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Tunneling-Enhanced Recombination in Polycrystalline CdS/CdTe Solar Cells

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Abstract

The dominant dark current transport mechanism in as-grown and $CdCl_2$ 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 $CdCl_2$ 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 $CdCl_2$-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 $Cu(In,Ga)(Se,S)_2$ 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 $\sim$240 K in both as-grown and $CdCl_2$ 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 $CdCl_2$:CH_3OH (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 $K_2Cr_2O_7$:H_2SO_4:H_2O 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

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

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 $Log\ I \propto qV/nkT$, 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^{-3} [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 ε_n and ε_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_2 (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

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

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, Φ_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 tunneling 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]:

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

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]

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

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 and $CdCl_2$-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.

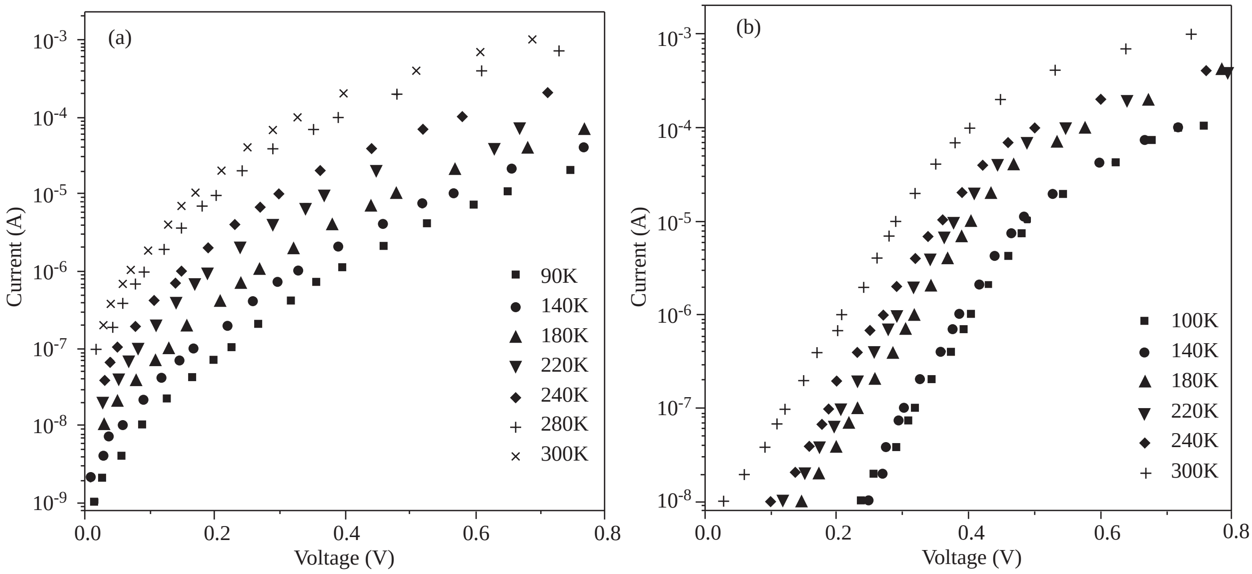

Figure 1. The dark I-V characteristics of (a) as-grown and (b) $CdCl_2$ processed solar cells for temperatures between 90 K and 300 K.

Table 1. The I_o, q/nkT and n values for the typical as-grown and $CdCl_2$ processed CdTe solar cells of Figure 1.

	As-grown			$CdCl_2$ Treated		
T (K)	I_o (A)	q/nkT (V^{-1})	n	I_o (A)	q/nkT (V^{-1})	n
90	3.6×10^{-9}	14.82	8.70	1.2×10^{-11}	26.90	4.79
100	5.0×10^{-9}	14.61	7.94	1.7×10^{-11}	26.96	4.30
120	5.8×10^{-9}	14.40	6.71	2.8×10^{-11}	27.08	3.57
140	7.5×10^{-9}	14.23	5.83	6.0×10^{-11}	27.16	3.05
160	1.3×10^{-8}	14.11	5.14	1.0×10^{-10}	27.24	2.66
180	2.0×10^{-8}	14.30	4.50	1.9×10^{-10}	27,36	2.35
200	3.6×10^{-8}	14.03	4.14	3.0×10^{-10}	27.51	2.11
220	6.0×10^{-8}	14.32	3.68	4.0×10^{-10}	27.73	1.90
240	9.5×10^{-8}	15.80	3.06	5.0×10^{-10}	27.78	1.73
260	1.0×10^{-7}	16.31	2.73	6.0×10^{-10}	27.83	1.60
280	1.6×10^{-7}	19.22	2.16	7.0×10^{-10}	28.56	1.45
300	3.4×10^{-7}	18.41	2.10	3.0×10^{-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 $CdCl_2$-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 Φ_b^p [15, 16].

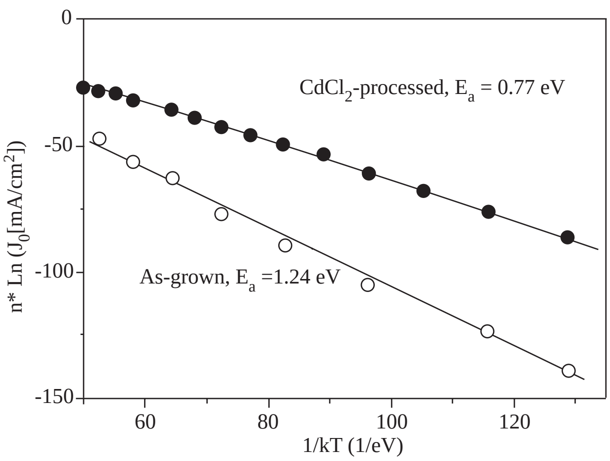

Figure 2. Corrected Arrhenius plot of the saturation current density J_o of as-grown and $CdCl_2$ processed CdTe solar cells.

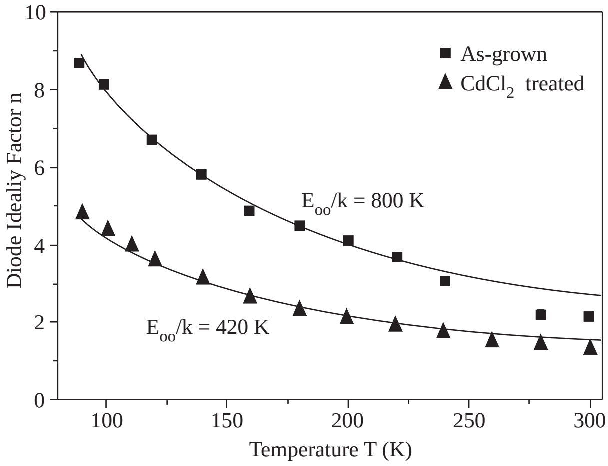

Figure 3. Diode ideality factor as a function of temperature and the fits to Eq. (4) for as-grown and $CdCl_2$ processed CdTe solar cells.

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 $CdCl_2$-processed cells, respectively. The reduction of the tunneling energy from the as-grown to the $CdCl_2$-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 $CdCl_2$-processed cells.

5. Conclusion

The electronic loss in both as-grown and $CdCl_2$-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 $CdCl_2$ processed CdS/CdTe solar cells.

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References

[1] X. Wu, et al. *High-efficiency CTO/ZTO/CdS/CdTe Polycrystalline Thin-Film Solar Cells*, Proceedings of the NCPV Prog. Review Meeting 14–17 October. (Lakewood, Colorado, 2001).

[2] H. Bayhan and Ç. Erçelebi, *Semiconductor Sci. and Tech.,* **12**, (1997), 600.

[3] D. M. Oman, K. M. Dugan, J. L. Kilian, V. Ceekala, C. S. Ferekides and D. L. Morel, *Solar Energy Mat.& Solar Cells.*,**58**, (1999), 361.

[4] D. L. Bätzner, M. E. Özsan, D. Bonnet, K. Bücher, *Thin Solid Films.*, **361–362**, (2000), 288.

[5] M. El Yacoubi, R. Evrard, N. D. Nguyen and M. Schmeits, *Semicond. Sci. Technol.*, **15**, (2000), 341.

[6] P. Nollet, M. Kontges, M. Burgelman,S. Degrave, R. Reineke-Koch, *Thin Solid Films.,* **431–432**, (2003), 414.

[7] U. Rau, A. Jasenek, H. W. Schock, F. Engelhard, T. Meyer, *Thin Solid Films.*, **361–362**, (2000), 298.

[8] V. Nadenau, U. Rau, A. Jasenek and H. W. Schock, *J. Appl. Phys.*, **87**, (2000), 584.

[9] H. Mamikoglu Ph. D. Thesis, METU (Ankara, TURKEY, 1994).

[10] A. L. Fahrenbruch R. H. and Bube, *Fundamentals of Solar Cells*, (Academic Press, Newyork, 1983).

[11] W. Shockley and W.T. Read, *Phys. Rev.*, **87**, (1952), 835.

[12] R. N. Hall, *Phys. Rev.*, **87**, **(**1952), 837.

[13] T. Walter, R. Menner, C.H. Köble, H.W. Schock, *Proc.12th PVSEC* (1994) p. 1755.

[14] R. Albert Enzenroth, K. L. Barth, W. S. Sampath., *J. of Physics and Chem. of Solids.*, **66**, (2005) 1883.