

Studies of ZnTe Back Contacts to CdS/CdTe Solar Cells

T.A. Gessert, P. Sheldon, X. Li, D. Dunlavy,
D. Niles, R. Sasala, S. Albright, and B. Zadler
*Presented at the 26th IEEE Photovoltaic
Specialists Conference, September 29B
October 3, 1997, Anaheim, California*



National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
A national laboratory of
the U.S. Department of Energy
Managed by Midwest Research Institute
for the U.S. Department of Energy
under contract No. DE-AC36-83CH10093

Prepared under Task No. PV704201

September 1997

STUDIES OF ZnTe BACK CONTACTS TO CdS/CdTe SOLAR CELLS

T.A. Gessert, P. Sheldon, X. Li, D. Dunlavy, D. Niles, National Renewable Energy Laboratory (NREL), Golden, CO. 80401
R. Sasala, Solar Cells, Inc., Toledo, OH, 43607
S. Albright, Golden Photon, Inc., Golden, CO 80401
B. Zadler, University of Wisconsin River Falls, River Falls, WI 54022

ABSTRACT

Ongoing research topics in CdS/CdTe photovoltaic (PV) device technology include development of a back contact demonstrating low resistance and stability, while using processes consistent with large-area manufacturing. In efforts toward this goal, we have developed a sequence of dry, high-temperature processes to provide this contact. The process eliminates the need for chemical etching, and is performed at $\sim 300^\circ\text{C}$ to aid in contact stability and adhesion. Applying this contact process to NREL-grown CdS/CdTe device material has resulted in efficiencies $>12\%$. Devices with efficiencies $\sim 10\%$ have also been produced using material supplied by Solar Cells, Inc., and by Golden Photon, Inc.

INTRODUCTION

To realize the full potential of PV solar cells based on thin-film CdTe, issues relating to the fabrication of environmentally stable, low-resistance, and readily manufactured ohmic contacts to p-CdTe must be addressed. Presently, most contacting techniques involve three process steps. First, a wet-chemical treatment of the CdTe surface is used to produce a surface of reproducible stoichiometry that is free of unwanted deposits (e.g., Cl or CdCl₂ residue, etc.). This treatment can also produce other beneficial results, including the formation of a Te-rich layer and/or desirable grain-boundary etching of the CdTe. Second, a contact interface layer (CIFL) is formed on the etched surface. The primary function of the CIFL allows the valence band of CdTe to equilibrate with the work function of an outer metallization through the formation of a (low-resistance) tunneling barrier. To serve this function, the CIFL must be either an appropriate semi-metal or degenerate semiconductor (e.g., HgTe[1], PbTe[2], Te[3], ZnTe[4,5]). Third, an outer metallization is deposited onto the CIFL. The metal provides an adherent connection to the CIFL, limits environmental penetration into the contact, and reduces sheet-resistance losses.

This contact process has numerous advantages for research and development activities. However, because most of these processes have been developed for research-size PV devices, they are not well suited for incorporation into a PV-manufacturing sequence. For example, it is problematic to incorporate a wet-chemical treatment into a dry, in-line process. Similarly, CIFL formation is often a low-temperature process that requires post-deposition annealing to form an optimum contact. Finally, the performance of the resultant device is typically sensitive to the temperature of metal deposition, with the

best performance often achieved for metal deposition at room temperature. Not only is this inconsistent with in-line processing, but it can limit efforts to optimize metal adhesion.

In the present study, we report on the development of a sequence of dry processes to contact the p-CdTe absorber layer of CdS/CdTe thin-film PV devices. The sequence uses a ZnTe-based CIFL, but incorporates several features that allow for enhanced device performance and stability. The contacting sequence also incorporates a dry treatment that enables contact fabrication directly onto CdCl₂- and Cl-treated CdTe without the need for wet-chemical etching.

EXPERIMENTAL

CdS/CdTe device materials were acquired from three different sources: Solar Cells, Inc. (SCI), Golden Photon, Inc. (GPI), and NREL. In many cases, contacts were deposited simultaneously on devices from at least two of these sources. The contact process is initiated by placing Cl- (i.e., CdCl₂, HCl- or Cl-gas) treated device material into a multi-source vacuum chamber, and evacuating the chamber to $\sim 8 \times 10^{-6}$ torr. Device temperature is maintained at $\sim 300^\circ\text{C}$ throughout the contact process. Dry pre-treatment of the CdTe surface is accomplished with a 3-cm ion gun, operating at a beam energy and current of 500 eV and 10 mA, respectively. The ion gun is mounted at 45° , and is operated with pure Ar at a chamber pressure of 2×10^{-5} torr. Source-to-substrate distance is ~ 12 cm and a neutralizer filament is used to reduce the ion component of the beam, thus avoiding substrate charging. This configuration results in a peak beam current density at the CdTe surface of ~ 0.6 mA cm⁻², yielding an etch rate of ~ 250 Å min⁻¹.

Following ion-beam (IB) exposure, the ZnTe CIFL layers are deposited by r.f.-magnetron sputtering in 10 mtorr of pure Ar. The first CIFL layer is undoped ZnTe (ZnTe) sputtered from a Sloan S-310 source fitted with a pressed-powder target. The layer is deposited at a peak rate of 200 Å min⁻¹, and nominal layer thicknesses between 0 µm and 3 µm were studied. Following ZnTe deposition, a layer of ZnTe containing ~ 6 at.% Cu is deposited (ZnTe:Cu)[5]. The ZnTe:Cu is sputtered from a 5.08-cm planar source fitted with a pressed-powder target, at a peak rate of 400 Å min⁻¹, and to a nominal thickness of 0.5 µm. Except for devices prepared for comparative adhesion studies, the outer metallization was d.c.-magnetron sputtered Ni. Ni was chosen because of its relatively high work function and compatibility with simple photolithographic processing. The Ni layer is deposited at a peak rate of 1000 Å min⁻¹ to a nominal thickness of 0.6 µm.

The ZnTe/ZnTe:Cu/Ni contact is sufficiently adherent and uniform in thickness to allow fabrication of individual devices using standard positive photolithographic procedures. A single chemical etching step with 39% FeCl₃:H₂O is used to isolate 0.25 cm² mesa cells for analysis. Light current-voltage (LIV) measurements for efficiency and stability analysis were performed at NREL using standardized methods.

Devices processed to compare the performance of chemically pre-treated surfaces were etched with 1 HNO₃ : 85 H₃PO₄ : 33 H₂O, for 15 sec. (NP etch). Structures fabricated to assess the adhesion of the sputtered Ni consisted of electron-beam (EB) evaporated Ni and Ti/Pd/Ag layers. In this case, samples were cooled after the deposition of ZnTe:Cu, removed from the sputtering system, and photolithographically processed to form transmission-line lift-off patterns. Ni and Ti/Pd/Ag were then deposited by EB evaporation.

RESULTS AND DISCUSSION

Developing a completely dry process to contact a thin-film CdTe PV device must address several issues. First, the wet-chemical etching of the CdTe surface must be eliminated. This also implies that beneficial aspects related to wet-chemical etching, such as grain-boundary etching or the formation of a Te layer, must be considered. Second, the process should be conducted at the highest possible temperature. This will enhance adhesion of the outer metallization, and force potentially detrimental interdiffusion of the contact to occur during contact formation rather than during the operating lifetime of the device. High-temperature processing also eliminates the need to cool the device prior to contacting, and can eliminate post-deposition annealing. Finally, if Cu is used in the CIFL layer, the contact should allow for control of Cu diffusion during contact formation.

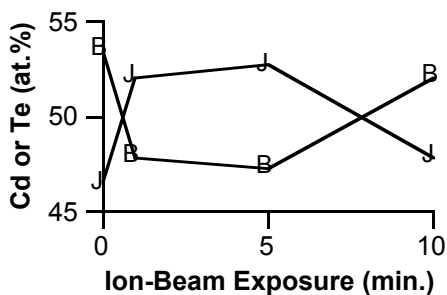


Fig. 1. X-ray photoelectron spectroscopy (XPS) analysis of the surface of an IB-exposed crystalline CdTe surface. Circles represent surface Cd, squares represent surface Te.

As shown in Fig. 1, the surface stoichiometry of a crystalline CdTe sample changes as IB exposure increases. Although the effect of IB exposure on thin-film CdTe surfaces will likely be different than for crystalline material, it is likely that the surface stoichiometry of thin-film CdTe will also depend on IB-exposure time, and these changes may affect the contact performance. Indeed, Fig. 2 shows that the IB-exposure time significantly

affects the open-circuit voltage (V_{oc}) of CdS/CdTe devices. The figure also shows the performance of SCI devices that were chemically etched to form a Te layer prior to IB exposure (NP etch). The comparison indicates that the IB exposure process can produce devices with similar V_{oc} as the NP-etch process (assuming an appropriate layer of undoped ZnTe is located between an IB-exposed surface and the outer contact layers). Although not shown, it is observed that the fill factor increases with voltage such that the V_{oc} represents a reasonable indicator of overall device quality.

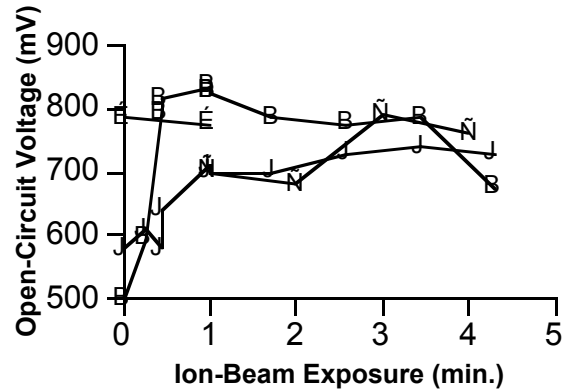


Fig. 2. Change in V_{oc} with increasing IB-exposure time: Solid squares = SCI-device material, solid circles = GPI-device material, open squares = NREL-device material. For SCI and GPI materials, nominal thicknesses of undoped ZnTe, ZnTe:Cu ZnTe, and Ni layer are 1.5 μ m, 0.5 μ m, and 0.6 μ m, respectively. For comparison, open circles show V_{oc} of SCI material that was chemically treated (NP etch) prior to IB processing.

The effect of increasing V_{oc} with increasing thickness of an undoped layer is shown in Fig. 3. For this set of experiments, the IB-exposure time was fixed at 3.4 min., so that reasonable-quality performance resulted for both SCI and GPI devices. At this time, the reason for the increase in V_{oc} is unclear. One explanation may be that the Fermi level at the IB exposed surface CdTe surface is pinned toward mid gap, and interdiffusion at the CdTe/CIFL interface allows the device to assume a greater built-in voltage. Another explanation is that the undoped layer moderates the beneficial effects of Cu diffusion from the outer layers of the CIFL. Although not shown, another curious observation is the fact that the series resistance does not increase systematically with ZnTe thickness except for devices with a nominal ZnTe thickness > 2.0 μ m. Fig. 3 also shows the performance of SCI devices that were chemically etched rather than IB exposed prior to contact formation (NP etch). This comparison suggest that, even for contact based on a chemically formed Te layer, the two-layer CIFL can provide a performance enhancement when contacts are deposited at 300°C.

Although we have not exhaustively studied the parameter space for the IB exposure and the two-layer CIFL, we have used the available data to determine IB and CIFL parameters that produce reasonable-quality devices for NREL, SCI, and GPI material. The best of these

devices are summarized in Table I, and the NREL device is shown in Fig. 4. These results indicate that the process can be adjusted for differences in the polycrystalline p-CdTe that result from various CdTe-deposition and post-deposition processes.

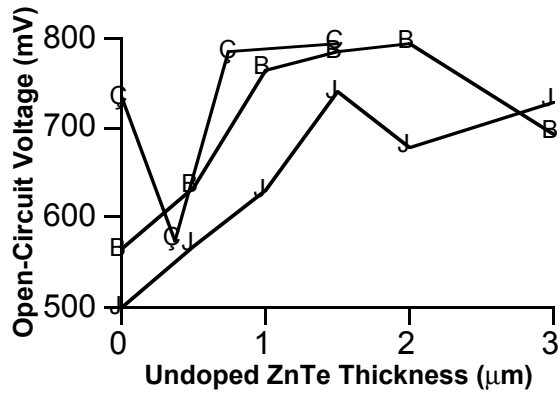


Fig. 3. Figure shows change in V_{oc} with increasing thickness of the undoped-ZnTe layer: Solid squares = SCI-device material, solid circles = GPI-device material. For circles and squares, ion-beam exposure time is 3.4 min. Open triangles show SCI-device material that was NP etched for 15 sec. rather than IB processed prior to ZnTe/ZnTe:Cu/Ni contacting.

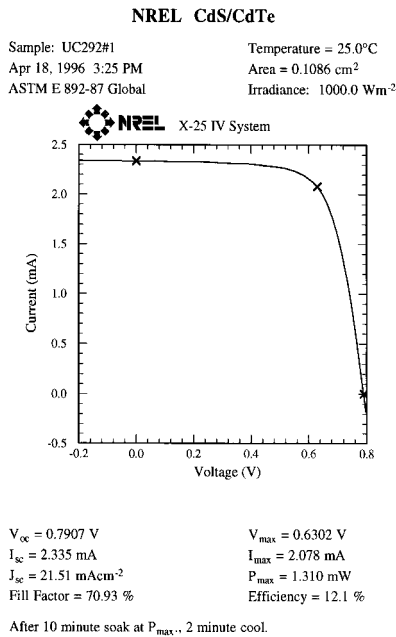


Fig. 4. Results from light I-V measurements performed under standard conditions at NREL for NREL-produced device material on a 1-mm thick Corning 7059 substrate, using CdS deposited by chemical bath, and CdTe deposited by close-space sublimation.

Table I. Standardized LIV measurements of NREL-, SCI-, and GPI-device material contact with IB/ZnTe/ZnTe:Cu/Ni.

Material Supplier	V_{oc} (mV)	I_{sc} (mA/cm ²)	FF (%)	Eff. (%)
NREL	791	21.51	70.9	12.1
SCI	813	18.61	71.1	10.7
GPI	701	22.49	59.7	9.4

In addition to allowing sequential contact fabrication immediately after previous high-temperature processes, it is believed that the ~300°C contacting temperature may benefit contact stability and metallization adhesion. Unfortunately, it is difficult to judge the stability of these contacts because few comparative data are available regarding how to perform a stability study on non-encapsulated CdS/CdTe devices. As an initial attempt to survey the stability of these devices, and to establish a baseline to which later device results can be compared, a stability study of SCI and GPI devices contacted with the dry-ZnTe process has been initiated. For this survey, a mechanical-convection oven is used to heat treat non-encapsulated devices in the dark, at 80.0°C, at V_{oc} , in air. Initial representative results from this survey are shown in Fig. 5. The results indicate that, although the dry contact process used for both devices is similar, the changes in performance parameters are different for the two devices. This may suggest that either the contact process interacts with the two device materials differently, or that the changes are not due solely to the back contact.

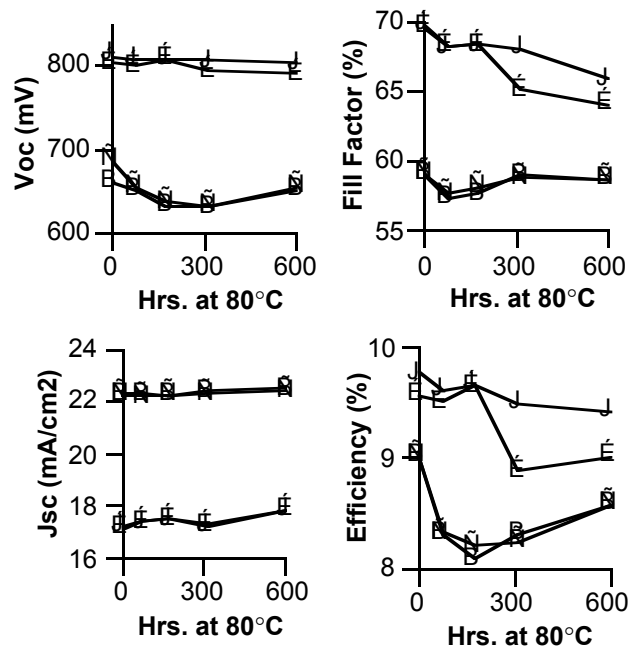


Fig. 5. Standardized LIV measurements for SCI (circles) and GPI (squares) devices annealed at 80°C in a mechanical-convection oven in air. In each figure, solid points indicate as-received measurements (i.e., storage state), and open points represents data for the same device after a 10-min. light soak at P_{mpp} followed by a 2-min. cooling cycle.

The stability study has also suggested that the Ni used as the outer metallization may not be as adherent as predicted. Indeed, Scotch-Tape pull tests, conducted on photolithographically produced devices, indicate that the Ni adhesion on NREL and SCI devices is poorer than for GPI devices. This could explain differences in fill-factor stability shown in Fig. 5, and may result from the back surface of the NREL-, and SCI-device material being smoother than the GPI material. Presently, we are investigating Ti/Pd/Ag as a metallization on the ZnTe:Cu. Preliminary experiments in which EB-evaporated Ni is compared with Ti/Pd/Ag indicate that the Ti/Pd/Ag is much more adherent. We are presently developing processes to test if the Ti/Pd/Ag contact can be incorporated into the dry-process sequence at 300°C.

CONCLUSIONS

We have developed a sequence of dry processes that can be used sequentially to produce ohmic contacts to CdS/CdTe PV devices at relatively high temperature (300°C). The steps of the contact process are ion-beam milling to condition the Cl-treated p-CdTe surface, deposition of undoped ZnTe, deposition of Cu-doped ZnTe, and deposition of Ni. Based on the available optimization data, we have produced devices with reasonable performance from NREL-, SCI-, and GPI-device material. We expect continued improvement in the performance of this contact as studies proceed.

Stability studies of non-encapsulated devices have been initiated. Although preliminary, these studies have begun to indicate the measurements necessary to observe important trends, and suggest contact design changes that are necessary to improve future stability studies. This study has produced a set of baseline data to which later devices will be compared. LIV data indicate that devices contacted with the dry process demonstrate reasonable stability when annealed at 80°C in air, but that differences in stability are observed between devices supplied from different sources.

Future studies will focus on more fundamental aspects of this contact system. Auger spectroscopy studies are presently underway to examine what effects the IB treatment has on a Cl-treated, thin-film p-CdTe surface. Secondary Ion Mass Spectroscopy analysis has also begun to examine how the diffusion of Cu proceeds from the ZnTe:Cu through the ZnTe and into the CdTe. Finally, we are investigating the possibility of using thinner CIFL layers to produce good-quality devices.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-83CH10093. Special thanks to T. Zhou, formerly of SCI, for preliminary samples.

REFERENCES

1. E. Janik and R. Triboulet, *J. Phys. D: Appl. Phys.* **16**, p. 2333 (1983).
2. K.W. Mitchell, U.S. Patent #4,734,381 (1986).

3. D.W. Niles, X. Li, D. Albin, D. Rose, T. Gessert, and P. Sheldon, *Prog. in Photovoltaics*, **4**, p. 225 (1996).
4. P.V. Meyers, *7th E.C. Photovoltaic Solar Energy Conference*, Sevilla, Spain (D. Reidel Publishing Co., Dordrecht, 1986) p. 1211.
5. T.A. Gessert, A.R. Mason, P. Sheldon, A.B. Swartzlander, and T.J. Coutts, *J. Vac. Sci. Technol. A* **14**, p. 806 (1996).