Analysis of Alloying and Built-in Voltage in Thin Film Chalcogenide Solar Cells using Modulation Spectroscopy

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***Abstract* — Modulation spectroscopy has been performed on superstrate CdS/CdTe solar cells prepared by close-spaced sublimation. Photoreflectance (PR) measurements were conducted near the CdTe E_0 band edge using a variable-wavelength probe beam in conjunction with a chopped pump beam. A fit to the observed PR spectrum was made using two third-derivative, low-field lineshapes. The band gap of the active material near the junction is 1.46 eV ($CdTe_{1-x}S_x$). The envelope function varied as 1 – V/V_{bi}. The PR spectrum shifted with a temperature coefficient of -0.31 meV/K. Photoreflectance spectroscopy offers a powerful method of determining absorber band gaps, alloying, and built-in voltage in thin-film solar cells.**

***Index Terms* — CdTe, chalcogenide, photoreflectance, solar cell, spectroscopy, thin film.**

I. INTRODUCTION

We have employed modulation spectroscopy in the form of photoreflectance (PR) to study completed thin-film CdS/CdTe solar cells in a non-destructive and convenient fashion near room temperature. The goal of this work is to detect and quantify compound formation near the CdS/CdTe interface and to explore the surface space charge region.

Modulation spectroscopy [1]-[6] has undergone a resurgence of interest. It has been applied to study systems such as semiconductor alloys, heterostructures, superlattices, quantum wells, and QD [7]-[11], and to map the composition of $Cd_{1-x}Zn_xTe$ crystals [12]. Also studied has been the surface field in InP solar cells [13], CdS-CdTe cells [14], strain effects in CIGS cells [15], and QD intermediate band solar cells [16].

II. EXPERIMENTAL

A. Cell Fabrication

Cadmium telluride solar cells were fabricated in the superstrate configuration: glass/SnO_2:F/HRT/n^+-CdS/p-CdTe/ graphite paste (ZnTe:Cu)/metal back contact [17]-[18]. The CdS was deposited by chemical bath deposition (CBD), and the CdTe by close-spaced sublimation (CSS) at T_s = 600 °C in 10-15 Torr He/O_2. The CdTe was treated using $CdCl_2$ at 400 °C. Solar cell efficiencies of 10 – 11% were obtained using baseline techniques, and 13 - 14% using a modified CBD CdS process and a carefully-controlled $CdCl_2$ process (Fig. 1).

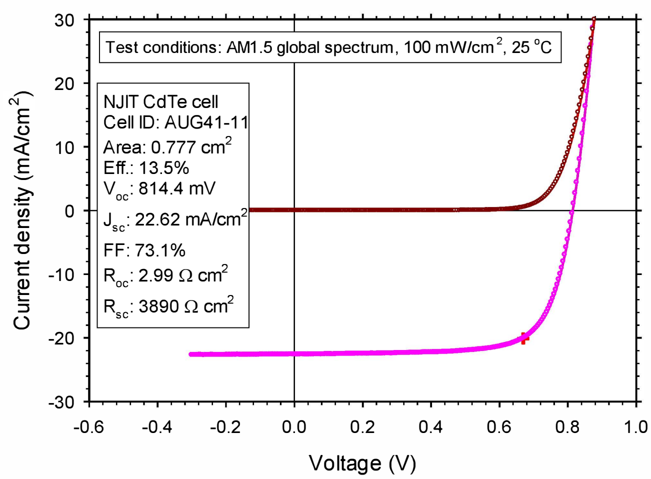

Fig. 1. Light and dark *J-V* curves for NJIT CdS/CdTe solar cell.

B. Photoreflectance Apparatus

The experimental set up for PR at NJIT is shown in Fig. 2. The variable-λ probe beam is generated using collimated light derived from a 150 W W-halogen bulb dispersed by a grating monochromator. The pump beam consists of above-gap light from a 15 mW HeNe laser (632.8 nm) that is passed through an optical chopper (692 Hz). The pump beam is incident on the sample in the same area that the probe beam is incident, but arrives at a different angle. The beams overlap in the plane of the thin-film structure. The reflected probe beam is passed through a HeNe notch filter to suppress scattered light from the pump beam and is directed to a c-Si photodiode. Optical baffling greatly limits spurious chopped light from reaching the photodiode. The current output from the photodiode is converted to a voltage signal in a preamplifier. The DC component of the output voltage is proportional to $I(\lambda)R(\lambda)$ where $I(\lambda)$ is the photon flux in the probe beam and $R(\lambda)$ is the (unperturbed) reflectivity of the cell; the AC signal is

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proportional to $I(\lambda)\Delta R(\lambda)$, where ΔR is the modulated reflectivity, and is measured using an SR510 lock-in amplifier. The ratio of these two signals is $\Delta R(\lambda)/R(\lambda)$. The voltage across the cell, V, can be fixed at will using an op-amp circuit.

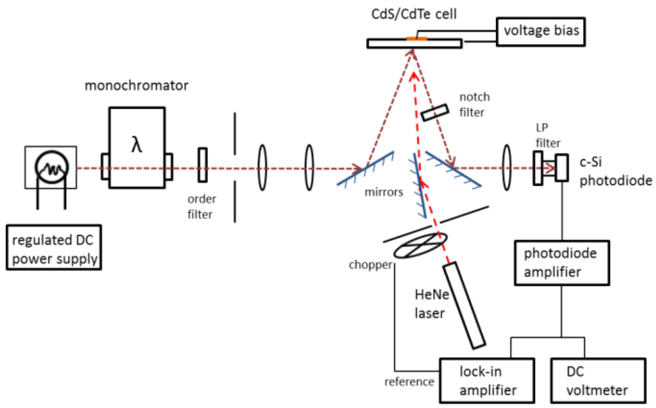

Fig. 2. Schematic of experimental setup for photoreflectance spectroscopy using 633 nm pump beam.

III. Background

In modulation spectroscopy, a repetitive stress, such as temperature T, pressure P, or electric field F, is applied to a semiconductor and its optical reflectivity is found to be modified in synchrony. Photoreflectance is conducted by modulation of the reflectivity using a chopped light beam. Electron-hole pairs generated by the pump beam reduce the electric field F in the semiconductor near its surface, thereby changing the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ via its dependence on F, and changing the reflectivity R [1, 4, 19]:

$$\frac{\Delta R}{R} = \alpha_s(\varepsilon)\Delta\varepsilon_1 + \beta_s(\varepsilon)\Delta\varepsilon_2 \tag{1}$$

where α_s and β_s are the Seraphin coefficients. Near the fundamental gap, $\beta_s \approx 0$. In our case, the semiconductor is nominally CdTe. Since photoreflectance probes the dielectric function but is a derivative technique, sharp peaks occur only at the interband critical points, e.g. at E_0, E_1, E_0', etc. [20].

IV. Experimental Results

A. Spurious Signal Cancellation

Even at room temperature the extremely small PR signal is exceeded by an in-phase signal originating from photoluminescence of the sample excited by the above-gap pump beam [21]. We have devised a method for suppressing this spurious signal. In principle, it can be used to suppress in-phase signals from the detector resulting either from scattered chopped pump light or light from PL. The essence of the method is to generate an out-of-phase signal that is equal in amplitude to the spurious signal. The sum of these signals is simply a DC term that is ignored by the lock-in amplifier. This is accomplished by generating a second "mock-pump" beam that is out-of-phase with the primary pump beam, and which is incident on the device adjacent to the probe beam but not overlapping it. This mock-pump beam gives rise to scattered laser light and PL just as the primary pump beam does, but does not modulate the reflected probe beam. The intensity of this beam is adjusted to null the in-phase spurious signal. The experimental arrangement is shown in Fig. 3 below where we have called the mock-pump beam the spurious signal cancellation beam. Several related techniques have been described in the literature, including the well-known "sweeping PR" technique introduced by Shen and Dutta [22].

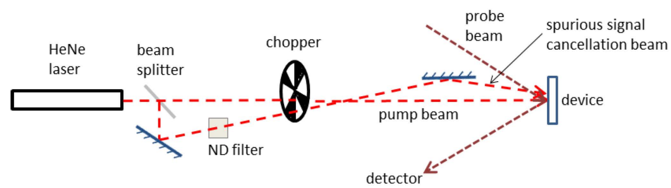

Fig. 3. Generation of a spurious signal cancellation beam to improve PR signal-noise ratio.

Application of our cancellation-beam technique was hampered by the use of a fixed ND filter whereas a variable ND filter (which was unavailable) should ideally be employed to enable exact signal cancellation. Nevertheless, we are confident that the method has merit as the raw lock-in readings were reduced through use of the scheme (e.g. from 5.22 to 3.29 at 838 nm), implying a reduction of the spurious signal.

B. PR Signal at Zero and Non-zero Cell Bias

Figure 4 (open circles) shows the PR spectrum obtained at room temperature with the cell held at $V = 0$. This spectrum denotes the presence of $CdTe_{1-x}S_x$, as we later show.

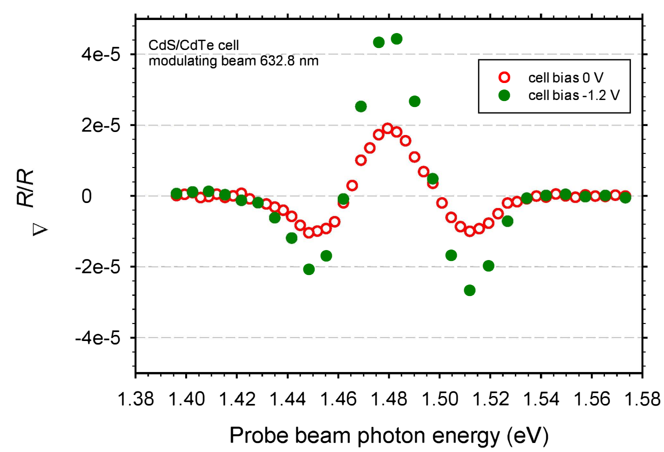

Fig. 4. PR spectra of CdS/CdTe solar cell at 300K near the band edge for voltage biases of 0 V and -1.2 V applied to the cell.

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It was found that the amplitude of the peaks, or the envelope function, is a function of cell bias, and hence of both the strength and extent of the electric field in the surface space charge region. Figure 4 also shows the spectrum under a reverse bias $V = -1.2$V. The PR signal increases under reverse bias. However, the energy spacing and location of the peaks do not change with cell bias or pump intensity. Franz-Keldysh oscillations are not seen. Upon application of a cell bias V, both the space charge width W and the peak electric field F_0 are multiplied by a factor $\sqrt{1-V/V_{bi}}$ relative to their values at zero bias [23]. Since $\Delta R/R \sim F_0^2$ (see section V), we would expect at V = -1.2 V the PR signal to increase by a factor $1 - V/V_{bi} = 2.2$ (with V_{bi} = 1V). This is precisely what is observed.

With the probe beam set at the wavelengths of two of the extrema in Fig. 4, we show in Fig. 5 the amplitude of the $\Delta R/R$ peaks as a function of applied voltage bias. While the reverse bias portion of the data for $\Delta R/R$ extrapolates to 0 for a V of about 1.0 V, consistent with the equation

$$\frac{\Delta R}{R} \sim F_0^{\,2} \sim 1 - \frac{V}{V_{bi}} \qquad (2)$$

derived above, in the forward bias direction $\Delta R/R$ (and by implication the peak electric field F_0) collapses almost to zero near V = 0.6 V, i.e. at about the cell open-circuit voltage under the HeNe laser. This is an interesting result. The peak surface field with the pump beam off is F_0. If the peak field with the pump beam on, $F_{0,\,on}$, is zero or a fixed fraction of F_0, the PR signal should vary as $(F_0 - F_{0,\,on})^2$ i.e. still as $\sim F_0^2$.

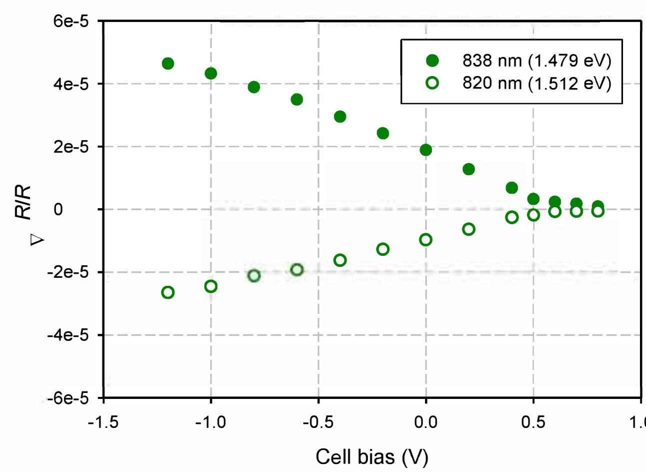


Fig. 5. Dependence of PR signals at 838 and 820 nm (wavelengths approximately corresponding to the +ve going and –ve going PR peaks) as a function of cell bias.

C. Dependence of PR Signal on Cell Temperature

PR spectra were measured at 298 K and at 313.1 K. This was accomplished by building a small enclosure containing a heater around the sample and measuring the sample temperature using a Pt thin-film sensor. For a ΔT of 15.1 K, a red shift in the PR spectrum of 4.6 meV was found, corresponding to an energy shift of -0.31 meV/K (see Fig. 6). This is close to the reported temperature coefficient of the CdTe bandgap (-0.4 meV/K).

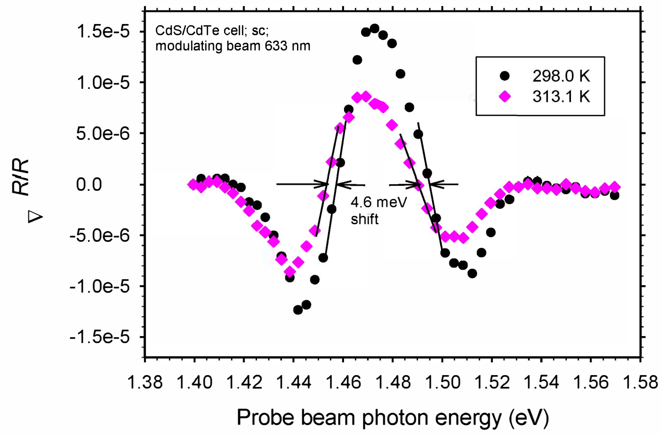


Fig. 6. Temperature shift of zero-bias PR spectrum; the shift is -0.31 meV/K.

V. Lineshape Analysis

The analysis of PR spectra depends on whether F corresponds to a high-field (>100 kV/cm) or a low-field condition. Pollak and Shen [19] identify the low-field case as satisfying $\Theta << \Gamma$, where Γ is the broadening parameter (see below) and Θ is the electrooptical energy:

$$\Theta = \left(\frac{e^2 F^2 \hbar^2}{2\mu}\right)^{1/3} \qquad (3)$$

Here F is the electric field and μ is the reduced mass. We calculate Θ = 7.5 meV in our cell for F = 1 x 10^4 V/cm, and later we find Γ = 20 meV. We therefore believe the low-field case is appropriate for this work. On the other hand, a group at NREL chose to use the high-field case [24]. In the low-field case, and for band-band transitions, Aspnes has shown that $\Delta\varepsilon$ has a third derivative form:

$$\Delta\varepsilon \sim \frac{\Theta^3}{E^2}\frac{\partial^3}{\partial E^3}[E^2\varepsilon(E - E_{cp}, \Gamma)] \qquad (4)$$

where E is the photon energy [5]. Since $\Theta^3 \sim F^2$, $\Delta\varepsilon$ is proportional to the square of the electric field. Assuming ε is a Lorentzian, $\Delta\varepsilon$ can be calculated, leading to:

$$\frac{\Delta R}{R} = \Re e\left[\sum_k C_k e^{i\theta_k}(E - E_{cp,k} + i\Gamma_k)^{-n}\right] \qquad (5)$$

In this equation, $\Re e$ denotes real part of, C is the amplitude, θ is the phase factor, E_{cp} is the critical point energy, Γ is the broadening factor, and the value of n represents the nature of the critical point [4, 19]. For the usual 3D band-band transition, $n = 2.5$, while $n = 2$ corresponds to bound state (e.g. excitonic) transitions and $n = 3$ to 2D band-band transitions.

We have derived the following explicit functional forms for third-derivative lineshapes. With $x = E - E_{cp}$, we find for the case $n = 5/2$

$$\frac{\Delta R}{R} = CK\left\{[\frac{1}{\sqrt{2}}\frac{G}{H} + \sqrt{2}x\frac{H}{G}]\cos(\theta) - [\sqrt{2}x\Gamma\frac{1}{GH} + \frac{1}{\sqrt{2}}\frac{(x^2-\Gamma^2)^2}{\Gamma}\frac{H}{G}]\sin(\theta)\right\} \tag{6}$$

where

$$K = \frac{\Gamma}{(x^2-\Gamma^2)^2 + 4x^2\Gamma^2}\;;\; G = \sqrt{x^2+\Gamma^2}\;;\; H = \sqrt{-x+\sqrt{x^2+\Gamma^2}} \tag{7}$$

For the case $n = 2$ we find

$$\frac{\Delta R}{R} = C\frac{(x^2-\Gamma^2)\cos(\theta) + 2x\Gamma\sin(\theta)}{(x^2-\Gamma^2)^2 + 4x^2\Gamma^2} \tag{8}$$

To fit the experimental data previously shown in Fig. 4 we have used one $n = 2$ lineshape and one $n = 2.5$ lineshape with appropriate values of E_{cp}, θ, and Γ. Normalized lineshapes using these parameters are shown in Fig. 7.

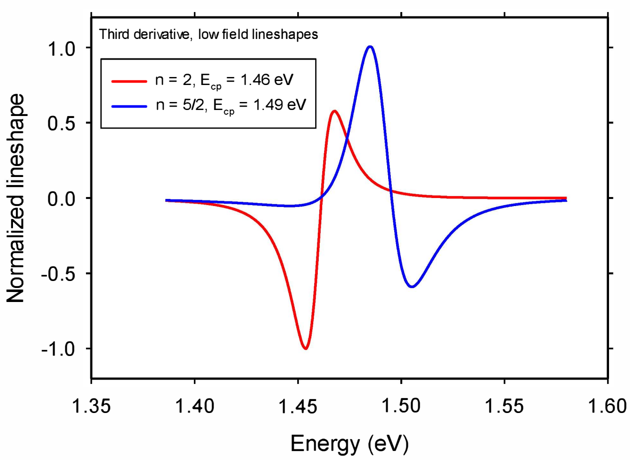


Fig. 7. Normalized lineshapes for $n = 2$ (excitonic) and $n = 5/2$ (band gap) transitions (with θ and Γ as given in Table I).

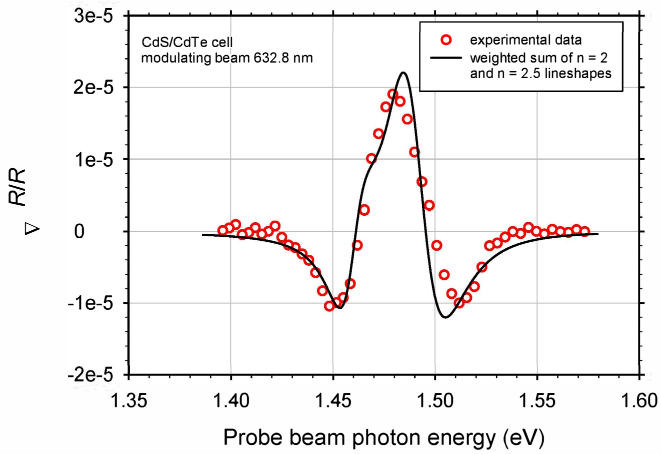
The values of these parameters are shown in Table I, case (a).

TABLE I
FITTING PARAMETERS FOR THE TWO LINESHAPES ACCOUNTING FOR THE PR SPECTRUM OF THE CDS/CDTE CELL IN FIG. 4.

Case	n	E_{cp} (eV)	θ	Γ (10^{-3} eV)
(a)	2	1.46	1.8	12
	5/2	1.49	1.7	20
(b)	5/2	1.46	5.5	20
	5/2	1.495	2.05	20

With appropriate weighting, the sum of these two lineshapes is shown in Fig. 8a, superimposed on the experimental data. Two $n = 5/2$ lineshapes yield the fit shown in Fig. 8b. The E_{cp}, θ, and Γ values for this case are shown in Table I, case (b).

(a)



(b)

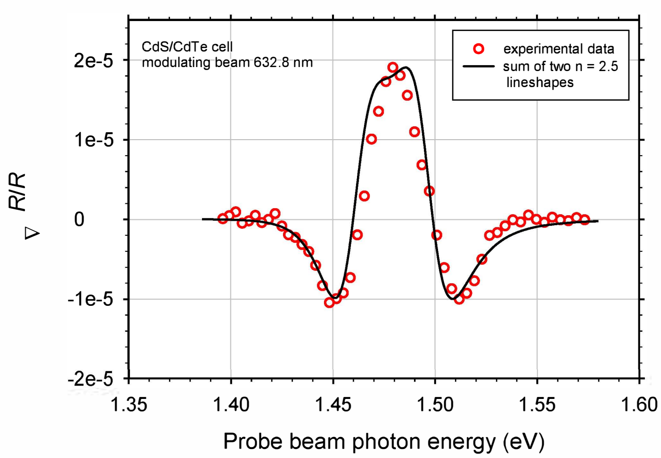


Fig. 8. Two-lineshape fits (solid lines) to experimental PR data on CdS/CdTe cell (red circles): (a) $n = 2$ and $n = 2.5$; (b) two $n = 2.5$ lineshapes.

VI. DISCUSSION

The above analysis (case (b)) shows that the bandgaps of the semiconductors responsible for the band-band transitions are 1.46 eV and 1.495 eV. The RT band gap of pure CdTe is known to be 1.51 eV [25]. The smaller gaps are those of $CdTe_{1-x}S_x$ resulting from the diffusion of sulfur from the CdS into the CdTe during the high temperature deposition of the CdTe and its subsequent treatment using $CdCl_2$. The bandgap $E_g(x)$ of the alloy $CdTe_{1-x}S_x$ may be written:

$$E_g(x) = 2.4x + 1.51(1-x) - bx(1-x) \tag{9}$$

where the bowing parameter b is generally taken to be 1.85 [17]. Hence:

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$$\Delta E_g = E_g(x) - E_g(0) = 1.85x^2 - 0.96x \qquad (10)$$

Experimentally we find ΔE_g = 1.46 – 1.51, i.e. ΔE_g = -0.05eV. Solving equation (10) to find the value of x for the $CdTe_{1-x}S_x$ alloy yields x = 0.059. Thus the test cell, prepared using a wet $CdCl_2$ treatment, contains $CdTe_{0.94}S_{0.06}$ in the active region. We previously reported evidence of such a layer from V_{oc} versus temperature measurements [17].

VII. Conclusions

PR spectroscopy was shown to be a powerful method of characterizing the surface field and alloying in thin-film solar cells. In reverse bias, the PR signal $\Delta R/R$ was shown to vary as the square of the surface field, i.e. as $F_0^2 \sim 1 - V/V_{bi}$. The presence of the mixed alloy $CdTe_{1-x}S_x$ was apparent and x = 0.06 was deduced from the relevant critical point. Explicit expressions were derived for the n = 2 and 5/2 lineshapes. A method involving a spurious signal cancellation beam was described to improve the signal/noise ratio through nulling of the PL signal. Additional measurements are planned using a single-crystal epitaxial CdTe layer.

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