Spatial uniformity of minority-carrier lifetime in polycrystalline CdTe solar cells

R. K. Ahrenkiel, B. M. Keyes, D. L. Levi, and K. Emery
National Renewable Energy Laboratory, Golden, Colorado 80401

T. L. Chu and S. S. Chu
Ting Chu & Associates, 12 Cuncannon Court, Dallas, Texas 75225

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Time-resolved photoluminescence was used to map recombination lifetimes in polycrystalline CdS/CdTe solar cells. Typical lifetime profiles indicated spatial variation by factors of 2–3 across 1 cm dimensions. Correlated device efficiency measurements indicated that spatial regions of lifetime minima dominated the open-circuit voltage.

Polycrystalline semiconductor thin-film solar cells have been under investigation for about 30 years; recently they have shown increasing promise for low-cost, terrestrial photovoltaic applications. Numerous groups have reported AM1.5 efficiencies exceeding 12% with devices made by several different deposition techniques. Recently, thin film devices with AM1.5 efficiencies near 16%[1,2] have been reported. Cadmium telluride (CdTe) may be the strongest candidate for flat plate modules for several reasons. As CdTe is a binary compound, stoichiometric material appears easier to produce than the competitive technology based on the ternary $CuInSe_2$. In addition, the important parameters for CdTe-based photovoltaic devices have smaller temperature coefficients. The uniformity of the films is unknown and crucial to scale-up considerations. However, several apparently inexpensive deposition techniques, including electrodeposition[3] and spray technology,[4] have been reported.

The photovoltaic (PV) characteristics of these devices are determined mainly by the microstructural and electronic properties of granules in the CdTe film. While laboratory devices are often 1 cm^2 or smaller in area, large-area devices, 10^3–10^4 cm^2, are required for modules. In consideration of the scale up required for commercial applications, the uniformity of the microstructure and electronic properties in CdTe is crucial. The relationship between open-circuit voltage and minority-carrier lifetime has been well documented.[5] In particular, the effect of low minority-carrier lifetime regions must be examined. The adverse effects of low lifetime regions may dominate the characteristics of large area devices. This work will show that the latter assumption is correct.

Standard efficiency measurements may be dominated by defective areas and are not able to detect these regions. Therefore, a nondestructive, spatially resolved measurement technique, that evaluates PV performance, is critical to detecting such defective areas. Most of the nondestructive techniques are not directly informative about device performance. The unique nondestructive technique that meets this criterion is the measurement of minority-carrier lifetime, using time-resolved photoluminescence (TRPL).[6,7] Analytical models[8] show that the open-circuit voltage is a direct function of minority-carrier lifetime.

Previous work[7] indicated a weak relationship between the minority-carrier lifetime and open-circuit voltage. In that work, the injection levels of the TRPL measurement pulses were not carefully controlled. New experimental data indicate that the relationship has been obscured by measurement artifacts, but it is indeed quite strong. This new experimental work on CdS/p-CdTe solar cells will be described in this letter.

The TRPL technique is well suited as an evaluation criterion of the uniformity of PV performance. Here, a focused laser beam (600 nm wavelength) was used to measure the local carrier lifetime and to provide a lifetime profile in CdTe films that are components of CdS/CdTe solar cells. By focusing of the incident laser beam to about a 50 μm diameter, one samples a volume as small as 5×10^{-9} cm^3. Assuming an average grain diameter of 1 μm, this measurement is an average of about 5000 individual grains. The experimental procedures and selected results are summarized in this letter.

The solar cell structure has the configuration p-CdTe/n-CdS/SnO_2:F/glass (substrate).[9,10] The p-CdTe films of 3–4 μm thickness were deposited onto CdS/SnO_2:F glass at 600 °C by the close-spaced sublimation technique.[11] The CdTe/CdS/SnO_2:F/glass structure was treated with a methanol solution of $CdCl_2$ and heated at 400 °C in an oxygen-containing atmosphere to promote grain growth and reduce grain recombination velocity.[12]

The analysis of TRPL data on single crystal material is well developed.[13] However, TRPL analysis of polycrystalline semiconductors is much more complicated due to the irregular geometries of the constituent grains. A recent article[4] used a spherical grain model with a bulk lifetime τ_B and a grain surface recombination velocity S. For small values of S ($S\ a/D<1$), the single grain photoluminescence lifetime is given by

$$\frac{1}{\tau_{\mathrm{PL}}}=\frac{1}{\tau_B}+\frac{2S}{a}, \quad (1)$$

where a is the grain radius and D is the minority-carrier diffusivity. For large values of S ($S\ a/D\gg1$), the single grain lifetime is

$$\frac{1}{\tau_{\mathrm{PL}}}=\frac{1}{\tau_B}+\frac{\pi^2D}{a^2}. \quad (2)$$

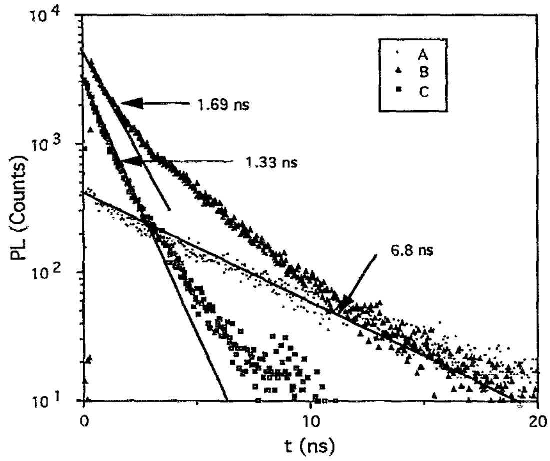

FIG. 1. TRPL decay curves for CdS/CdTe solar cell. Curves A, B, and C are data for injection levels of about 2×10^{14}, 2×10^{15}, and 2×10^{16} cm^{-3} electron-hole pairs, respectively.

Here, the lifetime is limited by the diffusion rate to the grain surface. For a distribution of grain sizes, the net lifetime will be a weighted average of the values corresponding to specific grain radii. The bulk lifetime consists of a Shockley–Read–Hall (SRH) component and a radiative component. Assuming that the injected density of electron-hole pairs is given by ρ (cm^{-3}), and the CdTe radiative coefficient is given by B, the bulk lifetime is

$$\frac{1}{\tau_B}=\frac{1}{\tau_{\mathrm{SRH}}}+2B\rho. \tag{3}$$

This formulation of the recombination lifetimes assumes that high-injection conditions concentration prevail.[13] This assumption is used when the lifetime measurements are made primarily in the depletion region of the heterojunction. Previous work has shown that in addition to recombination effects, shallow trapping is often present in these polycrystalline materials. These traps produce delayed luminescence with a rate determined by the trap emission rate. These traps tend to mask the true recombination lifetime if not properly treated during the measurement.

The effects of traps on the photoconductive decay measurement of recombination lifetimes in semiconductors has been known for many years.[14] The analysis of TRPL measurements on materials containing traps will be described in detail elsewhere.[15] In these studies, one must use care so that either the trap capture rate or the trap emission rate is not mistaken for recombination lifetime. Measurements and theory both show that determination of the recombination lifetime becomes difficult when the trap density exceeds the density of recombination centers. At smaller trap densities, the traps may be optically filled and the recombination lifetime will dominate minority-carrier decay. The experimental studies to be described here will illustrate such trap-filling techniques that are used to extract the true recombination lifetime.

The data of Fig. 1 are TRPL typical CdS/CdTe solar cell data for which the CdTe is excited through the glass and CdS window layer. The light source is an argon pumped, cavity dumped dye laser. The dye used here was Rhodamine 6G tuned to wavelengths of about 600 nm. The pulsewidth of the dye laser pulse is about 5 ps. Because minority electrons generated in the CdTe depletion region are rapidly swept out of the junction, the photoluminescence from the latter appears to be insignificant. The preponderance of light emission is likely from the quasineutral region of the p-CdTe.

This cell was found to have an open circuit voltage (V_{oc}) of 0.8457 V and a short circuit current of 15.6 mA/cm^2. The data indicate the technique used to account for the complications of trapping. In the figure, curve A is TRPL data obtained with an incident laser energy of .0625 nJ per pulse focused to approximately a 50-μm-diam spot size. Curves B and C correspond to intensity increases of 0.625 and 6.25 nJ/pulse, respectively. These three incident intensities correspond to 2.4×10^{10}, 2.4×10^{11}, and 2.4×10^{12} photons/cm^2, respectively. Assuming a 1.0 μm absorption length, the initial density of electron-hole pairs is about 2×10^{14}, 2×10^{15}, and 2×10^{16} cm^{-3}, respectively. As the CdTe is depleted of majority carriers in this region, the radiative recombination rate is probably described by high-injection conditions.

Curve A shows that the lowest incident intensity produces an exponential decay with a time constant of 6.8 ns. Studies of the TRPL lifetime indicate that this decay time increases as the temperature is lowered. Such behavior is indicative of trapping with an emission process controlling the radiative recombination rate. Curve B shows an initial fast decay (1.69 ns) followed by a decay slowing to greater than 5 ns. These data indicate initial trap filling with the PL decay being controlled by recombination. As the electron density decreases, the trap controlled emission process of curve A begins to dominate again. Finally, curve C shows trap saturation with the PL decay dominated by recombination over most of the observation range. The PL lifetime drops to 1.33 ns, probably because radiative component of Eq. (3) becomes significant at higher injection levels. The B coefficient for CdTe is unknown but is assumed to be relatively large because of the strong light emission from these films. Fitting these data with Eq. (3), one calculates the radiative component here as 6 ns and B as 2×10^{-9} $cm^{-6}\,s^{-1}$. This value is about a factor of 10 larger than the B value for GaAs. Factoring in the uncertainty in the injected carrier density for curve C, this estimate is reasonable.

At the injection levels found in one-sun solar cells ($\rho\ll1\times10^{16}$ cm^{-3}), the SRH mechanism appears to dominate the recombination lifetime. In these measurements, the lifetime is experimentally obscured by trapping effects in many devices. Many devices did not display the shallow trapping effects. In devices containing these shallow traps, sorting out the effective recombination lifetime at AM1.5, one-sun injection levels becomes difficult. In this work, the intensity dependence of the TRPL data is used to extract the recombination lifetime from trapping phenomena. The initial decay, at injection levels that saturate shallow traps, is taken to be the recombination lifetime that controls the open-circuit voltage of the device. This model will be applied to the subsequent TRPL data in this letter.

As noted earlier, spatial uniformity of response is basic to the probability of successful scale up. Figure 2 is a profile

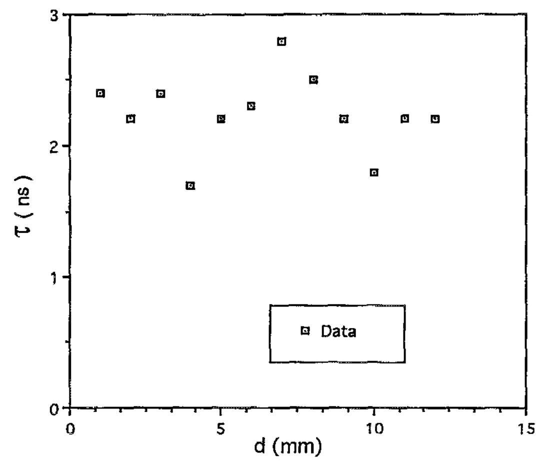

FIG. 2. Linear spatial profile of recombination lifetime across CdS/CdTe solar cell with net V_{oc} of about 848 mV.

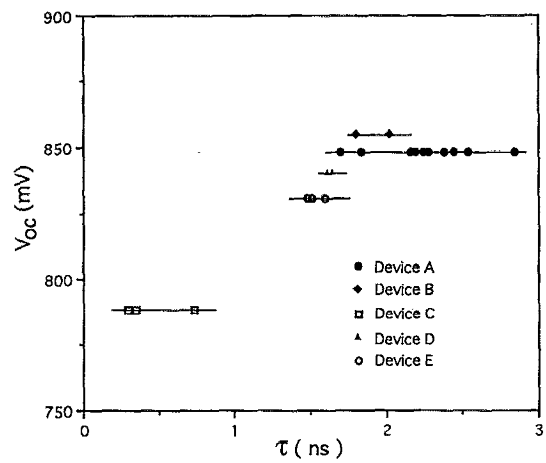

FIG. 3. Plot of V_{oc} of five CdS/CdTe devices vs sampled recombination lifetimes across the respective devices.

of the TRPL response along a 1.3 cm device. The circular data points represent the response of this device with intensities such that the traps are saturated. The recombination lifetime varies between 1.7 and 2.8 ns over this spatial scan. The trap emission lifetime varies considerably over this range but likely has little effect of PV performance. The V_{oc} of this cell is 847.9 mV and is among the better devices made here.

Figure 3 is a plot of V_{oc} of five devices (A-E) versus the measured TRPL lifetime. Lifetime profiles were measured for five devices using the TRPL technique. There was no significant relationship between the shallow trapping lifetime and V_{oc}. Device A is that for which the profile data of Fig. 2 were obtained and on which extensive measurements were made. Device B is the same as that described by the data of Fig. 1. The other devices shown had several measurements made across the active area. However, regions will either lower or higher lifetime might well exist but not have been measured. The injection level was chosen so that the traps are filled but the device is not driven into high injection. That compromise is often not easy to realize in practice.

The relationship between τ_{PL} and V_{oc} is clear from the data as one sees that the minimum lifetime of the active area controls V_{oc}. For example, device A had the largest measured lifetime (2.9 ns) but a lifetime minimum of 1.6 ns. The device V_{oc} falls below that of device B that had a measured lifetime range of 1.8 to 2.0 ns. Device E produced no lifetime regions with τ_{PL} greater than 1 ns and had the smallest measured V_{oc} of 788 mV. Device E, with lifetimes in the 1.5 ns range, had a measured V_{oc} of 830.5 mV. These data are consistent with the standard photodiode model, in which all devices are connected in parallel, to represent the various regions of the device. As the low voltage regions will determine the overall photovoltage, grain uniformity is extremely important.

There was no significant relationship between the density of shallow traps and V_{oc}. Some of the best devices had either no observable shallow traps while others had significant densities of traps. Thus, the recombination centers and the shallow trapping centers appear not to be related.

In conclusion, these data showed that V_{oc} appears to be controlled by the area with the minimum lifetime for the particular device. Using this model for a large-area polycrystalline system, lifetime uniformity is far more important than previously thought. The source of lifetime variation is unknown at this time, but is probably a function of grain morphology and surface recombination velocity.[4] The control of the lifetime uniformity of thin films will need to be a focus of future research in the maturation of this technology.

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