl<sub>2</sub> processed CdTe solar cells of Figure 1.

$T$ (K)	As-grown			CdCl <sub>2</sub> Treated		
	$I_o$ (A)	$q/nkT$ (V <sup>-1</sup> )	$n$	$I_o$ (A)	$q/nkT$ (V <sup>-1</sup> )	$n$
90	$3.6 \times 10^{-9}$	14.82	8.70	$1.2 \times 10^{-11}$	26.90	4.79
100	$5.0 \times 10^{-9}$	14.61	7.94	$1.7 \times 10^{-11}$	26.96	4.30
120	$5.8 \times 10^{-9}$	14.40	6.71	$2.8 \times 10^{-11}$	27.08	3.57
140	$7.5 \times 10^{-9}$	14.23	5.83	$6.0 \times 10^{-11}$	27.16	3.05
160	$1.3 \times 10^{-8}$	14.11	5.14	$1.0 \times 10^{-10}$	27.24	2.66
180	$2.0 \times 10^{-8}$	14.30	4.50	$1.9 \times 10^{-10}$	27.36	2.35
200	$3.6 \times 10^{-8}$	14.03	4.14	$3.0 \times 10^{-10}$	27.51	2.11
220	$6.0 \times 10^{-8}$	14.32	3.68	$4.0 \times 10^{-10}$	27.73	1.90
240	$9.5 \times 10^{-8}$	15.80	3.06	$5.0 \times 10^{-10}$	27.78	1.73
260	$1.0 \times 10^{-7}$	16.31	2.73	$6.0 \times 10^{-10}$	27.83	1.60
280	$1.6 \times 10^{-7}$	19.22	2.16	$7.0 \times 10^{-10}$	28.56	1.45
300	$3.4 \times 10^{-7}$	18.41	2.10	$3.0 \times 10^{-9}$	29.06	1.33

The slopes of the I-V curves are found to vary slowly with temperature, thus suggesting direct or trap-assisted tunnelling [13] cannot be considered as the dominating current transport mechanism over the full temperature range investigated here. However, since  $n(T) > 1$ , tunnelling may possibly contribute to the recombination as proposed by Rau et al. [7, 8]. The evaluation of the saturation current densities according to equation (2) and shown in Figure 2 yields activation energy values for as-grown and CdCl<sub>2</sub>-processed cells at about 1.24 and 0.77 eV, respectively. The values of  $E_a$  in both devices are different from the band gap energy of CdTe obtained from the transmission measurements ( $E_g = 1.51$  eV at 300 K) [9]. Hence, it is likely that the recombination process may be governed by the heterojunction interface and  $E_a$  represents the interface barrier height  $\Phi_b^p$  [15, 16].

**Figure 2.** Corrected Arrhenius plot of the saturation current density  $J_o$  of as-grown and CdCl<sub>2</sub> processed CdTe solar cells.



**Figure 3.** Diode ideality factor as a function of temperature and the fits to Eq. (4) for as-grown and CdCl<sub>2</sub> processed CdTe solar cells.

The validity of the proposed recombination path is also checked through the temperature dependence of the diode ideality factor, and is plotted for these cells in Figure 3, where it is in good agreement with the theoretical expression given by equation (3). The tunnelling energies were calculated as  $E_{oo} = 69$  meV and 36 meV for as-grown and CdCl<sub>2</sub>-processed cells, respectively. The reduction of the tunneling energy from the as-grown to the CdCl<sub>2</sub>-processed samples could probably be due to the decrease in the interface state density [2]. Previously published results [2] on similar solar cells indicated that, below 280 K, multistep tunnelling of carriers through the CdTe depletion region and subsequent recombination dominates the current transport. However, in this study, the analysis of the current-voltage data, using tunnelling enhanced bulk and interface recombination models, indicate that tunnelling enhanced recombination at heterojunction interface dominates the dark current transport mechanism in both as-grown and CdCl<sub>2</sub>-processed cells.

## 5. Conclusion

The electronic loss in both as-grown and CdCl<sub>2</sub>-processed cells can be explained by a relatively new approach which was developed for tunnelling-enhanced bulk/interface recombination in CIGS heterojunction solar cells. Comparison of the theoretical model to dark current-voltage data of the CdTe devices shows that this model consistently explains the low temperature ( $T < 240K$ ) transport properties of as-grown and CdCl<sub>2</sub> processed CdS/CdTe solar cells.

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