Dependence of carrier lifetime on Cu-contacting temperature and ZnTe:Cu thickness in CdS/CdTe thin film solar cells[☆]

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ABSTRACT

Cu diffusion from a ZnTe:Cu contact interface can increase the net acceptor concentration in the CdTe layer of a CdS/CdTe photovoltaic solar cell. This reduces the space-charge width (W_d) of the junction and enhances current collection and open-circuit voltage. Here we study the effect of Cu concentration in the CdTe layer on carrier lifetime (τ) using time-resolved photoluminescence measurements of ZnTe:Cu/Ti-contacted CdTe devices. Measurements show that if the ZnTe:Cu layer thickness remains constant and contact temperature is varied, τ increases significantly above its as-deposited value when the contacting temperature is in a range that has been shown to yield high-performance devices (~280° to ~320 °C). However, when the contacting temperature is maintained near an optimum value and the ZnTe:Cu thickness is varied, τ decreases with ZnTe:Cu thickness.

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1. Introduction

It is well known that Cu diffusion from the back contact of a CdS/CdTe thin film solar cell can significantly enhance device performance. It is also well known that this same Cu diffusion is often linked to device instability. Research using the ZnTe:Cu/Ti contact has enabled critical aspects of Cu diffusion to be studied using conditions that afford a high degree of process control. These studies have established that Cu diffusion from the ZnTe:Cu layer can increase the net acceptor concentration in the CdTe layer (N_A–N_D), thereby reducing the junction space-charge width (W_d). Optimum light current–voltage (LIV) performance is attained when W_d is narrow enough to produce a drift field in the CdTe absorber of sufficient strength to compensate for low values of τ, but still wide enough to limit effects of voltage-dependent collection (i.e., photocarriers should be generated primarily within the depletion region when the device is biased near the maximum power point [MPP]) [1]. Higher concentrations of Cu can produce Cu diffusion into the CdS layer that will reduce its net donor density (N_D–N_A) and also produce a manifestation of photoconductivity in this layer [2]. It is suspected that certain types of instability could be linked to similar (but longer-term) redistribution of Cu. In this investigation we use time-resolved photoluminescence (TRPL) mea-surements to study how Cu, in addition to affecting carrier density, may also affect τ.

2. Experimental

CdS/CdTe materials used in this study were produced by three different groups. The sample structures produced at NREL were 7059 Glass, CVD SnO₂:F, CVD SnO₂, Chemical Bath CdS, CSS CdTe, and Vapor CdCl₂ [3]. The second sample set was produced at Colorado State University (CSU) and utilized Tec 15 (soda lime) glass substrates and CdS, CdTe, and CdCl₂ vacuum processes consistent with CSU procedures [4]. The third set of samples incorporated Tec 15 glass, a commercial vapor transport deposition (VTD) process for the CdS and CdTe layers, and a wet CdCl₂ process. For all CdS/CdTe materials used in this study, no contact or pre-contact processes were performed prior to the application of the ZnTe:Cu/Ti contact.

The ZnTe:Cu/Ti contact was produced at NREL as follows: Samples were placed into a multi-source vacuum processing chamber and preheated for 120 min at the indicated contact deposition tempera-ture (25° to 360 °C) to achieve steady state thermal conditions. Prior to ZnTe:Cu deposition, ion-beam milling (IBM) was performed to removed CdCl₂ residue and establish a nearly stoichiometric surface. IBM was performed with a 3-cm Kaufman-type ion gun operating at a beam energy and current of 500 eV and 6 mA, respectively, using UHP-grade Ar. ZnTe:Cu layers (~9 at.% Cu) were deposited by r.f. sputter deposition to the indicated thicknesses (0.04, 0.1, 0.2, 0.5, and 1.0 μm). The sample heater was turned off following ZnTe:Cu deposition and allowed to cool to an indicated temperature of ~185 °C (except for the 25 °C contact), at which point 0.5 μm of Ti was deposited using d.c. magnetron sputtering. Several 0.25-cm² cells were defined
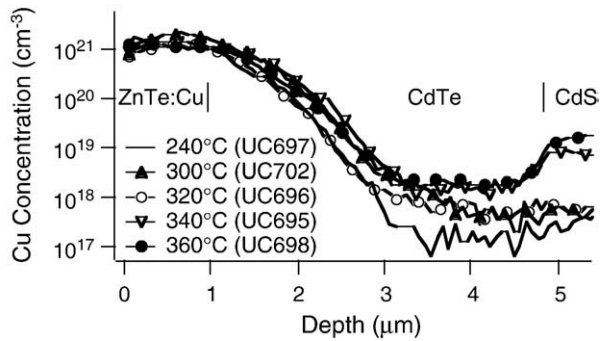
Fig. 1. Quantified SIMS depth profiles of Cu concentration in ZnTe:Cu/CdTe/CdS devices for indicated contact temperature. ZnTe:Cu thickness for all samples is 1.0 μm and analysis performed from the ZnTe:Cu side.

Fig. 3. TRPL analysis at 2.5 mW power for CdS/CdTe/ZnTe:Cu/Ti devices in which the ZnTe:Cu layers were deposited at the indicated temperature. Results are grouped to show sets of devices contacted at temperatures that produce "insufficient," "optimum," and "excessive" Cu diffusion.

photolithographically on each sample using a two-step chemical etching of TFT Ti Etchant (Transene Co. Inc., Rowley, MA) to remove the Ti, followed by an aqueous solution of 39% $FeCl_3$ to remove the ZnTe:Cu and CdTe. A perimeter contact to the SnO_2 layer was formed with soldered In.

Electrical analysis included light and dark current–voltage (LIV/DIV) measurements at room temperature using an XT-10 solar simulator adjusted to approximate Global AM1.5 current from a CdS/CdTe reference cell. Secondary ion mass spectrometry (SIMS) analysis was performed on some devices following chemical removal of the Ti layer with the TFT etchant. SIMS was performed from the contacted side of the devices using a Cameca IMS-3F instrument tuned for a mass resolution ($M/\Delta M$) of ~4000 to allow for separation of $^{63}Cu^+$ from $^{126}Te^{2+}$ species. TRPL was measured at 820 nm through the glass side of the devices using a 650-nm excitation wavelength and a beam diameter of ~1 mm at a 250 kHz rep rate. Measurements were performed at two different laser-injection intensities (0.25 and 2.5 mW average CW power) in the hope of observing and negating any effect that increasing electric field strength as a function of Cu incorporation may have on the measurement of τ. Low-temperature photoluminescence was performed at 4.25 K using an excitation wavelength of 633 nm and an average CW power of 1 mW.

3. Results and discussion

Figs. 1 and 2 show SIMS profiles confirming systematic variation in Cu diffusion into the CdTe layer due to contact temperature and Cu availability, respectively. Capacitance–voltage analysis has confirmed that CdTe net acceptor concentration (N_A–N_D) increases with both increasing contacting temperature and ZnTe:Cu thickness, while numerical simulation has linked the trends in device performance with changes in N_A–N_D [1,5]. Although compelling, this description of junction evolution during Cu contact formation does not account for reports linking Cu incorporation to τ reduction [6–8].
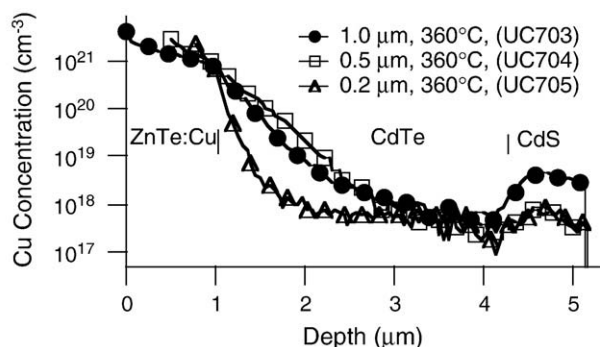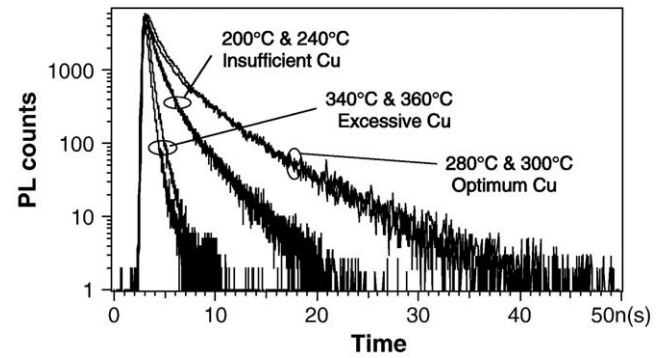

Fig. 2. Quantified SIMS depth profiles of Cu concentration in CdTe/CdS devices for indicated ZnTe:Cu thickness. Analysis performed from the ZnTe:Cu side.

The samples used to study the effect of contact temperature on τ are the same as those shown in Fig. 1. This set was produced using a commercial VTD process for the CdS and CdTe layers. Fig. 3 shows representative TRPL measurements for ZnTe:Cu contact interface layer deposition at temperatures between room temperature and 360 °C. Inspection of the PL decay curves for individual cells show that these samples demonstrate a gentle biexponential decay at 2.5 mW. At lower intensity (0.25 mW, not shown), the fast decay component makes the biexponential aspect of the decay more pronounced. Longer duration scans taken at even lower intensity (~0.07 mW, not shown) for two samples indicated a continuing decrease in lifetime with decreasing injection level (note that signal intensity becomes borderline at this injection level). This injection dependence is in contrast to that observed for cells measured at NREL with other types of contacts [6] and could be a sign of charge separation consistent with a stronger junction field in these devices relative to previously measured devices. However, trap recombination and saturation are also possible explanations.

Values of τ were calculated from biexponential fits for both the initial decay region (τ_1) and the longer-term decay (τ_2), and are shown in Table 1. The different functional forms suggest that τ_1 at 0.25 mW may be more representative of interface recombination kinetics, whereas the other τ values are more representative of bulk recombination. The results also indicate that some of these samples demonstrate very respectable lifetimes for CdTe PV devices. This is especially true at the higher injection level (2.5 mW) where the influence of junction field should be efficiently screened by the photoinjected carriers.

Trend analysis of τ with Cu diffusion (Fig. 4) shows that τ decreases slightly as the contacting temperature increases from room temperature to ~250 °C. Previous studies have shown that this temperature region yields a Cu concentration profile in the CdTe that is considered "insufficient" for high-performance devices. The most exciting result

Table 1
Measured short (τ_1) and long (τ_2) carrier lifetime at high (2.5 mW) and low (0.25 mW) power excitation for CdS/CdTe/ZnTe:Cu/Ti devices as a function of approximate temperature during contacting

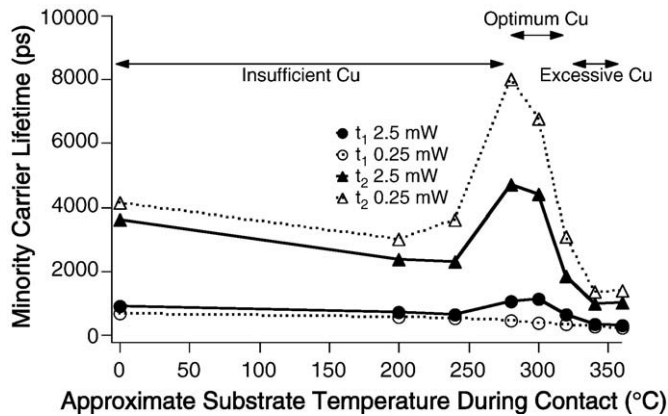| Approx. sub. temp. (°C)	τ_1 lifetime (ps)		τ_2 lifetime (ps)	
	2.5 mW	0.25 mW	0.25 mW	2.5 mW
0	897	663	4150	3620
200	704	574	2990	2360
240	651	519	3620	2280
280	1040	458	8000	4710
300	1140	364	6780	4410
320	631	328	3620	1850
340	340	268	1360	971
360	296	216	1390	998

Fig. 4. Minority carrier lifetime in the junction region of a CdS/CdTe/ZnTe:Cu/Ti device as a function of contacting temperature. Figure shows two different excitation intensities (2.5 and 0.25 mW) and fits of the fast (τ_1) and slow (τ_2) decay times. The temperature regions indicated as "Insufficient Cu," Optimum Cu," and "Excessive Cu" are consistent with those identified in Figs. 2 and 3.

of this study is observed in the contact temperature range of ∼280° to ∼320 °C, where τ is observed to increase significantly. Previous studies have shown this temperature range produces a Cu concentration profile that is "optimum" for producing high-performance devices. Finally, the figure shows that for substrate temperatures >∼300 °C, τ drops precipitously, consistent with a region previously identified as producing "excessive" Cu concentration in the CdTe, significant Cu diffusion into the CdS, and poor device performance [1]. The observed τ increase within the "optimum" temperature range not only helps explain why high-performance devices result in that temperature range for the ZnTe:Cu contact, but may suggest why other contact processes are optimized within this range. Further, the result may explain why the Cu-contact formation processes are often "forgiving" of changes in the contact process parameters (i.e., a contact process may yield a W_d that is non-optimum, but still produce a high-performance device because the longer τ will enable collection of photogenerated carriers from the lower-field regions of the junction).

The defect centers leading to the observed variation in lifetime were probed using low-temperature photoluminescence (LTPL). Fig. 5 shows that a broad luminescence peak at ∼1.4 eV emerges as the contact temperature increases from values that produce "insufficient" Cu and poor τ (25–250 °C) to "optimum" Cu and improved τ (∼280 °C). This broad peak has been assigned to a series of phonon replicas from a zero-phonon transition at 1.463 eV (i.e., 1.463 eV for VTD films, or 1.456 eV for films deposited by close-space sublimation [CSS] and crystalline material) [9]. It is believed to be associated with a defect complex involving interstitial Cu (Cu_i) and oxygen on a Te site

(O_{Te}). This peak has been observed only in devices with: a) higher Cu concentration near the front of the device, b) higher CdTe N_A–N_D, and c) higher performance. This study suggests further that the onset of the 1.463 eV peak is associated with higher τ CdTe material. As the contact temperatures increase to values that produce "excessive" Cu (360 °C), the relative intensity of the 1.463 eV peak increases still further and a peak at ∼1.53 eV emerges.

The observation that τ can increase with Cu diffusion appears to contradict existing reports that indicate τ decreases with increasing Cu diffusion into CdS/CdTe. [7,8] However, it should be noted that in these other reports, Cu incorporation into the CdTe and CdS layers was varied by changing the amount of Cu available from the contact while maintaining the diffusion temperature near its optimum value. For the study shown in Figs. 1, 3, and 4, the Cu diffusion was controlled by varying the contact temperature while maintaining a fixed amount of Cu available to the contact (i.e., the ZnTe:Cu thickness remained constant at ∼1.0 µm). Additionally, for most other types of contacts, the lowest amount of Cu that can be diffused into the CdTe is known to produce apparent quantum efficiency (AQE) under red-light bias that exceeds 100% in the CdS-absorbing region [2,7]. In contrast, the extent of Cu diffusion during the ZnTe:Cu/Ti contacting can be limited so that devices with optimum performance result, yet QE greater than expected from the CdS region does not result (i.e., Cu does not diffuse significantly into the CdS) [5,10]. A final difference is that Cu diffusion in the ZnTe:Cu contacting process occurs at a slightly higher temperature than is typical for Cu-based CdTe contacts (i.e., 280–350 °C, compared to ≤280 °C).

Considering the above results, additional TRPL measurements were performed on sample sets that more closely replicate the experimental design of the other TRPL reports, yet using the ZnTe:Cu contact. Specifically, ZnTe:Cu/Ti contacts were deposited at fixed temperature while varying the ZnTe:Cu thickness. Although some of these samples sets were produced at higher-than optimum temperature (i.e., ∼320°–360 °C), if the ZnTe:Cu/Ti contact behaved like contacts based on other Cu sources (i.e., Cu_xTe, metallic Cu, etc.), τ should decrease with ZnTeCu thickness. This study also included CdS/CdTe structures produced by several different groups to allow an investigation of how τ functionality may be affected by different materials (see Fig. 6).

The results of this second study (Fig. 5) are much more consistent with previous reports where other forms of Cu were used [6–8] and reveal a decrease in τ with increasing Cu concentration in the CdTe and CdS layers. The increase in τ for the VTD material for ZnTe:Cu thicknesses between 400–2000 Å is still being investigated. There is some evidence that trap emission related to Cu incorporation may be affecting the PL decay curves and lifetime values for the VTD samples. One should note that all values of τ within this study are relatively long compared to those resulting from non-optimum temperatures as shown in Fig. 5.
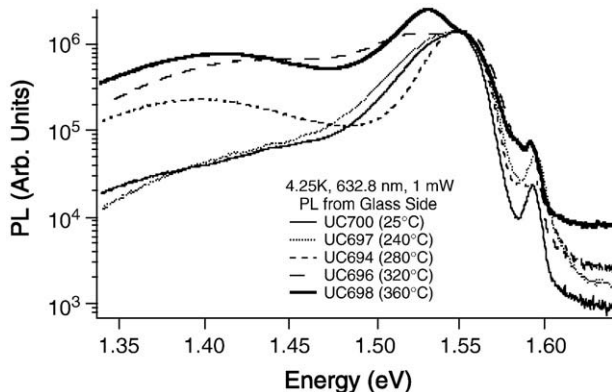

Fig. 5. Low-temperature PL showing evolution of radiative recombination as the ZnTe:Cu/Ti contact temperature increases.
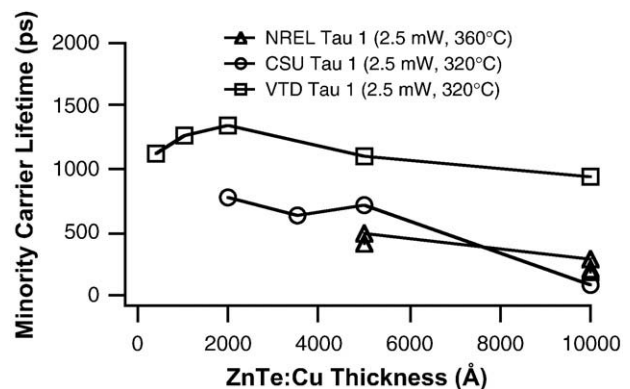

Fig. 6. TRPL analysis showing changes in τ_1 as a function of ZnTe:Cu thickness.

4. Conclusion

This study has shown that τ within the junction region of a CdS/CdTe PV device can increase or decrease during ZnTe:Cu/Ti contacting depending upon the amount of Cu that is diffused into the junction region and the temperature during this contact diffusion. These studies indicate that previous reports showing that Cu diffusion leads only to reduction in τ may not account for the fact that τ can be longer than as-deposited values when a near-optimum contact temperature is used.

Acknowledgements

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