The electron affinity difference in CdS/CdTe solar cells

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Abstract. The electron affinity difference $\Delta E_c = \chi_1 - \chi_2$, in CdS/CdTe solar cells fabricated by four different processes has been measured from observations of the variations of open voltages with temperature. For CdS/CdTe cells, the values of ΔE_c lie between 0·20 and 0·25 eV and are found to be independent of the process of cell fabrication. The use of CdZnTe in place of CdTe increases the value of ΔE_c to 0·49 eV. The method used for the measurement of ΔE_c is very simple. The values of the saturation current I_0 for the different types of cells have been estimated from the slopes of qV_{oc} versus kT plots and compared with those obtained from lnI versus V curves. The values of I_0 found for each cell by the two methods are in substantial agreement.

Keywords. Heterojunction solar cells; CdS/CdTe cells; close spaced sublimation; electron affinity difference.

1. Introduction

Heterojunction solar cells with a wide band gap window and a narrow gap absorber have been investigated in order to develop an efficient, stable and low cost cell. CdS/CdTe heterojunction solar cells are attractive from several points of view. CdS having an energy band gap of 2·42 eV, is one of the promising materials as wide band gap front layer above the absorber. A low resistivity of the CdS film can be easily achieved using film deposition methods. CdTe has the direct band gap near the optimum for solar photovoltaic conversion [1], and a high absorption coefficient which is enough to absorb photons within a few micrometers of the surface of the layer. Therefore, CdS/CdTe heterojunction has a high potential as a solar cell system. Fahrenbruch and his co-workers [2] theoretically estimated the solar conversion efficiency for CdS/CdTe heterojunction and obtained a value of 17%. Matsumoto and his co-workers [3] made a solar cell by the screen printing technique and obtained a conversion efficiency of 12·8%. To date, efficient CdS/CdTe thin films solar cells have been made by close spaced sublimation (CSS) [4,5]. Chu and his co-workers have achieved over 15% efficiency using CSS process [4].

The efficiency of the photovoltaic cell is related to its open circuit voltage V_{oc}, short circuit current I_{sc}, and the fill factor FF. To improve the V_{oc} of the cell, the parameters subject to change are, ΔE_c the electron affinity difference, S_i the interface recombination velocity, and A_1 the junction area. Work function and electron affinity are defined, respectively, as that energy required to remove an electron from the Fermi level

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vacuum level
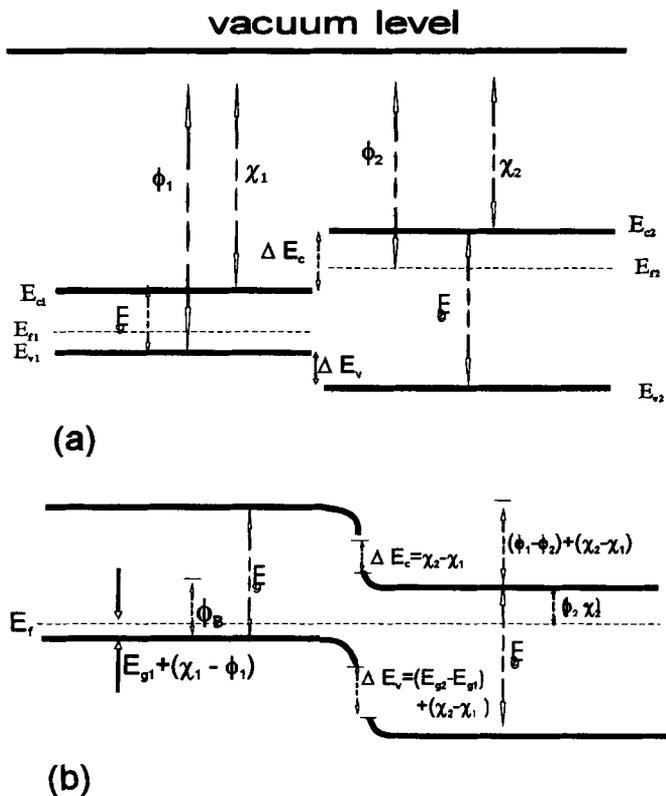
Figure 1. Energy band diagram of CdTe (subscript1)-CdS (subscript2);(a) before contact, and (b) after contact, E_g is the band gap, $E_c = \chi_2 - \chi_1$, is the difference in electron affinity, ΔE_c is the difference in the valence band edge, $\phi_1 - \phi_2 = eV_D$ is the work function difference, V_D is the diffusion potential and ϕ_B is the barrier height.

(E_f) and from the bottom of the conduction band (E_c) to a position just outside the material (vacuum level). The difference in energy of the conduction band edges in the two semiconductors is represented by ΔE_c and that in the valence band edges by ΔE_v. Figure 1 shows the origin of electron affinity difference when a *p-n* junction is formed of two semiconducting materials having different band gaps. Also shown in the figure are the barrier height ϕ_B, the work functions ϕ_1, ϕ_2, and ΔE_v. Since ΔE_c is directly related to fundamental material properties, it can be changed only by changing materials. The interface recombination can arise in many ways which may be reduced by lowering the density of interface states, except that this density is more or less fixed by the lattice mismatch between CdS and CdTe. The junction area A_1 is technology dependent and can be reduced by using special methods of cell fabrication.

In this paper, a simple method for measuring ΔE_c from the observation of the variation of V_{oc} with temperature is described. Measurements were made on CdS/CdTe cells fabricated by different processes[6] and also on CdS/CdZnTe cells. The purpose of this paper is to show that ΔE_c is directly related to fundamental material properties, can be changed by changing materials, and is independent of the process of cell fabrication.

2. Experimental

2.1 *Cell fabrication*

The following four types of cells have been fabricated for this study:

Type A: (*evaporated cell*)

CdTe thin films were prepared by a vacuum evaporation technique based upon the simultaneous evaporation of two materials on polycrystalline alumina substrates heated to 350–450°C. CdS films were then evaporated on CdTe films. After the deposition of undoped material, the CdS films were doped with In. This doping formed a very low resistivity region to be contacted by the grid structure. Molybdenum grid was then deposited by RF sputtering [7] which served as a front contact of the cell.

Type B: (*screen printed cell*)

CdS paste for screen printing was prepared by mixing 100g CdS powder with 10g $CdCl_2$ powder and an appropriate amount of propylene glycol. The CdS paste was screen-printed on borosilicate glass substrate and dried at 120°C for 1 h. The CdS film was sintered in N_2 atmosphere at 260°C for 1 h. Later, the sintered film was fired at a higher temperature (690°C) for 1 h (Cd + Te) paste was then screen printed on CdS layer and sintered in N_2 atmosphere at 620°C for 60 min. A carbon electrode was formed on CdTe film by screen printing and heat treatment. Ag and Ag + In electrodes were formed on the carbon electrode and CdS film respectively, by screen printing and heat treatment [8].

Type C: (*wet-processed cell*)

The barrier was formed by dipping CdTe single crystal into an aqueous solution containing cadmium acetate, ammonia, ammonium acetate and thiourea at 80°C for 15 min. Doped CdS films were deposited by adding boric acid to the reaction mixture. The $BO_3^=$/Cd^{++} molar ratio in the solution was 10^{-3}. A gold contact was then deposited on CdTe crystal, which served as a back contact of the cell, and In grid contact was deposited on CdS, which served as a front contact of the cell [5].

Type D: (*CdS/CdZnTe cell*)

ZnTe thin films were prepared by a vacuum technique based upon the simultaneous evaporation of two materials on polycrystalline alumina substrates. CdTe films were then evaporated on ZnTe followed by CdS films being evaporated on CdTe. Indium grid was then deposited by vacuum evaporation on CdS which served as a front contact of the cell.

2.2 *Measurement technique*

For the measurement of open-circuit voltages at different temperatures, amica insulated heating coil, surrounded by an aluminium heat sink (about 4 mm thick) was used. The temperature on the surface of the heat sink could be kept constant for a considerable time. Applying voltages from 5 to 50 VAC across the heater coil, temperature could be varied from room temperature to about 150°C. The temperature of the cell was measured by a copper-constantan thermocouple. The cell was illuminated by a 100 W tungsten lamp. The incident light was passed through a 4 cm thick water filter so that the cell was not heated by the incident radiation at the time of taking a reading. The open-circuit voltages were measured by a Kiethly electrometer model 619°C. Plots of qV_{oc} versus kT were then obtained.

Forward current voltage measurements at room temperature were made and $\ln I_f$ versus V_f plots were obtained. The short-circuit currents for different cells were also measured at room temperature. The cell was illuminated by an ELH lamp.

3. Results and discussion

Figure 2 shows the plots of qV_{oc} versus kT for four types of cells. They are all straight lines. When extrapolated to $kT = 0$, the curves for A, B and C meet the ordinate between 1·18 and 1·25 eV, while for type D cells this value is about 2·20 eV. The values of ΔE_c for different types of cells are found to be independent of illumination intensity.

Figure 3 shows $\ln I_f$ versus V_f plots for different types of cells. Each curve is drawn from the readings taken on one sample (of each type of cell), but is very close to the other. The curves indicate the diode-like conduction at applied voltages of above 0·3. At relatively low voltages (below 1V) the measured points are found to be relatively stable. As the forward voltage is increased, a drift with time (drift increasing with forward bias) is observed. Some of the experimental results obtained for different types of cells are shown in table 1.

Table 1.   Evaluation of qV_{oc} versus kT and I_f versus V_f characteristics. V_{oc} and I_{sc} measured at room temperature.

Cell	$E_{gl} - E_c$ eV	ΔE_c eV	V_{oc} V	I_{sc} mA	Diode quality factor	I_0 from $I_f - V_f$	I_0 from $qV_{oc} - kT$	No. of cells tested
Type A	1·22	0·23	0·743	21·4	1·9	3×10^{-8}	2×10^{-8}	3
Type B	1·25	0·20	0·747	22·25	1·5	2×10^{-8}	5×10^{-8}	3
Type C	1·20	0·25	0·30	15	2·5	1×10^{-7}	9×10^{-7}	3
Type D	2·00	0·49	0·61	19	3	5×10^{-9}	3×10^{-9}	3
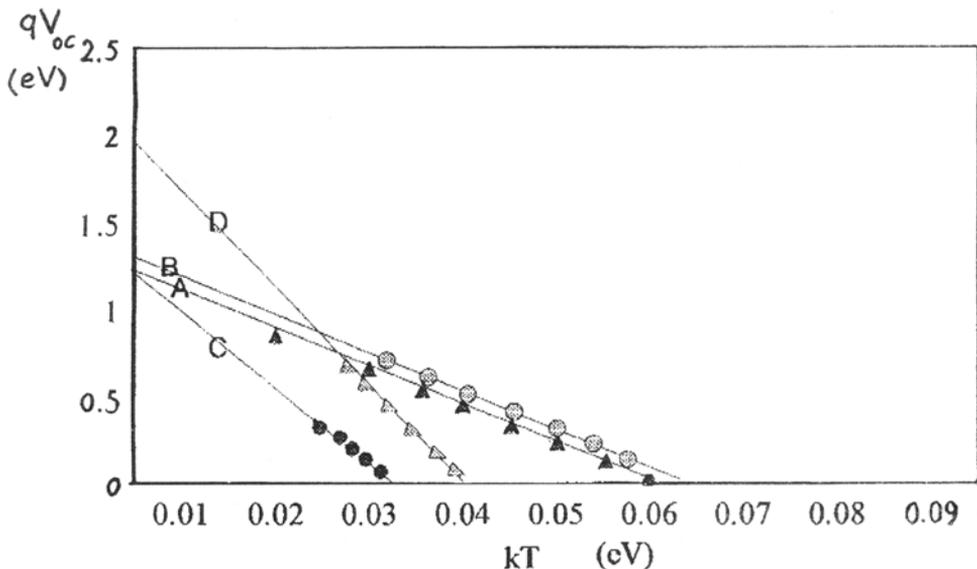
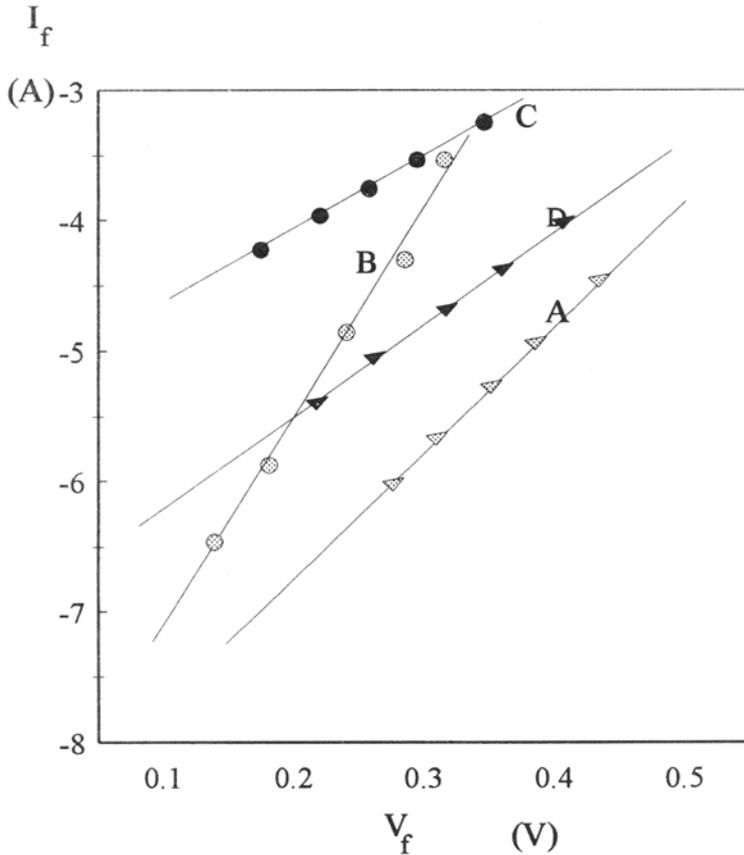**Figure 2.**   Plot of qV_{oc} versus kT for four types of cells.

Figure 3. Logarithmic plot of I_f versus V_f for four types of cells

According to interface recombination model [9], the expression for current in the cell is given by,

$$I = qA_iN_{c2}S_i\exp[-(E_g - \Delta E_c)/kT][\{\exp(V - IR_s)/nkT] - 1\} - A_1I_{sc}]$$ (1)

where q is the electronic charge, N_{c2} is the effective density of states at the CdS band edge, R_s is the series resistance and I_{sc} is the short-circuit current density of the cell.

From (1), the expression for open circuit voltage can be obtained for $I = 0$ and $qV_{oc} \gg kT$ as

$$qV_{oc} = (E_{g1} - \Delta E_c) + kT\ln I_{sc} - kT\ln q\, N_{c2}S_i - kT\ln(A_i/A_1).$$ (2)

Thus, a plot of qV_{oc} versus kT gives $(E_{gl} - \Delta E_c)$ as the $kT = 0$ intercept. Taking the band gap of CdTe as 1·5 eV, ΔE_c is calculated from the extrapolated value of $(\Delta E_{gl} - \Delta E_c)$. For cells A, B and C the values of ΔE_c are found to lie within $0·2 - 0·25$ eV.

From (2) it is seen that V_{oc} increases with the decrease of ΔE_c, S_i and (A_i/A_1). The electron affinity difference ΔE_c is related to fundamental material properties and can be changed only by changing materials. No change of ΔE_c with light intensity was detected. Lazarev [10] assumed that ΔE_c is independent of light intensity and applied

voltage and reported that this assumption is quite strong for heterojunctions with complex interface states. Bordure and co-workers[11] assumed that light modifies neither the space charge nor the height of spike in CdS.

Interface recombination can arise in many ways, but when it is related to the misfit dislocation density at the interface between CdS and CdTe due to the lattice mismatch Δa across the junction, it is given by the relation [12]

$$\sigma_i = v_{th} \sigma N_i^*.$$

Here, $N_i^* = 2\Delta a/a^3$ is the effective density of states, σ is the capture cross-section of the interface states and v_{th} is the thermal velocity of carriers and is given by the relation

$$v_{th} = (2kT/m)^{1/2}.$$

At room temperature its value is about $10^7 \, \text{cms}^{-1}$. Under the assumption that free carrier will be captured if it approaches sufficiently close to the centre so that the binding energy due to coulomb attraction is equal to or greater than kT, a simple estimate of the corresponding value of σ can be made [13]

$$(e^2/r\varepsilon^2) = kt$$

or, at room temperature, $\pi r^2 = \sigma = 10^{-10}/\varepsilon^2 \, \text{cm}^2$, where ε is the dielectric constant. Thus in the above case S_i is related to the fundamental material properties. There may be many states at the CdS/CdTe interface over ΔE_c. The hole concentration in CdTe is so large that the limiting process of interface recombination is the electron stage. The Boltzmann relationship is

$$n_0 = n_{b0} \exp(-\Delta E_c/kT).$$

With n_0 the concentration of electrons in the conduction band of CdTe at $x = 0$ and n_{0b} the concentration of electrons at the top of the barrier, is as valid in the case of a large number of interface states as it is in the case of few interface states[11]. The analysis made by Boer[14] indicates that the maximum reduction of the open-circuit voltage caused by interface recombination is about 0·1 V. The interface recombination is, thus, a minor effect for the better cells.

When CdZnTe is used in place of CdTe in type D cells, ΔE_c increases to a value of about 0·49 eV. This may be the reason for the observed higher V_{oc} for this type of cell. In type C cells, the CdS layer is formed by dipping, which results in a large value of A_i due to the formation of CdS in CdTe grain boundaries as shown in figure 4. This results in the decrease of V_{oc} according to the relation,

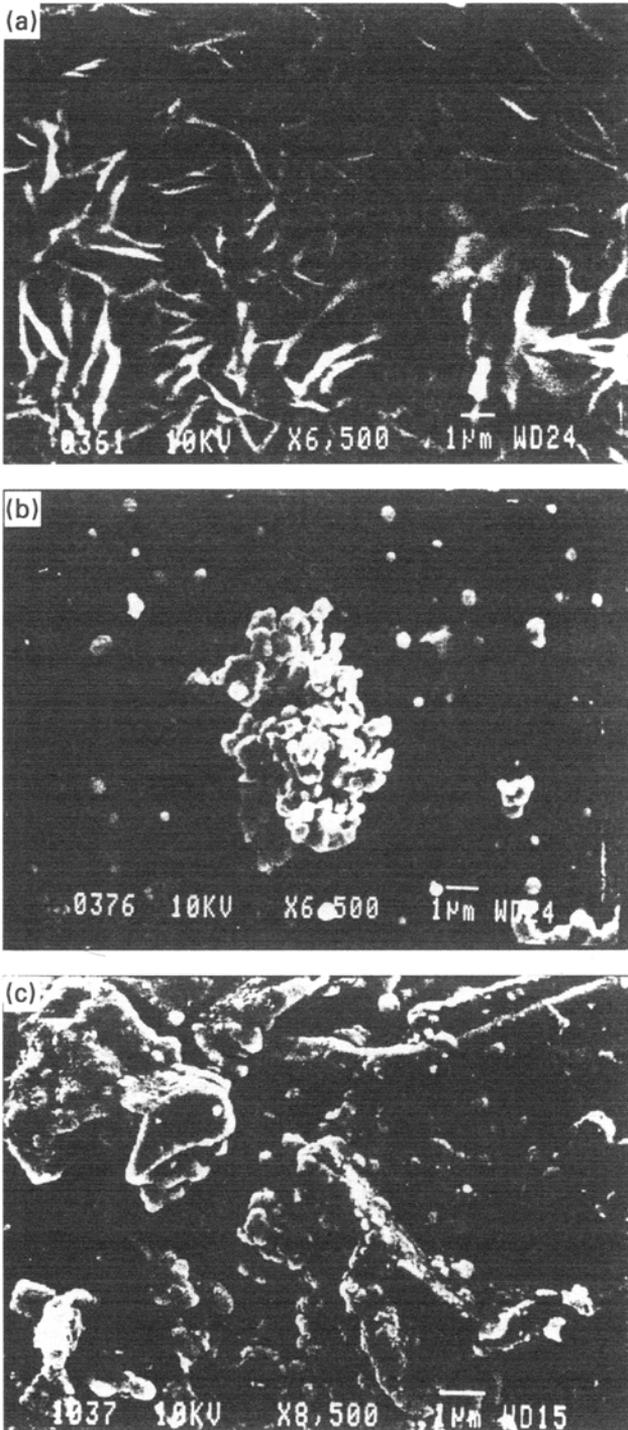$$V_{oc} = (kT/q)\ln(A_i/A_1).$$

This may be the reason for the observed low V_{oc} for type C cells. ΔE_c for this type is relatively high.

The method used for measuring ΔE_c is tested by conducting separate experiments with the same set of cells. For a small series resistance (1) may be written as

$$I = I_0 \exp[(qV/nkT) - 1] - I_{sc} \tag{3}$$

where the saturation current I_0 is given by

$$I_0 = qA_i/N_{c2} S_i \exp[-(E_{gl} - \Delta E_c)/kT].$$

Figure 4. Scanning electron micrographs of CdS films. (**a**) solution grown film, (**b**) screen-printed film and (**c**) evaporated film.

When $I = 0$, $V = V_{oc}$ and from (3) for $(I_{sc}/I_0) \gg 1$, we have

$$qV_{oc} = nkT\ln[(I_{sc}/I_0) + 1] = nkT\ln(I_{sc}/I_0).$$

Thus, a slope of qV_{oc} versus kT plots directly gives the value of $nln(I_{sc}/I_0)$. The I_{sc} for each cell is measured at room temperature with an ELH lamp of $50\,mW/cm^2$ intensity and a tungsten lamp of $50\,mW/cm^2$ intensity. Forward current-voltage measurements at room temperature are then made and ln I versus V plot are obtained. The current voltage relation may be expressed as

$$I = I_0\exp[(qV/nkT) - 1].$$

For an applied voltage greater than 0.3 V, the forward current can be expressed as [15]

$$I_f = I_0\exp(qV_f/nkT).$$

Thus, the ln I_f versus V_f curve will be a straight line. If we extrapolate the exponential portion to $V = 0$, we obtain I_0. The values of I_0 found for each cell by the two methods are in substantial agreement.

4. Conclusions

From the study of the observed results it may be concluded that for CdS/CdTe cells, the electron affinity difference is not dependent on the process of cell fabrication. It may be reduced only by changing material. The quantity (A_i/A_1) is technology dependent and can be reduced by an improved process of cell fabrication. The method used for measuring ΔE_c is very simple and may be extended for the estimation of the saturation current I_0.

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