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Role of Copper in the Performance of CdS/CdTe Solar Cells

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ROLE OF COPPER IN THE PERFORMANCE OF CdS/CdTe SOLAR CELLS *

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ABSTRACT

The performance of CdS/CdTe solar cells made with evaporated Cu as a primary back contact was studied through current-voltage (JV) at different intensities, quantum efficiency (QE) under light and voltage bias, capacitance-voltage (CV), and drive-level capacitance profiling (DLCP) measurements. The results show that while modest amounts of Cu enhance cell performance, excessive amounts degrade device quality and reduce performance. The analysis is supported with numerical simulations to reproduce and explain some of the experimental results.

Introduction

The performance of CdTe solar cells relies on the formation of a low-barrier back contact. This usually involves including Cu as a key element in the contacting process. The back-contact behavior and open-circuit voltage (V_{oc}) improve with the application of an optimal amount of Cu during the process. Unfortunately, rapid diffusion of Cu from the back contact toward the main junction is believed to contribute to degradation observed in long-term stability studies. Cu can form both deep interstitial donors Cu_i and substitutional acceptors Cu_{cd} in CdTe [1,2]. Cu can also migrate along grain boundaries toward the main junction. The standard back-contact process at NREL uses a $Cu_{1.4}Te$ and HgTe-doped graphite paste as a primary back -contact. This paste is a commercial product consisting of multiple compounds, carbon, and a polymer binder. This complexity makes it difficult to study, control, and reproduce. Nevertheless, high-efficiency, CdTe-based solar cells use similar Cu-doped graphite pastes [3,4]. In this study, the paste was replaced with a relatively simpler one in which Cu metal of varying thickness is evaporated on Te-rich CdTe surfaces. The effect of Cu on the back contact, the CdTe, and the CdS layer as it diffuses from the back - contact region toward the front of the cell are discussed.

Device fabrication

Devices were fabricated by depositing 80-nm-thick CdS and 9-μm-thick CdTe on SnO_2:F-coated glass substrates by chemical-bath deposition (CBD) and close-spaced sublimation (CSS), 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 nitric-phosphoric (NP) acid solution to remove surface oxides and to create a Te-rich CdTe surface. Cu metal of varying thickness was deposited by electron-beam evaporation, without intentional substrate heating, at deposition rates of 0.01-0.05 nm/s. The contact was then annealed in flowing helium at 280°C for 25 min to promote Cu diffusion and facilitate the formation of Cu_xTe to improve the back contact behavior. Devices were completed by evaporating 60 nm of Pd and 300 nm of Al as a current-carrying electrode.

Effect of Cu on the back contact

Cu is primarily incorporated at the back-contact layer to improve the electrical contact. The current-voltage characteristics of typical devices made with varying amounts of Cu are shown in Fig. 1.

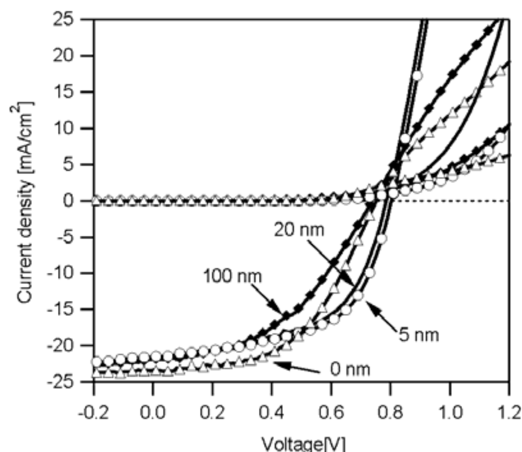

Fig. 1. JV characteristics of devices made with varying Cu amounts.

The device made with no intentional Cu and those made with excess Cu (100 nm) showed significant distortion (rollover) in their J-V curves. For devices made with optimal amounts of Cu (5-20 nm) the back-contact

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behavior is significantly improved and no distortion (rollover) is observed. JV parameters for the 5-nm Cu device are: short-circuit current density, J_{sc} = 21.5 mA/cm^2; V_{oc} = 803 mV; fill factor, FF = 57.5%; and total-area efficiency, η% = 10.0%. In general, Cu affects the back-contact behavior primarily through its series resistance. The high series resistance (low fill factors) observed in this set of devices, compared with devices completed with a Cu-doped graphite paste, could be due to excess Cu diffusion. Cu introduced in elemental form may represent a more mobile source of Cu than Cu introduced as $Cu_{1.4}Te$. The paste itself is also believed to contain ingredients that hinder Cu diffusion [5]. Interestingly, when devices made using Cu-doped paste contacts are stressed, the corresponding changes in J-V data resembles the J-V data of the unstressed devices shown in Fig. 1.

Effect of Cu on the absorber layer (CdTe)

The effects of Cu are not limited to the back-contact layer where it is deposited. Cu is known to be a fast diffuser in p-CdTe, and hence, a significant amount of Cu could be present in the CdTe layer in different forms. In the CdTe layer, Cu is known to form Cu_{Cd} acceptor state levels at about 0.12-0.3 eV from the valence band, which contributes to an increase in the carrier density [1,2]. Cu can also exist as Cu_i, which would compensate the CdTe. CV measurements, shown in Fig. 2, show that the apparent hole density in CdTe increases after the application of modest amounts of Cu (5-20 nm) at the back contact. As a result, higher V_{oc} is obtained. A further increase in Cu (100 nm) resulted in a higher apparent hole density, but a smaller depletion width and lower V_{oc}. In general, CV measurements show a wide depletion width and a low carrier density in the absence of Cu. When excess Cu is used, the depletion width becomes smaller, and thus the collection of photo-generated carriers is reduced, resulting in lower V_{oc} and FF.

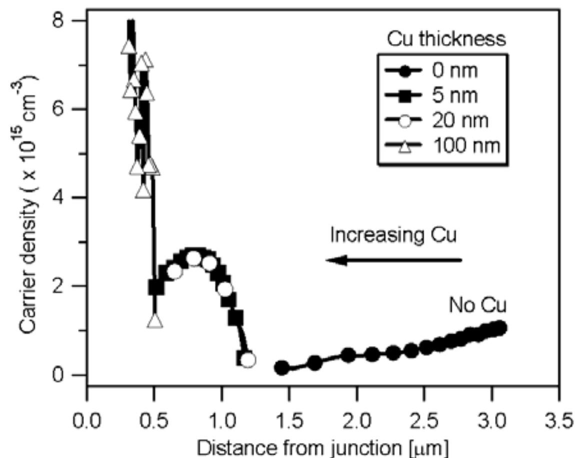

Fig. 2. Hole density as a function of distance from the junction estimated from CV measurement.

Since room temperature CV measurements may not yield the true hole density, DLCP measurements were performed to obtain a more accurate assessment of the free carrier and trap densities. In Fig. 3, the drive-level density (N_{DL}), determined as a function of the distance from the junction at different temperatures, is shown.

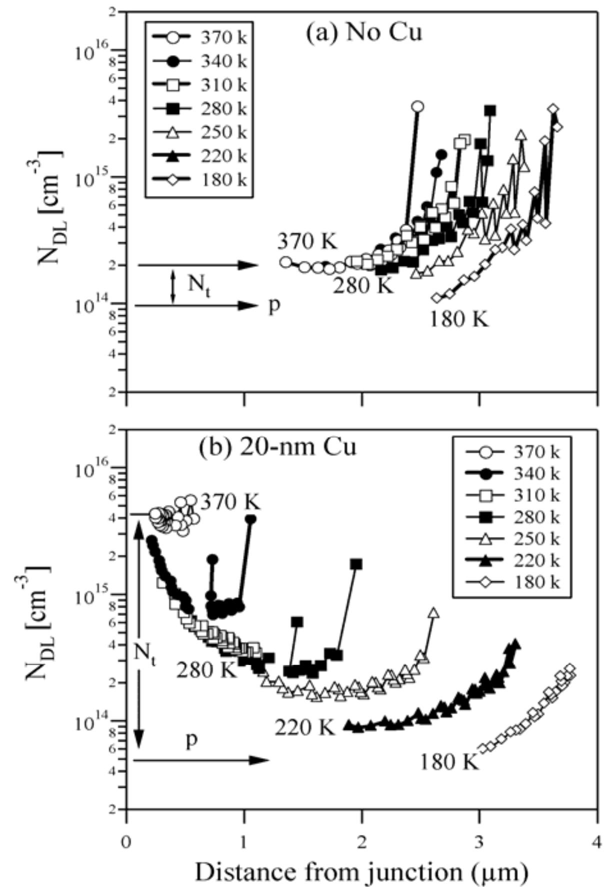

Fig. 3. Carrier density as a function of the distance from the junction estimated from DLCP measurement for a) no Cu and b) 20-nm Cu devices.

In the low-temperature limit, N_{DL} estimates the free carrier density (p), while the difference between high and low-temperature levels equals the density of trap states, N_t. It was observed that N_t, increased with increasing amount of Cu, which could explain at least partially the V_{oc} decrease with excess Cu.

JV measurements at different light intensities show apparent intensity dependence in leakage conductance. Figure 4 shows JV data at different intensities for devices made with and without Cu. All devices shown in Fig. 1 have dark shunt resistances larger than 10 kΩ-cm^2. However, under one sun illumination, the plots of dJ/dV vs. V near J_{sc} are not flat, and the upper-bound estimates of the "apparent shunt resistances" were in the range of 170-600 Ω-cm^2, dependent on the amount of Cu used. The apparent shunt resistance, R_{sh}, was found to decrease with increasing Cu thickness. It also decreased with increasing intensity. The increase in leakage conductance ($G = 1/R_{sh}$) with intensity is probably due to increased interface defect states whose occupancy is changed by the intensity of illumination.

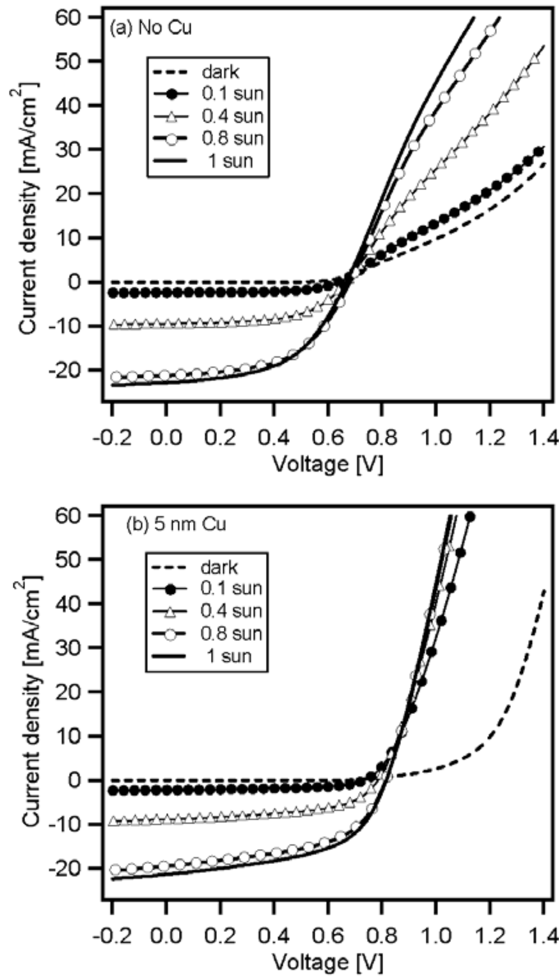

Fig. 4. JV curves as a function of illumination intensity for (a) no Cu and (b) 5-nm Cu devices.

The curved JV region below V_{mp} is a signature of a voltage-dependent collection. In Fig. 5, the QE curve as a function of applied voltage shows minimal voltage-dependent spectral response for devices made without Cu, and increasing voltage dependence when the amount of Cu was increased. This indicates that the photocurrent, obtained by integrating the QE curves over the wavelength, is voltage dependent. Defect levels in the CdTe that act as recombination centers play a major role in reducing the lifetime of photogenerated carriers. This reduces the collection of photogenerated carriers and results in a voltage-dependent collection. Time-resolved photoluminescence (TRPL) measurements on completed devices confirmed a decrease in bulk lifetime with increasing Cu concentration. AMPS-simulated JV curves [6], shown in Fig. 6, illustrate the correlation of smaller carrier lifetimes with increasing voltage-dependent collection. Current techniques for extracting JV parameters [7] without consideration of either voltage-dependent collection or spectral-dependent shunt resistance, may not yield credible results. For example, when applied to these results, these techniques predict diode quality factors larger than 3, which are not possible according to existing recombination theory.

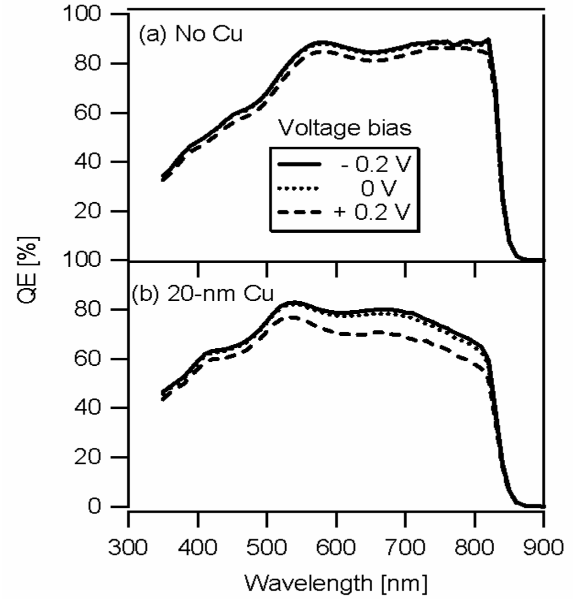

Fig. 5. QE curves as a function of voltage bias for (a) no Cu and (b) 20-nm Cu devices.

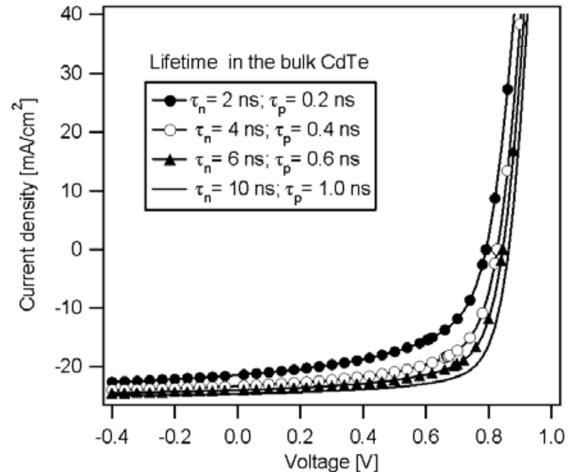

Fig. 6. Effect of lifetime on JV characteristics (simulated).

Effect of Cu on the window layer (CdS)

Cu is known to form acceptor states at about 0.34 and 1.2 eV (midgap) from the valence band in CdS [8]. The presence of these states impacts the photoconductivity of CdS. Deep acceptor states trap most of the free electrons contributed by donors, resulting in a low free-electron concentration, and hence, increased CdS resistivity in the dark. Under illumination, photons absorbed in the CdS layer increases the concentration of both free electrons and holes, increasing the conductivity of CdS. The photoconductivity of CdS is responsible for the light/dark crossover observed in devices made with Cu. In the absence of Cu, no significant crossover is seen.

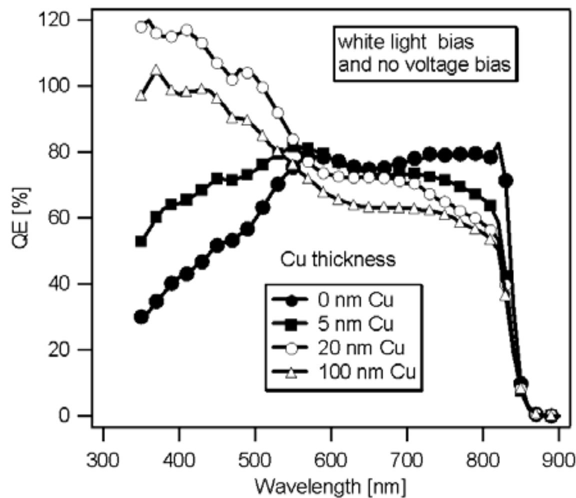

Fig. 7. QE curves under white light bias.

In the blue region (λ < 550 nm), apparent quantum efficiency (AQE) larger than unity under white-light illumination is observed in the presence of Cu, but not in the absence of Cu. A similar AQE observation under red-light illumination in CdS/CdTe solar cells has been reported [9]. The modulation of the barrier at the CdS/CdTe junction due to charge trapping by acceptor-like defect states in the CdS layer is responsible for the observed crossover and AQE effects. The impact on actual device performance, however, should be minimal.

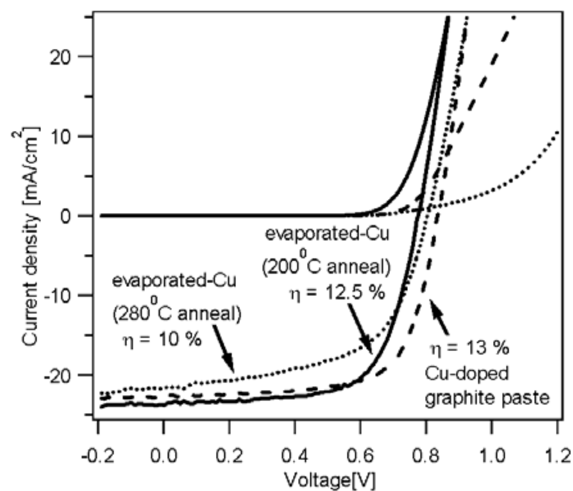

Fig. 8. Comparison of the JV curves of device with evaporated-Cu and Cu-doped graphite paste contacts.

Effect of back-contact annealing temperature

The optimum back-contact annealing temperature for our Cu-doped graphite paste contact was previously known to equal 280°C. The results from this study however show that this may be excessively high for contacts using evaporated Cu as the dopant. This was confirmed by a subsequent set of devices in which the evaporated Cu anneal temperature was reduced to 200 °C. Figure 8 compares the JV data for devices using evaporated Cu annealed at both 200°C and 280°C relative to a paste-based contact annealed at 280°C.

Conclusions

The results obtained show that Cu clearly enhances device performance, but that excess Cu can lead to significant collection losses. An optimal amount of Cu may increase the hole density of the CdTe by forming deep acceptor states. However, Cu also forms midgap defect levels that act as recombination centers, which lowers the lifetime, and consequently reduces V_{oc} and FF. The presence of Cu in the CdS layer is responsible for the dark/light crossover and apparent quantum efficiencies larger than unity. Under operating conditions (one-sun illumination), the presence of Cu in the CdS layer seems benign, but could in the extreme case contribute to an increased series resistance of the device. Though previous experience had indicated that paste contacts should be annealed at 280°C it was determined that evaporated Cu contacts required a much lower anneal temperature of 200°C. Cu in elemental form may be more mobile, relative to Cu incorporated as $Cu_{1.4}Te$ in our standard graphite paste contacts.

Acknowledgements

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