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ZnTe:Cu Contact Optimization Strategies for Single-Junction and Multijunction CdS/CdTe PV Device Designs

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ABSTRACT

The ability to produce high-performance CdS/CdTe photovoltaic (PV) devices that incorporate high-transparency back contacts for multijunction thin-film PV applications will require an even greater level of understanding than has been required for single-junction devices. This study reports some of our initial investigations at NREL to modify the ZnTe:Cu contact process previously developed for single-junction applications for optimal use as a transparent back contact. We have succeeded in producing devices incorporating a transparent ZnTe:Cu/ITO/metal-grid contact that demonstrates nominally identical light I-V (LIV) performance to the ZnTe:Cu/Ti contact used in single-junction devices. However, we have determined that the transparent conducting oxide (TCO), CdS, CdTe, and ZnTe:Cu layers are all factors in the optical absorption within the device. Finally, we have concluded that optimizing the transparent ZnTe:Cu contact for use with NREL-produced device material will require a more detailed understanding of the evolution of the junction region during the contact process.

1. Introduction

The present direction of the NREL High-Performance task includes development of thin-film materials with bandgaps of 1.55-1.8 eV, consistent with optimum top-cell operation. It has also recently been shown that the top-cell bandgap range may decrease to ~1.45-1.50 eV if cost-effective methods to use mild concentration can be identified (~2-3X), or if improved understanding leads to lower values of reverse saturation current density (J_o) [1]. Although succeeding in any of these strategies will require significant effort, it is further realized that additional challenges relate to producing a top cell with sufficient near infrared (NIR) transparency for efficient bottom-cell operation.

Many of the issues limiting top-cell NIR transparency are related to the back contact. Although several transparent contact alternatives have been suggested, including shorting junctions with n-type materials and the use of p-type TCOs, the only option that has produced reasonable cell performance thus far incorporates a ZnTe:Cu contact interface. For this contact, our present understanding suggests that low resistance transport at the CdTe/ZnTe:Cu interface occurs because the valance bands are aligned (i.e., the formation of a Cu_xTe layer or significant doping of the CdTe are not required), whereas transport at the ZnTe:Cu/metal outer interface is by tunneling. (Unlike the CdTe, the ZnTe:Cu doping is assumed to be degenerate.) However, even in this case, the effect(s) that the contact process has on junction formation is not well established. Therefore, a clear understanding of how modifications to the contact (which are intended to optimize NIR transparency) affect device performance is also not established. Nevertheless, we have found that efforts to produce transparent devices have provided some new insight into contact formation, and both one-junction and multi-junction devices may ultimately benefit from this enhanced understanding.

With regard to development of transparent CdS/CdTe top cells for use in mechanically stacked two-junction PV devices, many of the issues related to NIR transmission were identified ~15 years ago [2]. At that time, researchers at Ametek and IEC concluded that the main problem with high-performance tandem device operation was transmission through the top cell. It was further concluded that the ZnTe:Cu contact interface was a significant region of absorption, and that the optical properties of this material would require further development. As this present work will outline, even though we now have a better understanding of the material properties of the ZnTe:Cu contact interface layer, concerns about NIR optical transmission remain. Further, the extent to which we can minimize these optical issues will be closely linked to knowledge of how contact and junction formation are associated, and how they both affect ultimate device performance.

2. Experimental

CdS/CdTe materials used in this investigation were produced by both First Solar and NREL. For First Solar material (Run ID #20746), both CdS and CdTe layers were deposited by close-spaced sublimation (CSS) at ~580°C onto 5-mm-thick soda-lime glass to nominal thicknesses of ~300 nm and ~4.5 µm, respectively. This was followed by a wet $CdCl_2$ treatment at First Solar. Previous development of the NREL ZnTe:Cu/Ti contact on this type material has produced devices with open-circuit voltage (V_{oc}) of ~820 mV, fill factors of 76%, and device efficiency of ~10%-11% (performance is limited primarily by low current density due to thick CdS) [3]. The NREL CdS/CdTe device material utilized 1-mm thick 7059 glass substrates, a 450 nm SnO_2 bilayer formed by CVD of tetramethyltin and oxygen, ~100 nm thick CdS formed by chemical bath deposition, CdTe deposition [4]. CdTe thicknesses for NREL material were 4, 5, 6, 7, 8 and 10 µm. Representative efficiencies for the NREL devices (with 8-µm thick CdTe and a graphite-paste contact) were 11-12%.

The ZnTeCu back contact was produced using a sequential process involving 2-hr temperature equilibration at ~350°C, ion-beam milling the CdTe surface to a depth of ~100 nm, and r.f.-sputter deposition of ~0.4 µm of ZnTe:Cu (~6 at.% Cu) [3]. The ZnTe:Cu was contacted with either 0.5 µm of d.c.-sputter-deposited Ti (as the sample cooled from ~300° to 100°C), or with ~0.2 µm of d.c.-sputter-deposited ITO (at room temperature).

3. Results and Discussion

Prior to working with ZnTe:Cu-contacted devices, the optical properties of NREL-produced devices contacted

with the NREL graphite-paste contact were studied. Optical measurements indicated that after the HgTe:Cu and Ag layers were removed, these devices demonstrated essentially zero transmission at energies less than the CdTe bandgap. This was expected because it is known that the precontact chemical etch step (nitric acid/phosphoric acid) used in this graphite-paste contact process forms an optically thick Te layer on the back surface and into the bulk along near-surface grain boundaries [5]. Because the optical bandgap of Te is very small, very little light is expected to be transmitted.

Initial efforts to measure the optical characteristics of ZnTe:Cu-contacted devices utilized First Solar material contacted with ZnTe:Cu and a continuous layer of 500 nm of Ti. To allow for transparent operation, these devices were processed further using subtractive photolithography and a selective chemical etch (Transene TFT etchant) to form an "etched back" metallization pattern of 0.5-µm-thick Ti grids on the ZnTe:Cu-contact interface layer (grid area = 0.1 cm^2). In this design, the ZnTe:Cu layer acts as both the contact interface and lateral conduction layer.

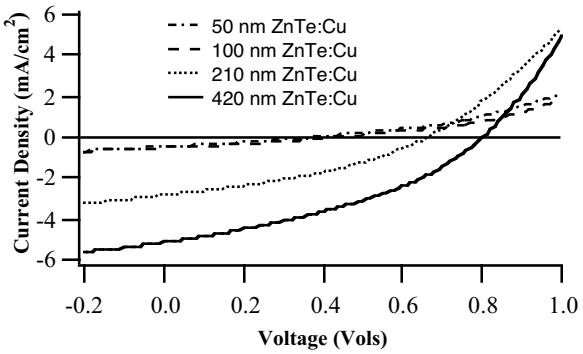

Figure 1. LIV characteristics of CdS/CdTe devices with a ZnTe:Cu contact interface and "etched-back" Ti grids.

As shown in Figure 1, the LIV characteristics of these initial devices is highly dependent on the thickness of the ZnTe:Cu layer, and the devices with the highest fill factor were produced using the thickest ZnTe:Cu layer investigated (~420 nm). These devices demonstrated a maximum efficiency of ~3%, and the LIV characteristic suggested that performance remained limited by series resistance. This was expected, because earlier studies had indicated that although the resistivity of ZnTe:Cu can be as low as ~10^{-1} Ohm-cm when deposited onto glass at 350°C, the ZnTe:Cu resistivity increases many orders of magnitude (to ~10^6 Ohm-cm) when deposited at similar temperatures onto CdTe material [6].

To test if ZnTe:Cu lateral resistance was indeed impacting series resistance significantly, a ~220-nm-thick layer of r.f.-sputtered ITO was deposited onto the top of the Ti grid structure for the device incorporating 420 nm of ZnTe:Cu. This ITO layer was optimized for high optical transparency and low resistivity, whereas the thickness was chosen to assist with antireflection of the NIR radiation at back surface. Further, because the ITO layer was relatively thin and demonstrated reasonably high mobility with moderate carrier concentration (~30 cm^2/V-sec, $4x10^{20}$ cm^{-3}, respectively), free-carrier absorption due to this layer was not expected to be a significant concern. As shown in Figure 2, the ITO layer improved the device fill factor such that the J_{sc} was no longer impacted by high series resistance (fill factor increased to ~45%) and produced devices with efficiencies of ~6%.

Although the performance improvement enabled by the ITO layer was encouraging, the more important result was evidence that the ZnTe:Cu/ITO interface was operating as a low-resistance shorting junction (this is the only way that the fill factor could improve significantly). Although this result is a critical step forward in our ability to optimize this device for tandem operation, the mechanisms of current transfer at the ZnTe:Cu/ITO interface remain poorly understood, and studies are being designed to investigate the process further.

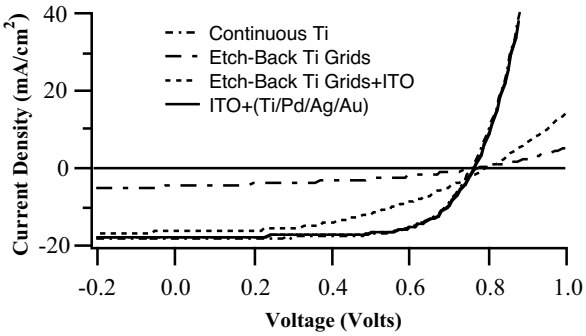

Figure 2. Light current voltage characteristics of First Solar material contacted with the NREL ZnTe:Cu contact (420 nm thick) and various finishing processes to test transparent operation.

Notwithstanding the success of the above experiments, the fill factor of the structure with etched-back Ti grids and ITO (~45%) remained much lower than that measured on the reference device with a continuous Ti outer contact layer (~70%). To investigate if the remaining series resistance could be reduced, a second device design was conceived. This design would test if either/or the cell-to-grid contact or the grid-metal resistance was dominating the series resistance. For this study, devices that were nominally identical to the already discussed First Solar material and contacted previously with ZnTe:Cu/Ti were used. However, instead of forming 0.5-µm-thick Ti grids from the 0.5-µm-thick continuous layer of Ti, the Ti layer was removed completely using the Ti etch, and a ~240 nm of ITO was deposited. Next, a 0.41 cm^2 metallization pattern was formed onto the ITO using a shadow mask (the grid pattern was identical to that used for the CIS bottom cell on which this type of top cell will be placed). The grid metallization was a contact stack of electron-beam-evaporated Ti/Pd/Ag/Au (50 nm/60 nm/1 µm/60 nm), and therefore was much thicker than the Ti metallization used in the initial cell design. This structure (LIV shown in Figure 2) produced an efficiency of 8.9%, as measured under standard conditions, with fill factors of ~65%. As also shown in Figure 2, the LIV of the transparent CdS/CdTe/ZnTe:Cu/ITO/metal-grid device was very similar to the nominally identical reference device that incorporated an outer contact of continuous Ti.

The above results indicate that we have identified a pathway to produce a transparent top cell with nominally identical performance to a nontransparent devices. With this technology "in hand," the next step was to study the extent of NIR transparency resulting from the particular device materials and contacting process used. To this end,

optical studies were performed after the various steps used in producing the above devices. Figure 3 shows that the NIR transparency of the completed devices is ~30% – significantly lower than required for reasonable two-junction operation. These results are similar to the earlier Ametek/IEC results [2].

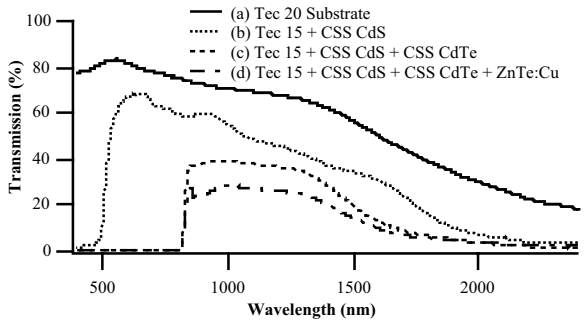

Figure 3. Transmission characteristics of CdS/CdTe/ZnTe:Cu/ITO/metal-grid device showing various processing stages; (a) LOF Tec 20 superstrate on 3 m glass. (b) CSS CdS (First Solar) on substrate similar to that shown in (a). (c) CSS CdS/CdTe (First Solar) on LOF Tec. 15. (d) NREL ZnTe:Cu on First Solar CSS CdS/CdTe shown in (c).

As seen in Figure 3, much of the loss between 850-1400 nm is due to the type of TCO used for the substrate incorporated into the First Solar material (note that NIR loss is not a central issue for single-junction devices). As will be discussed, efforts have begun to use NREL CdS/CdTe devices that incorporate a TCO with much higher NIR transparency (due to higher mobility and lower carrier concentration), and we believe this absorption component will be reduced significantly. A second component of NIR absorption can be traced to the CdS layer. We expect this absorption also will be reduced when NREL device material is used because the NREL CdS layer is thinner (~100 nm compared to ~300 nm). The CdTe layer produces noticeable absorption, and efforts are under way to identify the origin of this. Finally, it is noted that absorption in the ZnTe:Cu layer is also high. This was somewhat unexpected, because, unlike some thin-film ZnTe:Cu layers that we have observed, the NREL-produced ZnTe:Cu layers used for this study demonstrate a carrier concentration of ~$1x10^{20}$ cm^{-3} (and so the plasma frequency should be farther into the NIR) and had been optimized to be visually transparent, consistent with a bandgap of ~2.26 eV.

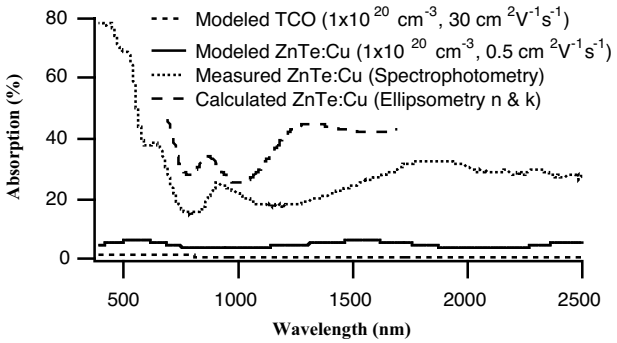

Figure 4. Measured and modeled absorption of ZnTe:Cu compared to modeled absorption of a typical TCO.

We considered that the high-NIR absorption in the ZnTe:Cu may be linked to the relatively small carrier mobility (≤~1 cm^2/V-sec). This is because the low mobility will broaden the plasma absorption signal significantly more than observed for a typical TCO (with mobility ≥ 20 cm^2/V-sec). However, as shown in Figure 4, efforts to model this effect for ZnTe:Cu using measured values of the required parameters [i.e., effective mass (0.35 m_e), high-frequency dielectric permittivity (8.2), hole concentration ($1x10^{20}$ cm^{-2}), and hole mobility (0.5 cm^2/V-sec)] [7] have suggested that the absorption measured with both spectrophotometry, as well as the calculated from the n and k values measured using spectrophopic ellipsometry, cannot be accounted for by free carrier absorption alone.

To minimize this absorption, one may consider using a thinner layer of ZnTe:Cu (because the low-resistance lateral current flow is enabled primary by the ITO layer). Unfortunately, and as supported by the LIV performance shown in Figure 1, previous studies have found that, even when a continuous Ti layer is used, the device cannot be optimized unless the ZnTe:Cu layer is at least ~400 nm thick [3]. The reason for this appears to be linked to the fact that a sufficient amount of Cu must be available from the contact to diffuse into the CdTe during the 350°C contacting process to enable adequate junction formation. Once this process is better understood, it may be possible to use much thinner ZnTe:Cu layers (or to eliminate the layer entirely!) to improve NIR transmission. In lieu of this understanding, we have recently had some success using ion-beam milling to remove some of the ZnTe:Cu layer prior to depositing the outer-contact layers (i.e., the ITO and metal grid). However, we have not yet established if the optical quality of the ZnTe:Cu is altered following ion-beam milling.

As suggested in the preceding discussion, we believe that several of the NIR absorption issues may be minimized by the use of NREL CdS/CdTe devices as compared to First Solar material (N.B. The First Solar material was optimized for criteria different than transparent top cell operation). To begin these studies, a set of NREL CdS/CdTe device structures were prepared with thickness ranging from 4-10 µm. These devices represent of new study area to the NREL activity because only devices with CdTe thickness of 8-10 µm have been optimized with the NREL graphite-paste contact process. Therefore, it is not known if the vapor $CdCl_2$ process used for this set of NREL devices is appropriate for all CdTe thicknesses. Nevertheless, initial results from studies in which these NREL devices were completed with ZnTe:Cu/Ti reveal some interesting results.

LIV results show that all the NREL material contacted with the ZnTe:Cu/Ti contact have much lower shunt resistance than the First Solar reference device (e.g., the shunt resistance for the First Solar reference device shown in Figure 5 is ~$4.5x10^7$ Ohm-cm^2, whereas the highest shunt resistance for any of the NREL devices is ~$3.5\ x10^3$ Ohm-cm^2). Furthermore, Figure 5 shows that the devices processed on 4–5-µm-thick CdTe suffer from severely low shunt resistance. This is an interesting result because the CdTe layer of the First Solar material that demonstrates high shunt resistance is also approximately 4 µm. The fact that the $CdCl_2$ process for the NREL devices has not been optimized for the thinner CdTe layers may explain some of these observations. Additionally, it also can be concluded

that either the NREL CdTe processes produce material that demonstrates lower shunt resistance, or the NREL material is more susceptible to diffusion from the contact – or both.

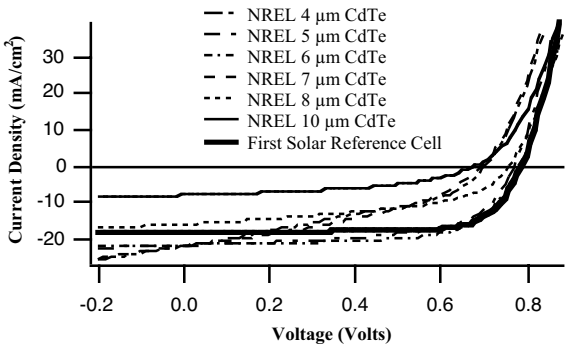

Figure 5. LIV characteristics comparing NREL CdS/CdTe material contacted with the ZnTe:Cu/Ti contact. Characteristic of First Solar device contacted in same deposition run is also shown.

A potentially much more insightful result from the NREL devices concerns how the contacting process affects junction formation. Figure 5 shows that significant voltage-dependent collection is observed for cells produced on CdTe layers that are 8 and 10 μm thick. Efforts are ongoing to understand this observation (including voltage-dependent quantum efficiency and capacitive-voltage measurements). Preliminary analysis indicates that the depletion width at zero bias is much deeper (by as much as ~2-3 μm farther from the CdSCdTe interface) for devices processed using the thicker CdTe layers. This may imply that, prior to sufficient diffusion from the contact, the depletion width is too large (i.e., the electric field is too small) to compensate for the (short) minority carrier lifetime resulting near the junction. Note that, for devices with these thick CdTe layers (8 and 10 μm), it is possible that very little diffusion from the contact has reached to the junction region because the process was optimized for a CdTe thickness of ~4 μm. This proposed scenario that the device performance improves if additional diffusion from the contact decrease the depletion width (increase the electric field), and/or if contact diffusion increases the minority-carrier lifetime. Presently efforts are underway to study both the diffusion from the contact on these thicker devices (using SIMS) and differences in the depth-dependent luminescence (using cross-sectional spectroscopic cathodoluminescense). These analyses may help determine if changes in the recombination processes can be correlated to impurity diffusion, and ultimately with device performance.

3. Conclusions

Understanding what happens within a CdS/CdTe device during various contact processes is critical to understanding not only device performance and stability, but also to identifying design options for producing transparent contacts for multijunction PV device designs. This study has confirmed previous results indicating that the ZnTe:Cu thickness must be optimized to produce high-performance devices. Unfortunately, the thickness of the ZnTe:Cu layer required for optimum LIV performance severely limits the NIR transparency of the device. Efforts are ongoing to determine if ion-beam milling can be used to remove most of the ZnTe:Cu layer prior to the application of the outer contact layers (i.e., the ITO and the metal grid). We believe this engineering solution may limit the NIR absorption in the ZnTe:Cu layer while retaining the (albeit poorly understood) benefits linked to diffusion from the ZnTe:Cu contact interface. We have also determined that NIR losses associated with the front TCO and CdS layers should be reduced significantly by using a ZnTe:Cu-based contact on NREL CdS/CdTe device material. However, initial studies indicate that the ZnTe:Cu contact process produces very different results on the NREL and First Solar materials, and further work will be required before the benefits of the ZnTe:Cu contact can be exploited fully on the NREL material.

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REFERENCES

[1] T. Coutts, J. Ward, D. Young, K. Emery, T. Gessert, R. Noufi, To be pub. Prog. Photovolt: Res. Appl.

[2] P. Meyers, C. Liu, L. Russell, V. Ramanathan, R. Birkmire, B. McCandless, and J. Phillips, Proceedings of the 20th IEEE PV Specialists Conf., September 26-30, Las Vegas, NV, pp1448-1450.

[3] T.A. Gessert, M.J. Romero, S. Johnston, B. Keyes, and P. Dippo. Spectroscopic Cathodolumiescence Studies of the ZnTe:Cu Contact for CdS/CdTe Solar Cells, Proceedings of the 29th IEEE PV Specialists Conf., May 20-25, 2002, New Orleans, LA.

[4] D. Rose, F. Hasoon, R. Dhere, D. Albin, R. Ribelin, X. Li, Y Mahathongdy, T. Gessert, and P. Sheldon, Prog. Photovolt: Res. Appl. **7**, 3312-340 (1999).

[5] X. Li, D.W. Niles, F.S. Hasoon, R.J. Matson, and P. Sheldon, *J. Vac. Sci. Technol. A* **17** (3), 805 (1999).

[6] T. Gessert, A. Duda, S. Asher, C. Narayanswamy, and D. Rose, Proceedings of the 28th IEEE PV Specialists Conf., Sept 15-22, 2000, Anchorage, AK pp. 645-657.

[7] T. Gessert, A. Mason, P. Sheldon, A. Swartlander, D. Niles, and T. Coutts, J. Vac. Sci. Technol. A 14 (3) 806-812 (1996).

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