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Local electrical characterization of cadmium telluride solar cells using low-energy electron beam

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ABSTRACT

We investigate local electronic properties of cadmium telluride solar cells using electron beam induced current (EBIC) measurements with patterned contacts. EBIC measurements are performed with a spatial resolution as high as ≈20 nm both on the top surface and throughout the cross-section of the device, revealing a remarkable degree of electrical inhomogeneity near the *p–n* junction and enhanced carrier collection in the vicinity of grain boundaries (GB). Simulation results of low energy EBIC suggest that the band bending near a GB is downward, with a magnitude of at least 0.2 eV for the most effective current-collecting GBs. Furthermore, we demonstrate a new approach to investigate local open-circuit voltage by applying an external bias across electrical contact with a point electron-beam injection. The length scale of the nanocontacts is on the length scale of a single or a few grains, confining current path with highly localized photo-generated carriers.

1. Introduction

Chalcogenide and chalcopyrite photovoltaic (PV) materials are attractive options for thin film solar cells due to their effective optical absorption and inexpensive fabrication processes [1,2]. Among these thin film PVs, cadmium telluride (CdTe) solar cells represent one of the most successful solar energy technologies on the market today. However, at ≈13% efficiency, commercial module performance is still well below the theoretical maximum value (≈28% under 1 sun) [2]. The underlying physical mechanisms for the discrepancy between the actual and theoretical efficiencies are presently not well understood. Grain boundaries, for example, are known to have a high concentration of defects and impurities which generally increase carrier recombination and thus adversely affect cell performance. In contrast, it has been suggested that compositional non-uniformity and/or surface states present at grain boundaries in the CdTe absorber induce a space-charge region, which can be beneficial for minority carrier collection [3,4]. The effect of grain boundaries on the open-circuit voltage (V_{oc}) is another important consideration, as V_{oc} for these materials is still well below its theoretical maximum [5,6]. Therefore, the details of how microstructure affects macroscopic performance must be addressed in order to optimize performance of PV materials comprised of a high density of grains.

Characterization techniques based on scanning probe and focused electron beams are increasingly used for investigating microstructures, compositions, and optoelectrical properties of thin film solar cells [7,8]. Electron beam induced current (EBIC) is one such method, and is frequently used to map hot carrier recombination in semiconductors by rastering an electron beam in a scanning electron microscope (SEM) while selectively collecting minority carriers using a Schottky or a *p–n* junction [9]. The EBIC contrast reflects the local efficiency of carrier collection, which is determined by local built-in and applied electric fields, as well as the carrier recombination rate. To improve the signal-to-noise ratio and decrease the effects of surface recombination, high energy beams (> 10 keV) are typically used for EBIC measurements [10].

In this work, we extend traditional EBIC measurements on photovoltaic devices in three ways: (1) use of low energy beams (< 5 keV) in order to map the photocurrent response with a spatial resolution adequate to probe the material inhomogeneity, (2) use of a patterned contact on the CdTe layer to confine the current path, and (3) application of external bias across the electrical contacts, which enables the measurement of current–voltage (*I–V*) characteristics for these confined current paths with highly

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localized photo-generated carriers. Using these techniques, we find substantial inhomogeneity in material properties within the p–n junction, and a band bending exceeding 0.2 eV near GBs which most effectively facilitate charge collection. The paper is organized as follows: in Sections 2 and 3 we describe experimental and modeling details, respectively. In Section 4, we first present low energy cross-sectional EBIC data, followed by top-down EBIC data with a patterned top contact. We then discuss simulation results, showing that the low energy EBIC signal is sensitive to the magnitude of the local electric field, and the top-down EBIC signal line-shape can be used to estimate the band bending near a grain boundary. Finally, we present I–V data obtained with a nanocontact.

2. Experimental

All measurements in this work were performed on thin film solar cell fragments extracted from a commercial solar module, consisting of p-type CdTe (≈3.5 μm)/n-type cadmium sulfide (CdS; ≈50 nm) sandwiched between two glass substrates (≈3 mm). The large module was cut into small pieces (< 3 cm × 3 cm), and the polymeric layer (ethylene vinyl acetate) was slowly peeled off a tempered glass, exposing a stack of p-CdTe/n-CdS/transparent conductive oxide (TCO) films on top of the other glass substrate. To make Ohmic contact to the p-CdTe, we either used the native metallization remaining on the surface after the extraction process or deposited platinum (Pt) contacts using a focused ion beam (FIB) with a size down to ≈0.5 μm × 0.5 μm. The second common contact to the TCO layer was made using indium solder. Electrical measurements are performed in a SEM equipped with a nano-manipulator used for placement of a tungsten probe (100 nm tip radius) on top of the contacts to p-CdTe. I–V data were collected using an external source-measuring unit, while EBIC images were obtained using a low-noise current amplifier under computer control.

3. Model details

To assist in interpreting the experimental results, we perform 2D finite element simulations. The model consists of coupled drift-diffusion and Poisson equations, with Shockley-Read-Hall recombination. The generation bulb is a Gaussian, with length scale set by the beam energy according to: $R = 0.043 \times (E_{beam}/\rho)$[g cm^{-3} keV μ$m$], where ρ is the material density. The distance between the top surface and the excitation peak is 0.3R, while the width of the excitation is $\sigma = R/\sqrt{15}$ [19].

We consider two geometries: the first is a simple p–n junction with large contacts, which we use to study the low energy cross-sectional EBIC signal (see Fig. 3a). The second geometry has a localized contact on the p-type region, a back contact on the entire length of the n-type region, and a grain boundary (see Fig. 4b). We model the grain boundary (GB) by imposing a fixed electrostatic potential difference ΔE between the neutral p-region and the GB center [17]. We vary the band bending ΔE, and the recombination velocity at the GB center S_{GB}. The model parameters are given in Table 1. The values of top surface and hole contact recombination velocity were obtained by fitting high energy EBIC data (> 10 keV) to analytic models, as in Ref. [20].

Table 1
Model parameters.

Parameter	CdS	CdTe
Layer thickness [μm]	0.12	3.6
Band gap [eV]	2	1.5
Conduction band offset [eV]	0	−0.1
Doping density [cm^{-3}]	10^{17}	10^{15}
Hole mobility [cm^2 V^{-1} s^{-1}]	320	320
Electron mobility [cm^2 V^{-1} s^{-1}]	40	40
Minority carrier lifetime [ns]	0.8	0.8
Majority (minority) carrier recombination velocity at contact [cm/s]	$10^8(10^8)$	$10^8(3 \times 10^4)$
Generation rate [cm^{-3} s^{-1}]	n/a	6×10^{24}
Top surface recombination velocity [cm/s]	1.8×10^6	1.8×10^6

4. Results and discussion

The baseline PV performance of the extracted CdTe specimens evaluated under 1000 W/m^2 (1 sun) is ≈12% efficiency, with a J_{sc} of 23.3 mA/cm^2, a V_{oc} of 820 mV, and fill factor of 64%, indicating that device properties are mainly preserved after the extraction processes. Fig. 1(a) shows an SEM image of the cell. The grain size varies from ≈0.1 μm to ≈2 μm with a peak-to-peak surface roughness of ≤0.5 μm, indicating highly inhomogeneous microstructure, typical of a polycrystalline CdTe absorber. A simultaneously collected EBIC image at 5 kV is shown in Fig. 1(b). The current is collected with a probe tip positioned on an isolated flake of the native metallization (contact area ≈5 μm × 10 μm). The bright contrast seen at many grain boundaries (GBs) indicates higher minority carrier collection for excitations at grain boundaries than at grain interiors (GIs), consistent with prior work [11]. A line scan corresponding to the EBIC signal collected for two adjacent grains is plotted in Fig. 1(c), where the current peaks (≈6 nA) at each GB and reaches a minimum (≈1 nA) at the center of the GI. As we discuss later, we use the magnitude of signal enhancement at the GB (a factor of 5 to 6) in order to estimate the band bending at these GB. The decay length of the EBIC signal is characteristic of (at least) two length scales: the space-charge depletion width and the minority carrier diffusion length. Some grain boundaries show a plateau (< 200 nm) at the peak of the EBIC current, which we attribute to the depletion width (Fig. 1c, ①). The decay of the peak EBIC signal from the GB toward the GI can be fit with a simple exponential $I_{EBIC} \approx \exp(-x/L_c)$, where L_c is an effective minority carrier diffusion length. The extracted value of L_c from the EBIC line scan is in a range of ≈100 nm to ≈800 nm.

To characterize the local response throughout the entire p–n junction region, we use a FIB to cut a cross-section through the device. The FIB process additionally results in a smoother surface compared to the native top surface, minimizing the effect of surface roughness [13]. Simultaneously obtained SEM and EBIC images on the cross-sectioned device are shown in Fig. 2(a) and (b), respectively. The magnitude and line shape of the EBIC signal near the p–n junction can be similar to that near some grain boundaries. However, the plateau width and decay length in the signal at different grain boundaries or at different positions along the p–n junction vary significantly throughout the sample.

To assist in interpreting these data, we perform two sets of simulations: the first simulation geometry is shown in Fig. 3(a), and is intended to clarify the cross-sectional EBIC data taken at low energies. At low energies, the length scale of the excitation bulb is smaller than that of the material inhomogeneity. Analytic EBIC models are derived for homogeneous materials [12], so that their application to strongly inhomogeneous materials like CdTe is not straightforward. Fig. 4 shows the simulated signals for a range of beam energies, along with the signal predicted by the commonly used EBIC models of Refs. [18,21]. For high beam energies, the analytical model agrees well with the simulation results. However, for low beam energies there are deviations between the analytic expression and the simulation, especially near the edge of depletion region. The source of this discrepancy is the approximation made in the analytic treatments that all carriers within the depletion region are collected. In fact, the collection probability for carriers within the depletion region is less than