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*Presented at the National Center for
Photovoltaics Program Review Meeting
Denver, Colorado
September 8-11, 1998*



National Renewable Energy Laboratory
1617 Cole Boulevard
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A national laboratory of the U.S. Department of Energy
Managed by Midwest Research Institute
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under contract No. DE-AC36-83CH10093

Work performed under task number PV904201

October 1998

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Analysis of Cu Diffusion in ZnTe-Based Contacts for Thin-Film CdS/CdTe Solar Cells

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Abstract. Ohmic contacts to thin-film CdS/CdTe photovoltaic devices have been formed using a two-layer contact interface of undoped ZnTe (ZnTe) and Cu-doped ZnTe (ZnTe:Cu), followed by Ni or Ti as an outer metallization. Secondary ion mass spectroscopy (SIMS) is used to study Cu diffusion within this back-contact structure, and also, to monitor Cu diffusion from the contact into the CdTe. When Ni metallization is used, the ZnTe:Cu layer becomes increasingly depleted of Cu, and Ni diffusion into the ZnTe:Cu increases as the contact deposition temperature increases from 100°C to 300°C. Cu depletion is not observed when Ni is replaced with Ti. Diffusion of Cu from the ZnTe:Cu layer into the ZnTe layer also increases with contact deposition temperature, and produces a buildup of Cu at the ZnTe/CdTe interface. High-mass resolution SIMS indicates that, although Cu levels in the CdTe remain low, Cu diffusion from the contact proceeds into the CdTe layer and toward the CdTe/CdS junction region.

INTRODUCTION

Photovoltaic (PV) solar cells based on thin-film CdTe are leading candidates for large-scale manufacturing (1). However, to realize the full potential of this technology, mass-production methods to produce stable and low-resistance electrical contacts to p-CdTe must be demonstrated. Forming low-resistance ohmic contacts to p-type CdTe is difficult for several reasons. First, no metals have a work function large enough to produce an ohmic contact to p-CdTe (2). Moreover, studies suggest that the surface Fermi level is pinned, limiting the extent to which CdTe will obey Mott-Schottky theory. Finally, acceptor compensation in p-CdTe results in low doping efficiency, limiting the effectiveness of contacts that must rely on quantum-mechanical tunneling. Even though these limitations present considerable obstacles to forming ohmic contacts, reasonable cell efficiencies have been obtained using a variety of contacts such as Au/Cu metal films (3) or graphite paste doped with HgTe and Cu (4).

Another contacting technique incorporates an interfacial layer between the p-type CdTe and a metal contact. The interfacial layer must provide both a negligibly small valence-band discontinuity with p-CdTe and enable high p-type doping to facilitate low-resistance quantum-mechanical tunneling. ZnTe is a recognized candidate for such an interfacial layer. Studies on crystalline materials have indicated small valence-band offsets for ZnTe/CdTe (5), and p-type doping of polycrystalline ZnTe with Cu has been demonstrated to $>10^{18} \text{ cm}^{-3}$ (6). Although ZnTe contacts have demonstrated reasonable success and stability (7), the use of Cu in back contacts of CdTe/CdS thin-film devices has been a subject of considerable debate. Cu has been linked to enhanced device performance by reducing series resistance and increasing open-circuit voltage.

However, Cu is also known to be a fast diffuser in most materials and will diffuse even more quickly along the polycrystalline grain boundaries. For these reasons, Cu-containing contacts have been associated with various types of instability in CdTe devices (8). In the following study, SIMS is used to assess variations in Cu concentration in the ZnTe and CdTe layers. These results are linked to device-performance characteristics typically observed when the ZnTe bilayer contact is used.

EXPERIMENTAL

The CdS/CdTe devices used for this study were grown using close-spaced sublimation (CSS) on 4.5-mm-thick soda-lime glass at Solar Cells Inc. (SCI, Toledo, OH). All the samples were treated with CdCl₂ using a wet process at SCI. Except where noted, the CdTe surfaces were chemically etched with 1 HNO₃ : 85 H₃PO₄ : 33 H₂O, for 15 s (NP etch), and the deposition temperature was maintained at ~300°C. ZnTe and ZnTe:Cu contact interface layers were deposited sequentially using r.f. magnetron sputtering. The outer metallization was deposited using d.c. magnetron sputtering to a thickness of ~0.5 μm. Additional experimental details are provided elsewhere (7). Two different contact metals, Ni and Ti, were studied. Following contact deposition, several 0.25-cm² devices were fabricated on each substrate using photolithography and chemical etching. Ni-metallized devices were patterned using a 39% FeCl₃ aqueous solution to remove the unwanted Ni, ZnTe:Cu, ZnTe, and CdTe layers in one ~3-min etching step. For Ti-metallized devices, the Ti layer was removed first with “TFT Ti Etchant” (Transene Co., Inc.), followed by the 39% FeCl₃ solution to remove the ZnTe, ZnTe:Cu, and CdTe layers. Devices were characterized using light current-voltage (I-V) measurements prior to SIMS analysis.

Earlier SIMS analysis indicated that non-uniform sputtering of the contact metallization reduced depth resolution significantly in the underlying ZnTe and CdTe layers. To avoid this problem, the Ni and Ti metallizations were removed prior to SIMS analysis. The low adhesion of the Ni to the ZnTe:Cu allowed its removal using Scotch tape. The adhesion of Ti to ZnTe:Cu is significantly greater, and its removal required the use of the previously noted TFT chemical etchant. Following metal removal, the exposed sample surfaces were cleaned with acetone and methanol, and dried using N₂. SIMS depth profiling was performed from the contacted side of the devices with a Cameca IMS-5F unit using 60 nA, 10 keV Cs⁺, a primary ion-beam impact energy of 5.5 keV, an incidence angle of 42°, and tuned for a mass resolution (M/ΔM) of ~300. The beam was rastered over a 250-μm² (crater) area. The effect of crater edges on depth resolution was limited by collecting positive secondary ions normal to the sample surface, and only from a central ~35-μm-diameter region of the crater. The signal was limited further by a 50% electronic gate. For high-mass resolution analysis, 12.5 keV O₂⁺ was used as the primary ion (8 keV impact energy, 39°), and the instrument was tuned for a mass resolution (M/ΔM) of ~4000.

RESULTS AND DISCUSSION

All SIMS profiles in the following figures have been scaled to an average of the Te signal within the CdTe layer. Previous studies have shown that the Te concentration in r.f. sputtered ZnTe:Cu is maintained at 51 ± 1 at.% for Cu concentrations up to ~ 8 at.% (9). Although small changes in the Te concentration with increasing substrate temperature have been observed, the Te concentration for ZnTe:Cu films containing ~ 5 -6 at.% Cu remains at 51 ± 1 at.% within the substrate temperature range investigated here ($100^\circ - 300^\circ\text{C}$) (6). The detection sensitivity of SIMS can also vary depending on the matrix from which the element is sputtered. Although complications related to the outer metallization have been eliminated (by removing the metal prior to SIMS analysis), a matrix difference remains between sputter-deposited ZnTe and CSS-deposited CdTe. Without information on the Cd/Te ratio or sputter yield of Cu in CSS CdTe relative to sputtered ZnTe, we have assumed that the effect on the Cu ion yield between ZnTe and CdTe is small.

The approximate location of interfaces between ZnTe:Cu/ZnTe and ZnTe/CdTe layers are indicated on the figures. Because the as-received surfaces of these devices are rough (surface roughness ~ 200 nm), broadening of the interfaces will result. Variation in layer thickness is also expected between samples. Furthermore, there is a slight difference in SIMS sputter rates between the sputtered ZnTe layers and the CSS CdTe layer. Finally, in cases where data from multiple samples are plotted together, the depth scales have been shifted to align the maximum of the Cu signal near the ZnTe/CdTe interface. Because of these issues, the interface locations shown on the figures are only rough estimates of the exact location.

Figure 1 compares two devices that have nominally identical contacts, except that the contact deposition temperatures are 100°C and 300°C (NP etching, $1.5\text{-}\mu\text{m}$ ZnTe, $0.5\text{-}\mu\text{m}$ ZnTe:Cu, $0.5\text{-}\mu\text{m}$ Ni). At the ZnTe:Cu outer surface (i.e., the surface that was the Ni/ZnTe:Cu interface prior to Ni removal), one sees that Cu is depleted and Ni diffuses inward at the higher temperature. Previous studies have shown that the low-resistance tunneling interface between the Ni and ZnTe:Cu becomes more resistive when the Cu concentration in this layer falls below ~ 4 at.%. Therefore, the Cu depletion may contribute to the “rollover” seen in stability studies of these devices.

Integration of the Ni signal in Figure 1 indicates that there is ~ 6 times more Ni for the contact deposited at 300°C compared to 100°C . The increased Ni in the ZnTe bilayer supports the conclusion that diffusion of Ni from the outer metallization is occurring. The figure also shows a Ni signal at the ZnTe/CdTe interface. At this time, the origin of this signal is uncertain because it also appears on devices contacted with Ti. As deposition temperature increases, Cu diffusion from the ZnTe:Cu layer is seen to proceed through the ZnTe layer. A significant increase of Cu is generally observed in the (undoped) ZnTe layer, and this concentration increases further with deposition temperature. However, Cu diffusion does not proceed systematically into the CdTe, but rather, builds up at the ZnTe/CdTe interface.

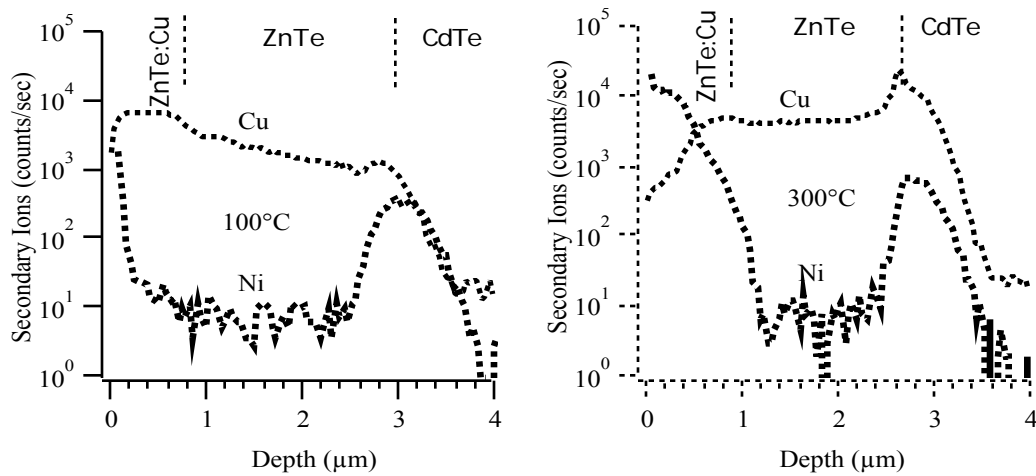


FIGURE 1. SIMS profiles showing effect of substrate temperature (100°C on left, 300°C on right) on Cu and Ni diffusion.

Figure 2 compares Cu profiles from nominally identical contacts (NP etch, 300°C, 0.5 μm ZnTe:Cu) except for the thickness of undoped ZnTe (0.4, 0.8, 1.5, and 3.0 μm). The figure also shows the Cu profile for a “control” device contacted with Ni (i.e., no Cu in the contact). The figure shows that Cu depletion at the metal/ZnTe:Cu interface persists, regardless of ZnTe thickness. Although the Cu buildup at the ZnTe/CdTe interface decreases for a ZnTe thickness of 3.0 μm , the Cu concentration in the bulk CdTe is roughly equal that of the control device, regardless of ZnTe thicknesses. A peak in Cu concentration is observed near the CdS layer. Although this peak is observed even for the control device, it increases systematically as the ZnTe thickness decreases. The data suggest that the undoped ZnTe acts as a sink for Cu diffusion from the ZnTe:Cu layer and can limit the Cu buildup near the CdS layer. Although significant Cu diffusion from this contact is not observed in the CdTe, the CdTe layer may act as a conduit for Cu diffusion toward the CdS layer.

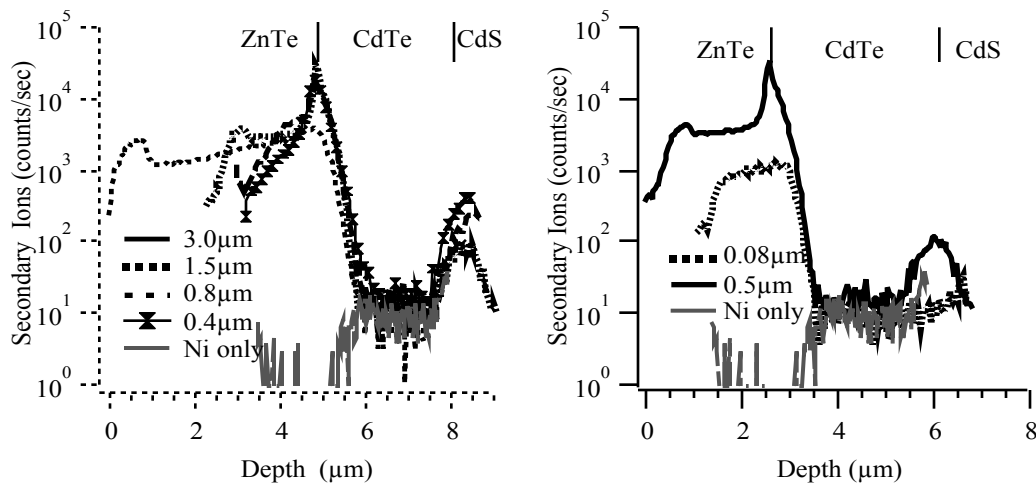


FIGURE 2. (Left) SIMS profiles showing the effect of undoped ZnTe layer thickness on Cu diffusion. The nominal thickness of undoped layer is indicated on figure.

FIGURE 3. (Right) SIMS profile showing effect of ZnTe:Cu layer thickness on Cu diffusion. The nominal thickness of ZnTe:Cu layer is indicated on figure.

Figure 3 compares Cu profiles from nominally identical devices contacted with different thicknesses of ZnTe:Cu (ZnTe:Cu = 0.08 and 0.5 μm , ZnTe = 1.5 μm) and a control device contacted with Ni only. The figure shows that Cu diffusion through the ZnTe layer, and Cu buildup at the ZnTe/CdTe interface, are present in both contacts. However, the concentration of Cu in the ZnTe layers is less for the contact with a thinner ZnTe:Cu layer. Also, although the Cu concentration for both Cu-containing contacts is roughly the same in the CdTe layer as in the control sample, the profiles show that the amount of Cu near the CdS layer is lower for the thinner ZnTe:Cu layer.

Figure 4 compares Cu profiles from nominally identical devices contacted with Ni and Ti. For both these devices, the CdTe surface was ion-beam milled (rather than NP etched) prior to deposition of the ZnTe and metal layers. The figure also shows Cu profiles for an as-received device and a crystalline CdTe sample. Unlike previous profiles, these data are collected using high-mass resolution dynamic SIMS, and the two device profiles are plotted to align the outer ZnTe:Cu interface. The figure illustrates that a significant difference between the metallizations is the absence of Cu depletion in the ZnTe:Cu layer for the Ti contact. The difference in depletion may suggest why the Ti-contacted devices appear to suffer less from rollover of the I-V characteristics. Comparing the Cu concentration in the CdTe for the as-received device indicates an increase in Cu level caused by the back contact. Furthermore, although a peak in the Cu level is observed near the CdS layer for the as-received device, this peak increases significantly when the contact is added, supporting the observation mentioned earlier.

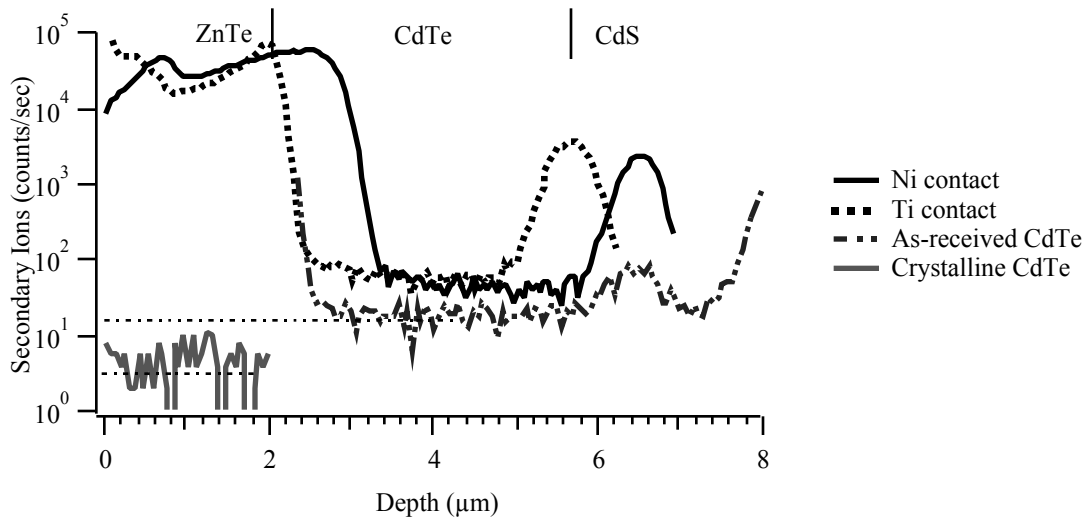


FIGURE 4. High-mass resolution SIMS profiles comparing the effect of Ni and Ti metallizations on Cu diffusion from the ZnTe contact. Figure also shows the SIMS-measured Cu concentration for a non-contacted CdTe device and a crystalline CdTe substrate.

CONCLUSIONS

The ZnTe bilayer contact interface originally was developed assuming the presence of an undoped ZnTe layer between ZnTe:Cu and the CdTe would control Cu diffusion into the CdTe and, thereby, improve device stability. We also assumed that the tunneling interface between the ZnTe:Cu layer and the outer metallization would not be affected significantly by the particular type of metallization used. Using standard and high-mass resolution dynamic SIMS profiling of Cu diffusion from this contact, this study has investigated the extent to which these assumptions are correct.

When Ni is used as the outer metallization, Cu is depleted from the ZnTe:Cu layer near the ZnTe/metal interface while Ni diffuses into the ZnTe layers. Cu depletion and Ni diffusion increase with increasing deposition temperature. Replacing Ni with Ti significantly reduces Cu depletion in the ZnTe:Cu layer. A significant amount of temperature-dependent diffusion of Cu from the ZnTe:Cu layer into the ZnTe layer is observed for both Ni and Ti metallizations. The Cu diffusion produces a build up of Cu at the ZnTe/CdTe interface, but standard-resolution SIMS does not show increased Cu concentration in the CdTe layer. Cu concentration near the CdS layer increases when the thickness of the ZnTe:Cu increases, or when the thickness of the undoped ZnTe layer decreases. This suggests that the undoped ZnTe layer can act as a sink for Cu diffusing from the ZnTe:Cu layer and that the CdTe may act as a conduit for Cu diffusion to the CdTe/CdS junction region. High-mass resolution SIMS confirms the trends of increased Cu concentration near the CdS layer, and further reveals a slightly increased Cu concentration in CdTe relative to a non-contacted device. The types of Cu diffusion noted in this study provide insight into the mechanism of device instability observed in some CdS/CdTe devices.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy under Contract #DE-AC36-83CH10093 and Subcontract #ZAX-4-14013-01 (U. of Toledo). The assistance of R. Powell of SCI in supplying device material is gratefully acknowledged.

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