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# Copper in Contacts to CdTe

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## ABSTRACT

Cu from the back contact of a polycrystalline CdS/CdTe solar cell does more than assist in forming a low-resistance contact. In this study we use a sputtered ZnTe:Cu/Ti contact and show that the $V_{oc}$ increases from ~400 mV to >800 mV as the contact deposition temperature increases from ~200°C to ~400°C. High-resolution SIMS analysis shows very little change in Cu within the CdTe layer, yet reveals a systematic increase in Cu within the CdS layer as the deposition temperature increases. Concurrent TLM measurements of specific contact resistance of the ZnTe:Cu/Ti interface shows the fill factor is limited by resistance at this interface for deposition temperatures <~320°C.

## 1. Introduction

It is well known that most back contacts to polycrystalline CdS/CdTe solar cells contain Cu. Nevertheless, there is very little solid information regarding what function(s) the Cu performs during contacting. It has been suggested that Cu diffusion leads to the formation of a $p^+$ region near the CdTe outer surface. However, efforts to dope crystalline CdTe to the degenerate levels to enable tunneling have thus far been unsuccessful. Another possibility is that the formation of $Cu_xTe$ is important to contact formation. Although these speculations may shed light on how low resistance is achieved, they do little to explain other observations related to contact formation. These include changes in $V_{oc}$ as the amount of available Cu from the back contact is altered.

In this paper, we describe one study in which the fill factor and $V_{oc}$ of the device increase significantly as the deposition temperature of a ZnTe:Cu/Ti contact is increased from ~200°C to ~400°C. Measurements of specific contact resistance indicate that most of the fill factor increase can be attributed to changes at the metal ZnTe:Cu interface. SIMS analysis of these devices reveals an increase in Cu concentration in the CdS layer with increasing deposition temperature. To our knowledge, this is the first time that this coincident trend has been clearly identified.

## 2. Experimental

The CdS/CdTe device material used in this study was produced at First Solar LLC. The CdS and CdTe layers are deposited at ~580°C on 5-mm soda-lime glass by the close-space sublimation (CSS) process to thicknesses of ~300 nm and ~4.5 μm, respectively. Following active layer deposition, a wet $CdCl_2$ treatment was performed at First Solar similar to that described elsewhere[1]. Except where noted, all devices used in this study were cut from the same First Solar sample plate (#20746F3).

ZnTe contacting is performed by cutting a small sample (~10 cm$^2$) from the larger plate, rinsing the sample with methanol, and placing it into a multi-source vacuum deposition system. The system was pumped to ~5x10$^{-8}$ torr, after which the substrate heater (boron-nitride element) is energized at a predetermined and constant voltage. The sample is maintained at the substrate temperatures throughout contacting. The temperatures noted in this study were calibrated by placing a 0.32 cm thick Al block with an imbedded thermocouple onto the deposition platten, and allowing the block to equilibrate for 2 hours at constant heater voltage. Devices were contacted at ten different substrate temperatures ranging between ~200°C and ~400°C. Contact formation was a sequential, three-step process involving ion-beam milling the CdTe surface to a depth of ~100 nm, r.f.-sputter deposition of ~0.5 μm of ZnTe:Cu (~6 at.% Cu), and d.c.-sputter deposition of ~0.5 μm Ti. Following deposition and sample cooling, an array of individual 0.25 cm$^2$ cells are defined photolithographically on each sample. Cell definition was by chemical etching the Ti layer using TFT etchant (Transene Inc.), followed by ZnTe:Cu- and CdTe-layer etching using an aqueous solution of 39% $FeCl_3$. The front contact is formed with a perimeter of In solder around the entire array of cells (typically six cells per array).

Devices used for secondary ion mass spectroscopy (SIMS) were contacted as above, except that the Ti layer was removed prior to analysis using the TFT etchant. High-resolution SIMS was performed from the contacted side of the devices using a Cameca IMS-5F unit using 12.5 keV $O_2^+$ as the primary ion (8 keV impact energy). The instrument was tuned for a mass resolution (M/ΔM) of ~4000 to allow for separation of Cu from Te and S species.

## 3. Results and Discussion

Figures 1 and 2 show the effect of substrate temperature on device fill factor and $V_{oc}$. The effect of 80-day laboratory storage is also shown, indicating this storage does not significantly alter the light current-voltage (LIV) parameters. These devices were not subjected to accelerated stressing conditions. Figure 1 shows that the substrate temperature during contact formation has a significant effect on the fill factor. To study this dependence, contact-resistance measurements (Transfer-Length Method) were performed on Ti/ZnTe:Cu/glass samples that were deposited at the same time as the devices shown in Figure 1. This analysis revealed that the specific-contact resistance ($r_c$) at the Ti/ZnTe:Cu interface may become a significant resistance component at substrate temperatures <~320°C (i.e., >0.1 Ohm-cm$^2$), and the dominant resistance component at substrate temperatures <~290°C C (i.e., >1.1 Ohm-cm$^2$)[2].

Figure 2 shows a much more surprising result: The substrate temperature has a significant effect on the device $V_{oc}$. This observation is consistent with anecdotal evidence

from other Cu-containing contact processes and suggests that the junction region may be altered during contacting.
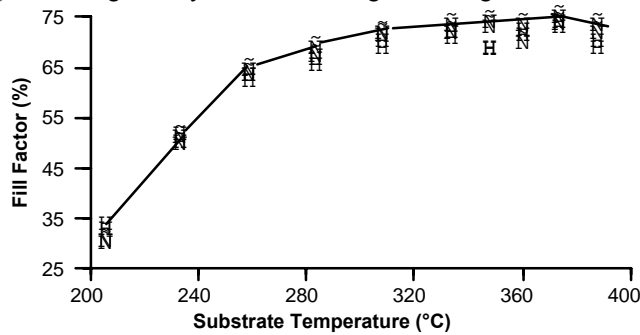


Figure 1. Fill Factor vs. substrate temperature during contact formation. Squares represent range of initial data for the 4 - 6 devices in the array of cells, and triangles represent the range of data after 80-day storage.
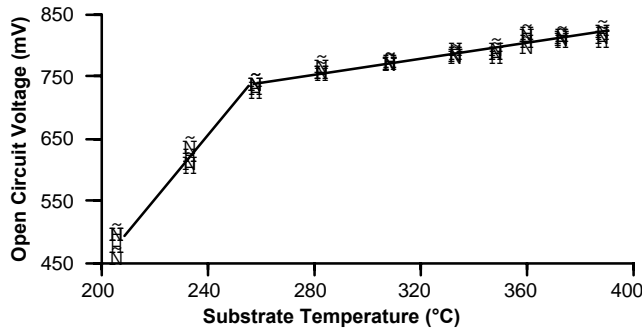


Figure 2. $V_{oc}$ vs. substrate temperature during contact formation. Squares and triangles are same as in Figure 1.

SIMS depth profiles performed at several of the heater temperatures are shown in Figure 3. These data clearly show that, although higher substrate temperatures leads to a systematic increase in Cu concentration in the region of the CdTe layer, there is a much more significant increase in the region of the CdS layer. Indeed, as shown in Figure 4, plotting the device $V_{oc}$ vs. the SIMS-measured Cu concentration in the CdS layer illustrates this coincidence.
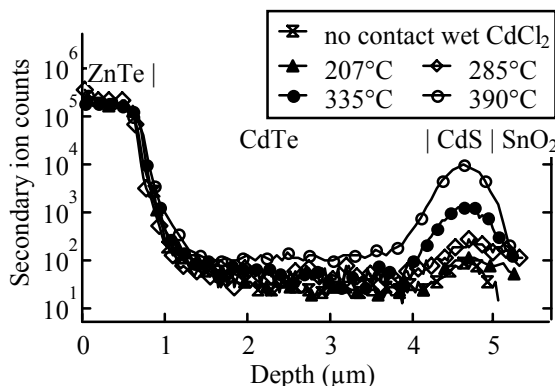


Figure 3. High-resolution, depth-profile SIMS of Cu in devices contacted at various heater temperatures. Note that the control device (with no contact) was produced using vapor-transport deposition at First Solar (#K98072435F6).

At this time, the potential effects of Cu in the CdS layer on the operation of a CdS/CdTe heterojunction are uncertain. It is acknowledged that much of the Cu observed in both the CdS and CdTe layers may reside on grain boundaries.

Unfortunately, at this time, measurement techniques do not exist that have both sufficient spatial resolution and elemental sensitivity to answer this question. It has also been reported that Cu can act as an acceptor in both crystalline CdS and in films grown by CBD[3]. Other possible causes that could relate $V_{oc}$ to substrate temperature include: effects due to the smaller, yet observable, increase in Cu concentration in the CdTe layer; temperature-related changes to defect-complex formation; changes in dopant activation or passivation; or changes at a back-contact barrier. In any event, the findings presented here suggest that one appropriate avenue for future investigations may be to study devices fabricated using Cu-doped CdS and contacted with Cu-free contacts.
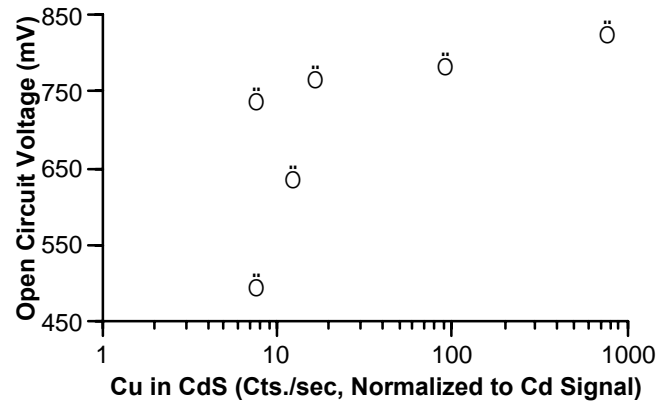


Figure 4. Device $V_{oc}$ vs. SIMS-measured Cu concentration. Data normalized to SIMS Cd signal

## 3. Conclusions

Numerous observations suggest that Cu from the back contact of a CdS/CdTe device does more than enable the formation of a low-resistance contact. Our studies reveal an increase in Cu concentration in the CdTe and CdS layers from a ZnTe:Cu contact that is coincident with a significant increase in device $V_{oc}$. The data also reveals that most of the $V_{oc}$ increase is coincident with a very small amount of Cu in the CdS. This study should be viewed as a preliminary step in understanding the role of Cu in device formation in the thin-film CdS/CdTe PV device.

## 4. Acknowledgements

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