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Cu-related recombination in CdS/CdTe solar cells

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Abstract

Cu used in the back contact of CdS/CdTe solar cells is known to improve contact behavior and open-circuit voltage. A study of devices made with varying Cu amounts confirmed these observations. However, Cu was also found to be deleterious to current collection. Time-resolved photoluminescence measurements of CdTe devices show that carrier lifetime decreased with increased Cu concentration. Drive-level-capacitance-profiling and low-temperature photoluminescence suggest this decrease in lifetime was associated with increased recombination center density introduced by Cu in the CdTe layer. The resulting impact of increased Cu on device performance was a voltage-dependent collection of photogenerated carriers that reduced fill-factor.

Keywords: Cadmium telluride; Solar cells; Photoluminescence; Capacitance profiling

1. Introduction

High performance CdTe-based solar cells require the formation of a low-barrier, low-resistance contact, which is frequently accomplished by incorporating Cu at the back contact [1,2]. In general, the back barrier is minimized, and the open-circuit voltage (V_{oc}) is increased, with the application of an optimal amount of Cu. However, Cu can form both deep donors Cu_i and acceptors Cu_{Cd} in CdTe [3]. Substitutional Cu (Cu_{Cd}) dopes the CdTe more p-type, and interstitial Cu (Cu_i) compensates the p-CdTe. Trap levels due to deep donors caused by formation of Cu complexes in p-CdTe have been reported [3–5], but there has been no direct evidence that Cu increases recombination in CdTe solar cells. Cu diffusion is also reported to be responsible for long-term degradation [6], though recent work suggests that this can be stabilized [7]. In this study, the effect of Cu on CdTe devices was studied by systematically evaporating Cu metal of varying thickness directly onto Te-rich CdTe surfaces prior to application of Pd/Al metal back contact layers.

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2. Device fabrication

Conventional superstrate solar cell devices were fabricated at NREL by depositing 80-nm CdS and 9-μm CdTe on SnO_2:F coated glass substrates by chemical-bath deposition and close-spaced sublimation, respectively. Prior to the application of the back contact, the structures were heat treated in a vapor mixture of $CdCl_2$ and O_2. After the $CdCl_2$ treatment, all devices were etched in a nitric–phosphoric acid solution to remove surface oxides, and to create a Te-rich CdTe surface. Cu metal layers with thicknesses varying from 0 to 100 nm were then deposited by electron-beam evaporation onto unheated device structures with a deposition rate of 0.01–0.05 nm/s. The contact was then annealed in helium at 280 °C for 25 min to promote Cu diffusion. X-ray diffraction confirmed the formation of $Cu_{1.4}Te$ during this latter step. The control samples, which had no intentional Cu introduced at the back contact, underwent an identical anneal. All devices were completed by evaporating 60 nm of Pd and 300 nm of Al to form the final current carrying electrode.

3. Experimental results and discussion

Current density–voltage (J–V) curves for typical devices are shown in Fig. 1. Devices made without intentional Cu were

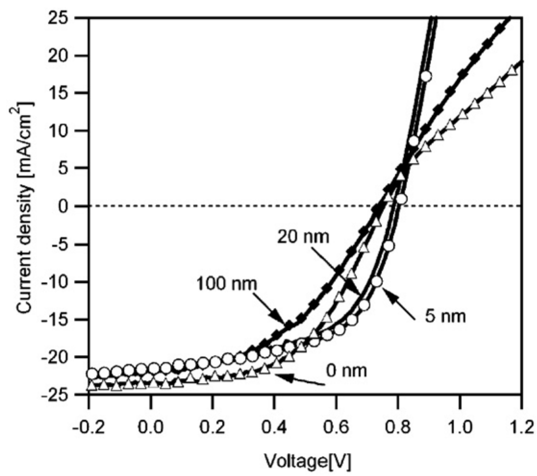

Fig. 1. Current–voltage curves for devices with different Cu amounts.

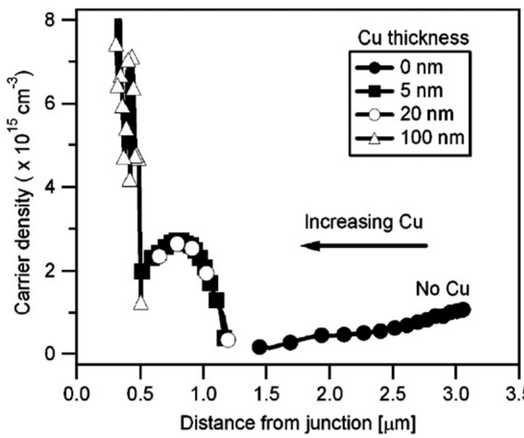

Fig. 3. Carrier density as a function of distance from the junction extracted from capacitance–voltage measurement.

characterized by low V_{oc}, high short-circuit current density (J_{sc}), and current limitation (roll-over) in the 1st quadrant (characteristic of a back contact barrier). The addition of only 5 nm of Cu improved V_{oc} by 50 mV, eliminated roll-over, but reduced J_{sc} by 1–2 mA/cm^2. Device efficiency increased moderately from 9.1 to 9.7%. Further increase in Cu above the 5 nm, "optimal" amount empirically observed for this set of devices, systematically reduced V_{oc}, fill-factor (FF), and overall performance. Lower J_{sc} values were observed for all devices using Cu relative to the Cu-free control samples.

Room-temperature photoluminescence (PL) decay curves were measured through the glass side using time-correlated single-photon counting [8]. Photoexcitation at 633 nm was provided by an optical parametric amplifier pumped by the output of a titanium:sapphire laser system with a regenerative amplifier. This wavelength has an effective penetration depth of approximately 220 nm into the CdTe. The final laser output consisted of a 250 kHz pulse train with an average power of 250 μW, a beam diameter of about 0.5 mm, and a pulse width of several hundred fs. This corresponds to peak photoexcited carrier density of about 10^{16}–10^{17} cm^{-3}. At these levels, the loss in PL caused by the separation of electrons and holes at the junction is negligible relative to the PL decay caused by Shockley–Read–Hall and interface recombination [9,10].

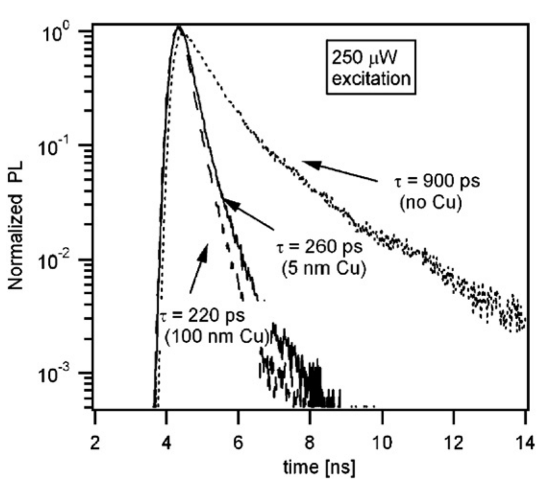

Fig. 2. Normalized time-resolved photoluminescence (TRPL) decay curves as a function of Cu thickness.

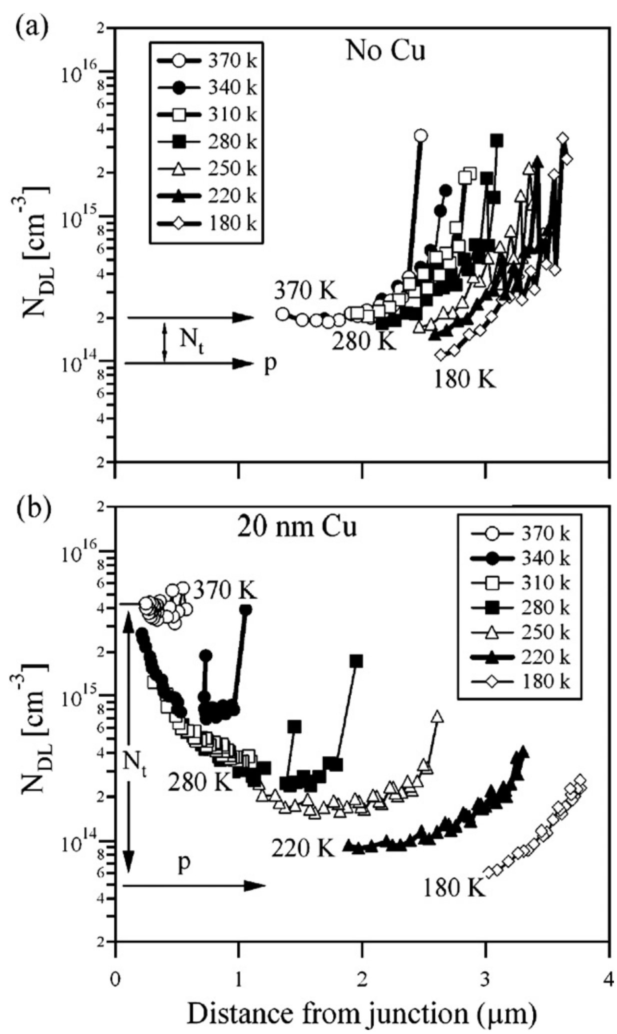

Fig. 4. Carrier density as a function of the distance from the junction estimated from DLCP measurement (p and N_t are the free carrier density and trap density, respectively). a) No Cu and b) 20 nm Cu device.

Lifetimes were determined by nonlinear least-squares iterative reconvolution of the system response with a model single exponential fit [11].

The PL decay curves for devices with different amounts of Cu are shown in Fig. 2. Increasing or decreasing (when there was sufficient signal) the injection level by an order of magnitude did not significantly affect the decay rates. As shown in Fig. 2, the time-resolved photoluminescence (TRPL) determined lifetime decreased significantly with even a 5 nm addition of Cu and then systematically decreased by small amount with further Cu additions. It should be noted that the lower lifetimes shown in Fig. 2 are somewhat smaller than what we ordinarily measure when Cu-doped graphite paste is used [10]. This may be due to the differences in Cu incorporation. In this study, Cu was introduced in simple elemental form as a distinct layer between the CdTe and the back contact and then diffused in with a heat treatment. In our standard device Cu is introduced in compound form, either as $Cu_{1.4}Te$ or as a crystalline dopant (Cu:HgTe) concurrent with graphite-paste (dag) layers [12].

The 5 nm case is particularly interesting in that a large lifetime decrease occurred simultaneously with a large increase in device V_{oc} (Fig. 1). Generally, there is a strong correlation between decreased lifetime and lower V_{oc} [10]. So in addition to the changes in lifetime, the incorporation of Cu must have other physical effects that increase V_{oc}. Carrier density as a function of distance from the junction was extracted from room-temperature capacitance–voltage (C–V) measurement taken at 100 kHz. Fig. 3 shows an increase in net carrier density and a decrease in depletion width with increased amounts of Cu. Similar trends were observed in an earlier study [2].

Drive-level-capacitance-profiling (DLCP) measurements were used to more accurately ascertain the density of traps and the spatial profiles of defect states as a function of distance from the CdS/CdTe junction. DLCP technique determines the depletion charge density in the vicinity of the location χ_e, where χ_e is the location at which $E_F - E_V = E_e$. Here E_F is the Fermi energy, E_V is the valence band edge, and E_e is the energy at which the occupation of a gap state can change just rapidly enough to follow the applied alternating bias at a given frequency [13]. In the DLCP measurements; a dc bias is applied to the device, while the amplitude of the ac probe signal (drive-level) is varied. In this fashion, the drive-level defect density, N_{DL} can be determined [13]. Spatial profiles of defect states are obtained by varying the dc bias. The activation energy for thermal emission from a deep defect can be ascertained by changing temperature or frequency, since the latter determines which gap states contribute to the capacitance. At relatively low temperature, or high frequency, the response from deep trap states is minimal, hence N_{DL} is due to free carrier density, and as temperature is increased or frequency is lowered, the value of N_{DL} increases because of the ionization of deep trap states. The difference between N_{DL} at high and low temperatures thus yields an estimate of the concentration of trapping states N_t. DLCP measurements were taken at a frequency of 20 kHz and temperature was varied from 180 K to 370 K. It should be noted that CV measurements were taken at 100 kHz. Since room-temperature capacitance–frequency curves (not shown) were nearly flat between 10–300 kHz, the effect of the difference in frequency at which CV and DLCP were taken should be minimal. Differences in DLCP measurements observed for devices without and with Cu are shown in Fig. 4a and b, respectively. An order of magnitude increase (10^{14} cm^{-3} to 10^{15} cm^{-3}) in trap state density was observed as Cu at the back contact was increased from 0 to 20 nm. In general, the defect state concentration was found to increase with the amount of Cu used. This increase in defect states was also corroborated by low-temperature photoluminescence (PL) measurements at 4.2 k that recorded a two-order-of-magnitude reduction of PL intensity as well as an additional sub-band gap peak in the presence of Cu (Fig. 5). Shallow-level defects can contribute carriers at room-temperature and hence improve device performance, while deep-level defects can enhance recombination which is detrimental to performance. The increase in deep-level trap density is a plausible explanation for the reduced lifetimes with increasing Cu concentration (Fig. 2).

Strongly reduced carrier lifetimes and depletion widths with increasing Cu had a significant effect on current collection. In Fig. 6, the external quantum efficiency (QE) measured at zero

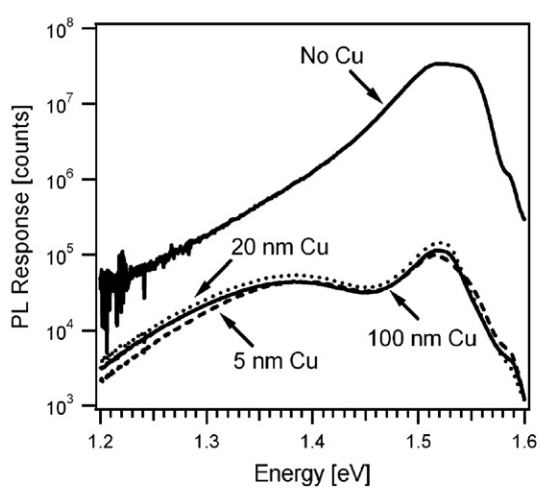

Fig. 5. Low-temperature (4.2 K) photoluminescence responses of devices made with and without Cu.

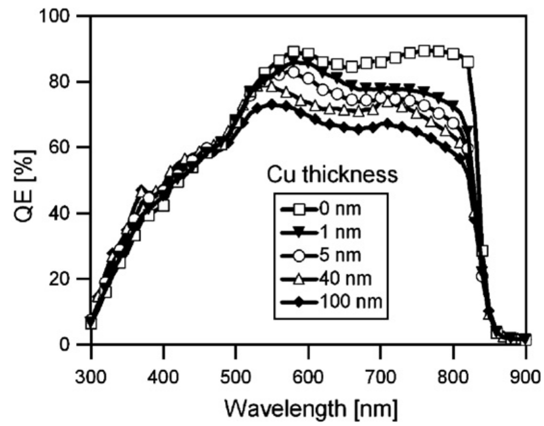

Fig. 6. QE curves as a function of Cu thickness.

bias as a function of Cu thickness is shown. The primary feature observed is the reduction in longer wavelength response with increasing Cu. In the absence of Cu, a significantly higher long-wavelength response is observed. This again strongly suggests higher recombination of photogenerated carriers in the CdTe layer when Cu-related defects are present.

The QE measured as a function of applied voltage (not shown) indicates minimal voltage-dependent spectral response for devices made without Cu, and increasing voltage dependence when Cu is increased. The observed voltage-dependent collection is consistent with the reduced fill-factor in the light J–V curve shown in Fig. 1.

The multiple effects of Cu revealed by PL, TRPL, DLCP, and C–V measurements together can describe both the J–V and QE characteristics shown in Figs. 1 and 6. From 0 to 5 nm, there is a significant decrease in the current collection because of the abrupt decrease in lifetime by traps and the reduced depletion width caused by increase in carrier concentration. This same increase in the carrier concentration resulted in increased V_{oc}. From 5 nm to 20 nm the changes were small. At 100 nm (excess Cu), FF was reduced dramatically and a current-limiting effect (roll-over) started to appear. It is possible that this is due to the formation of a rectifying contact at the back-contact layer that impedes hole transport, but this requires further systematic study.

4. Conclusions

This study clearly shows that even though small amounts of Cu (5 nm) improve performance by increasing V_{oc} and improving back barrier properties, Cu can also have a detrimental effect on current collection. Increased Cu resulted in a strong but systematic decrease in minority carrier lifetime caused by an increase in deep-level trap density. The combination of reduced lifetime and decreased space charge measured by C–V indicates a strong signature of field-assisted collection of photogenerated carriers that was corroborated by voltage-dependent QE measurements. This voltage-dependent collection effectively reduced J_{sc} and contributed to reduced fill-factors and overall reduced performance.

Acknowledgements

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