Temperature dependent electroreflectance study of CdTe solar cells

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ABSTRACT

Cadmium telluride is a promising material for large scale photovoltaic applications. In this paper we study CdS/CdTe heterojunction solar cells with electroreflectance spectroscopy. Both CdS and CdTe layers in solar cells were grown sequentially without intermediate processing by the close-space sublimation method. Electroreflectance measurements were performed in the temperature range of T = 100–300 K. Two solar cells were investigated with conversion efficiencies of 4.1% and 9.6%. The main focus in this work was to study the temperature dependent behavior of the broadening parameter and the bandgap energy of CdTe thin film in solar cells. Room temperature bandgap values of CdTe were $E_g = 1.499$ eV and $E_g = 1.481$ eV for higher and lower efficiency solar cells, respectively. Measured bandgap energies are lower than for single crystal CdTe. The formation of $CdTe_{1-x}S_x$ solid solution layer on the surface of CdTe is proposed as a possible cause of lower bandgap energies.

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1. Introduction

Cadmium telluride is a promising material for thin-film solar cells due to its direct optical bandgap with energy of about $E_g = 1.5$ eV and high absorption coefficient $> 5*10^5$/cm [1–4]. Record conversion efficiency of 17.3% was recently reported by First Solar for polycrystalline CdTe thin-film solar cell [5]. However, the record efficiency of CdTe solar cells is much less than its theoretical maximum (~29%). One possible reason for this could be related with problems in p–n junction between CdS and CdTe. It is proposed that the formation of $CdS_{1-x}Te_x$ solid solution layer with lower bandgap energy somehow affects the behavior of CdS/CdTe solar cells [6]. Also, the interface and bulk recombination reduces solar cell efficiency. Among other methods the electroreflectance spectroscopy (ER) is proven to be quite a powerful technique for investigation of junction properties. Room temperature ER studies were performed in several papers, mainly the bandgap energy and crystal quality were investigated [3,7,8]. Dhere et al. [9] performed room temperature ER measurements of CdTe solar cells and showed the presence of a high field region of 32 kV/cm in the CdS/CdTe interface layer. At the same time it could be interesting to study also temperature dependent electroreflectance behavior and find differences between different solar cells.

In the present work two CdS/CdTe heterojunction solar cells with different properties were studied. Differences between studied cells were in fabrication parameters and in back contact preparation. We used temperature dependent electroreflectance for characterization of CdTe solar cell junction properties. In addition to ER measurements,

the results of current–voltage (I–V) curve measurements and external quantum efficiency measurements (QE) are presented.

2. Experimental details

Thin film CdS/CdTe solar cells were fabricated on glass substrates with an area of 2×2 cm^2 covered with a SnO$_2$ layer with a sheet resistivity of about 10 Ω/□. SnO$_2$ served as the transparent front contact to CdS. Both undoped CdS and CdTe layers were grown sequentially without intermediate processing by the close-space-sublimation (CSS) method. CdS had the resistivity of 2–3 Ω·cm and transparency over 80%. The CdTe layers had the resistivity in the range of $~5*10^5$ Ω·cm. After the CdTe layer was deposited, the structures were held in CdCl$_2$:H$_2$O saturated solutions and then annealed in the air at 410 °C for ~30 min. To minimize the back contact barrier, an additional layer (~300 nm) of Te for one cell (Cell 1) or Cu for another cell (Cell 2) was used. In Cell 1 the CdTe was deposited at the substrate temperature of 440 °C, in Cell 2 at the temperature of 430 °C. The CdTe source temperature in both cases was 580 °C. All cells were completed with a Ni metal contact thermally deposited in vacuum. Both types of the solar cells have been fabricated in a superstrate configuration, and more details were given in [10].

Before ER measurements, I–V and QE measurements were made. I–V curves were measured at room temperature with illumination of 100 mW/cm^2 using the Oriel class A solar simulator 91159A. For electroreflectance measurements the DC- and AC-voltage was applied to a solar cell under study via back and front contact by a pulse generator with frequency of 275 Hz, AC value of ±0.8 V and DC component of −0.8 V. Computer controlled grating monochromator SPM-2 (f = 40 cm) together with a 250 W halogen bulb was used for illumination. The ER signal was detected using a Si detector and a lock-in

amplifier (SR 810). Solar cells under study were mounted into a closed-cycle He cryostat to perform temperature dependent ER measurements in the range of T = 100–300 K.

3. Results and discussion

3.1. I–V curves and QE of solar cells

Typical I–V curves of thin film CdS/CdTe heterojunction solar cells under the illumination are presented in Fig. 1. As it can be seen, Cell 1 shows better solar cell parameters with open circuit voltage $V_{OC} = 783$ mV, short circuit current density $J_{SC} = 23.1$ mA/cm^2 and conversion efficiency of 9.6%. The Cell 2 has quite different parameters, but still the open circuit voltage is $V_{OC} = 661$ mV and the short circuit current density is $J_{SC} = 18.2$ mA/cm^2, whereas the cell efficiency is lower, only 4.1%.

A comparison of the external quantum efficiency measurements, see Fig. 2, shows that Cell 1 has much steeper QE spectrum at long wavelength side than Cell 2. In the long-wavelength range the spectra restricted to the value of the CdTe bandgap energy which is equal to 1.499 eV (827 nm) for Cell 1 and 1.481 eV (837 nm) for Cell 2 at room temperature as measured by ER. The steeper shape of Cell 1 QE spectrum at long wavelength side leads to the steeper bandgap edge and could be one reason for better junction properties.

3.2. Temperature dependence of electroreflectance

Electroreflectance is a modulation spectroscopy where the external AC voltage is applied to the structure in order to modulate internal electric field.

Electroreflectance can be classified into three categories: weak, intermediate and strong field regimes, depending on the strength of a local electrical field in the junction. ER spectra with a weak field approach can be well fitted with a third derivative functional form (TDFF) given by Aspnes [11]:

$$\frac{\Delta R}{R} = Re\left[Ce^{i\phi}\left(E - E_g + i\Gamma\right)^{-m}\right], \qquad (1)$$

where E is the photon energy ($h\nu$), C is an amplitude parameter, ϕ phase parameter, E_g energy of the bandgap and Γ a broadening parameter, that reflects structural and compositional disorders. The exponent m depends on the type of the critical point and determining its proper value is of particular importance in analyzing ER spectra. Enloe and Parker [3] and Yu et al. [8] have improved their electroreflectance and photoreflectance fits by using m as independent variable and we used the same logic. Value m = 2.5, corresponding to a three-dimensional critical point, did not give a good fitting result. Therefore m = 3, corresponding to a two-dimensional critical point, was used for the fitting of all ER spectra since this value yielded an
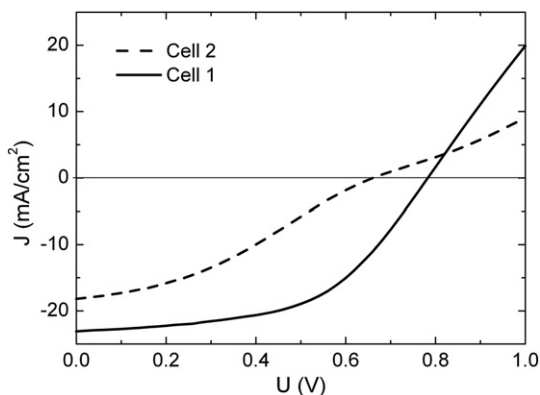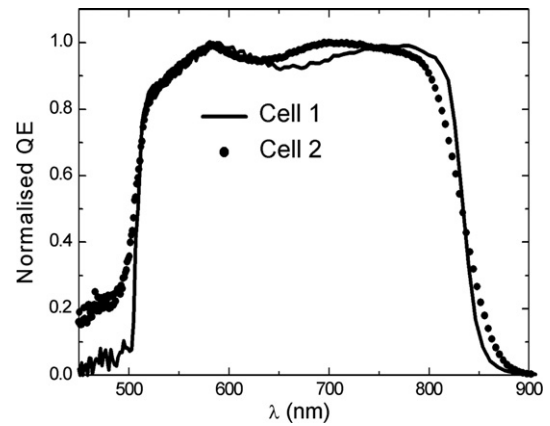

Fig. 2. Normalized QE curves of the studied solar cells.

excellent fit for majority of our data. To use m = 3 there are two possible explanations. A better fit is expected since the electron effective mass is significantly larger in one symmetry direction than the other two near the X point. Actually, neither n = 2.5 nor m = 3 can be strictly correct since both were derived under the assumption of a parabolic-band structure. Another possibility is that excitonic effect may be contributing to the transition in high-quality CdTe samples. The influence of excitons can cause a three-dimensional transition to appear as a two-dimensional in nature [3]. Temperature dependent ER spectra together with Aspnes fit (Eq. (1)) of Cell 1 and Cell 2 are presented in Figs. 3 and 4. It is clearly seen that the spectrum shifts towards higher energies with decreasing temperature and the ER signal intensity increases as can be seen from scale factors.

Temperature dependence of bandgap energies obtained from the fittings with Eq. (1) is plotted in Fig. 5. E_g values are considerably lower than reported reference values of monocrystalline CdTe, see Fig. 5 [1]. Temperature coefficients were found to be $dE_g/dT = -3.1 \times 10^{-4}$ eV/K for Cell 1 and $dE_g/dT = -3.5 \times 10^{-4}$ eV/K for Cell 2. These values are in good agreement with the results obtained by Mathew et al. [12].

It is seen that the obtained bandgap energies are smaller than those found for monocrystalline CdTe in other papers [1,2]. The smaller bandgap energies in our cells can be explained by assuming a formation of CdTe$_{1-x}$S$_x$ solid solution in the p–n junction region. Sulfur has incorporated into CdTe during the thermal treatment. Hädrich et al. [6] have found that the dependence of the bandgap energy of the CdTe$_{1-x}$S$_x$ solid solution is given by the empirical equation:

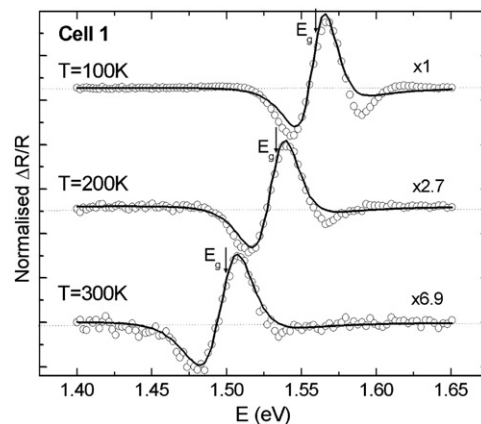$$E_g(x) = 2.4x + 1.51(1-x) - 1.8x(1-x). \qquad (2)$$

Fig. 3. ER spectra of sample Cell 1 at 100 K, 200 K and 300 K. Dots show the experimental result and continues lines are the fitting results with Eq. (1).
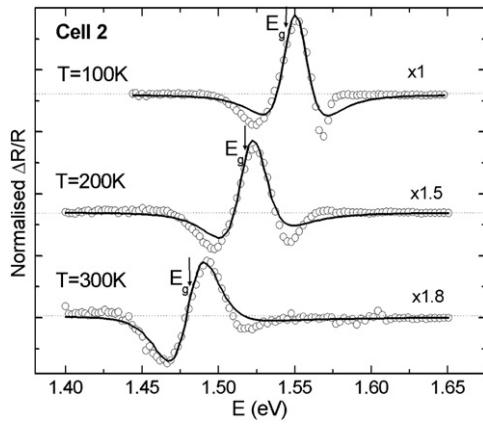

Fig. 1. I–V curves of the studied solar cells under illumination at room temperature.

Fig. 4. ER spectra of sample Cell 2 at 100 K, 200 K and 300 K. Dots show the experimental result and continues lines are the fitting results with Eq. (1).

Fig. 6. The temperature dependence of the broadening parameter Γ with fittings (solid curves) using Eq. (3).

At room temperature we found bandgap energies $E_g = 1.499$ eV and $E_g = 1.481$ eV for Cell 1 and Cell 2, respectively. According to Eq. (2) we have a $CdTe_{1-x}S_x$ solid solution with average sulfur content of $x = 0.01$ for Cell 1 and $x = 0.03$ for Cell 2. It is obvious that the solid solution layer does not have any abrupt edge and probably we have a layer with varying concentration of sulfur. Cell 1 with smaller sulfur content in solid solution, showed a better solar cell performance, as we saw from I–V measurements. Similar behavior was described also by Hädrich et al. [6].

The broadening parameter Γ is often used as a measure of crystal quality since its magnitude is primarily determined by lattice defects such as disorders, vacancies, and impurities [3]. In our experiment, as it can be seen from Fig. 6, Γ is found to be 29 meV for Cell 1 and 27 meV for Cell 2 at room temperature and it is decreasing with decreasing temperature. Comparing our results with other authors, it can be concluded that CdTe samples with a broadening parameter value around 30 meV and less can be classified into good quality samples category [3].

The effect of temperature provides not only the shift of the bandgap energy but also the change in the broadening parameter. If we grant the electron–phonon coupling as a main broadening mechanism, its parameter value can be written, by taking into account the Bose–Einstein occupation factor, as in [13]:

$$\Gamma(T) = \Gamma_1 + \left(\frac{\Gamma_0}{e^{\Theta_\Gamma / T} - 1} \right), \tag{3}$$

where Γ_1 represents the broadening due to temperature-independent mechanism such as crystalline imperfections and surface scattering, Γ_0 represents the strength of electron–phonon coupling, Θ_Γ is an average phonon temperature.

Fig. 6 shows the ER broadening parameter Γ as a function of temperature and least-squares fits (solid curves) with the Eq. (3) together with fitting parameters. The obtained Γ_1 values of 23 meV and 21 meV for samples Cell 1 and Cell 2, respectively, indicate relatively high quality of the CdTe thin film. Calculated values of $\Gamma_0 = 12$ meV and $\Theta_\Gamma = 338$ K for Cell 1 and $\Gamma_0 = 8$ meV and $\Theta_\Gamma = 233$ K for Cell 2 are comparable for both solar cells. It is interesting that solar cell with lower efficiency shows also a lower value of Γ_1. This difference between broadening parameters could also be an important factor in properties of the respective p–n junction. However further studies are needed in order to clarify this assumption.

4. Conclusion

Temperature dependent ER measurements (T = 100–300 K) were performed with two different CdS/CdTe solar cells. All ER spectra were fitted using Aspnes third derivative functional form. Room temperature bandgap energies $E_g = 1.499$ eV and $E_g = 1.481$ eV for Cell 1 and Cell 2, respectively, were found. The low value of the broadening parameter Γ for both solar cells shows a good quality of CdTe absorber layers. The formation of $CdTe_{1-x}S_x$ solid solution in the p–n junction region was detected for both solar cells. However, Cell 2 had smaller broadening parameter value, but Cell 1 showed a better solar cell performance. In conclusion, we showed that the temperature dependent ER measurements could give valuable information about the junction properties of solar cells.
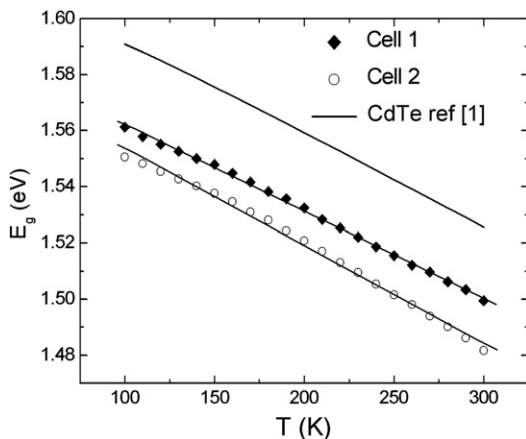
Fig. 5. Bandgap energy values found from ER fittings as a function of temperature. The upper curve represents the bandgap energy of the monocrystalline CdTe from ref. [1].
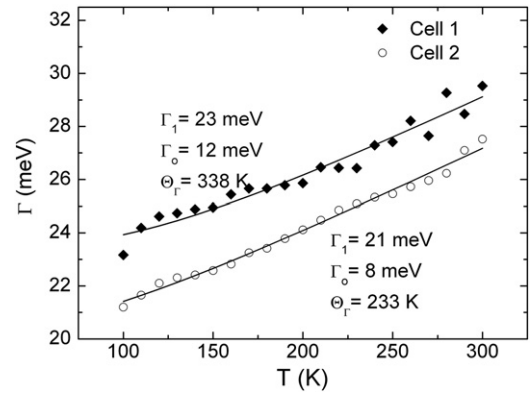
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