June 21, 2004

Ken Zweibel
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Re: NREL Subcontract #ADJ-1-30630-12

Dear Ken:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period
from May 9, 2004 to June 9, 2004, under the subject subcontract. The report highlights progress
and results obtained under Task 1 (CdTe-based solar cells).

Task 1 CdTe-Based Solar Cells

Improving CdS/CdTe Solar Cell Performance

Increasing V_{OC}

The V_{OC} in thin film CdTe/CdS devices is influenced by both junction and back contact
processing. Back contact processing of CdTe cells facilitates formation of a low barrier for hole
transport, between the robust conductor and CdTe, and by forming a transitional layer, consisting
of Te and/or Cu_2Te. Devices are completed by application of a current-carrying conductor. This
layer is also a source of Cu for doping the CdTe and raising V_{OC}. In this period, a procedure was
developed to directly form Cu_xTe contacts with different composition by co-evaporation of Cu
and Te using electron beam sublimation from elemental source crucibles. Depositions were
carried out over a range of Cu/Te compositions onto glass, ITO-coated glass, and VT CdTe/CdS
substrates. Energy dispersive x-ray spectroscopy (EDS) and glancing incident x-ray diffraction
(GIXRD) measurements are being made to determine the composition and phase content, and
cells are being fabricated. It is hoped that the electrical and optical properties of the equilibrium
phases found in working solar cells, namely Cu_2Te, Cu_7Te_4, Cu_7Te_5, and CuTe, can be
elucidated from these thin-film samples, since only the Cu_2Te phase has a literature basis.

Effect of CdTe Defects on Device Performance

The AMPS model has been used by Colorado State University (CSU) and Alan L. Fahrenbruch (ALF), among others, to gain insight into effects of back contact barriers, carrier density, band alignment etc., on device behavior. We have begun to develop expertise in AMPS modeling to interpret a range of experiments, including V_{OC}-T and defects from drive level capacitance. Here, we present some preliminary results. We used an input parameter set comparable to those published by CSU,[1] and achieved similar device performance: V_{OC}=0.830, J_{SC}=22 mA/cm^2, FF=80%, eff=14%. We have validated these input parameters by comparison to measurements of light and dark J-V, V_{OC}-T, and QE.

It is well established that low temperature J-V curves tend to show blocking contact behavior in forward bias. This problem often gets more pronounced after stressing and is attributed to an increase in the back barrier leading to reduction in electron current injection. Figure 1 shows the J-V curves at 250K for two simulated defect densities, midgap (MG) and MG plus donor and acceptor. The back barrier was the same for each case, 0.4 eV. At 300K, they behaved similarly at forward bias, with no rollover. Yet, at 250K, the case with additional shallow traps shows the typical rollover commonly attributed to the back barrier. Inspection of the internal hole and electron current density profiles indicated that the electron current was strongly reduced. Since it is well known that defect densities or carrier recombination increase with stress, it is possible to explain the observed increase in rollover without invoking an increase in back barrier height. We are continuing to use AMPS to interpret other measurements.
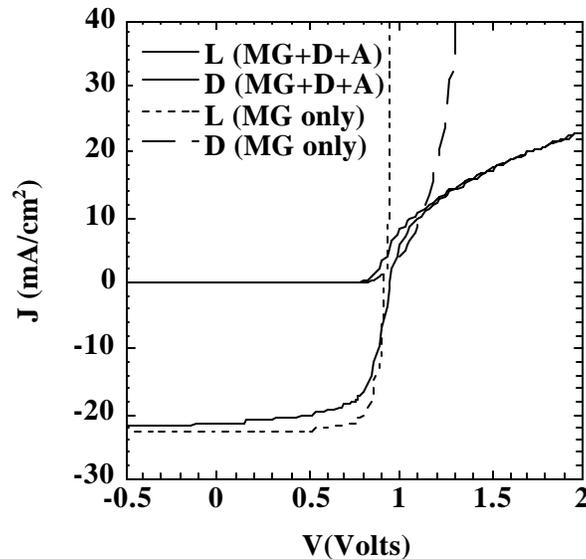

Figure 1. Light and dark J-V curves at 250K for two defect distributions, MG only (1x10^{14}/cm^3) and MG plus 2x10^{14} donors and 1x10^{15} acceptors.

CdTe Surface Chemistry

Aniline-based Electrolyte Treatment

Investigations into understanding the chemical mechanisms of the University of Toledo's aniline surface treatment have continued. All investigations had been carried out using CdTe/CdS/TCO/glass substrates illuminated during treatment through the glass side, though similar results are obtained when the CdTe is illuminated directly. The CdTe was deposited by vapor transport at IEC. To investigate the role, if any, of the other substrate layers during aniline treatments of CdTe, different substrates; CdTe/SnO_2/glass (no CdS) and CdTe/glass (no CdS or TCO), were used. The CdTe films received no post deposition $CdCl_2$ treatments. Using standard aqueous aniline bath conditions, 0.1 M aniline, 0.01 M *para*-toluenesulfonic acid (p-TSA) and 1 M NaCl, samples were treated with illumination on the glass or CdTe side for 90 mins. Variable angle spectroscopic ellipsometry (VASE) was used to determine presence of a Te layer. In each case, a Te-rich CdTe surface was produced, though the reaction was significantly faster when the CdTe is directly illuminated. This effect is also observed to some extent for $CdCl_2$-treated CdTe/CdS/TCO/glass structures, though the difference in reaction rate is not as significant. These results indicate that the CdTe is the only device layer involved in the reaction during aniline treatment.

A set of experiments were carried out where the p-TSA was substituted with a range of different acids, including oxalic, maleic, phthalic, ascorbic, acetic, phosphoric and hydrochloric acids and EDTA. The pH of each bath was 5-6. CdTe/SnO_2/glass substrates, with no post-deposition $CdCl_2$ processing, were treated for 90 mins with illumination on the CdTe film. Each bath produced a Te-rich CdTe surface, similar to the standard bath. However, for the HCl bath, some etching of the surface may have been due to the HCl itself. These results indicate that the nature of the acid is not critical to bath behavior, though concentration and pH must be controlled. Previously, we have reported that increasing the [p-TSA] of the bath attenuated the surface reaction. This may be due to the acid competing with or blocking the adsorption of aniline to the CdTe. When the acid is not added to the bath, the reaction does not proceed. We conclude that the University of Toledo aniline surface treatment is a promising pathway to achieving a Te-rich layer for device contact processing.

Mechanism of Nitric Acid / Phosphoric Acid Etching

We have previously described investigations of the surface chemistry of CdTe during treatment with the HNO_3/H_3PO_4 (NP) etchant. While it is known that this etch results in a thick, 50-100 nm, Te-rich surface layer, the chemical mechanism of the reaction is not understood.

It was found that when etching with fresh NP solutions, consisting of 1:70:29 HNO_3:H_3PO_4:H_2O, the etch rates were very slow. The expected bubbling, usually observed ~20s, did not occur until 45 – >60s immersion. Subsequent etches in the same solution showed faster bubbling times, ca. 20-30s, eventually reaching a minimum bubbling time of ~15s. Bubbling is an indication of formation of NO and/or NO_2 as the reaction proceeds. Adding pieces of CdTe or Te to a fresh solution also resulted in a shortening of the time for bubbles to appear. This decrease in bubbling time can be assumed to be due to the formation of a catalytic or active species, which is

directly involved in the reaction, during treatment. To confirm if this species was Cd or Te related, a small amount of Cu powder was added to a fresh NP solution. HNO_3 reacts with Cu similarly to CdTe. Following addition of Cu to a fresh NP solution, the bubbling time during CdTe etching decreased to 10s. This observation confirms that the active species produced during etching is, in fact, a product of the decomposition of HNO_3. Oxidation by HNO_3 is known to be autocatalytic,[2] where a reaction product is also a catalyst for the reaction. Autocatalytic processes begin very slowly, and after an incubation period, dramatically increase in rate, as seen during NP etching by the delay in the appearance of bubbles.

Sodium nitrite, $NaNO_2$, was also used to charge the etch solutions. NO_2^- decomposes in acid, with a similar reaction to that of HNO_3 treatments, and has been used as a catalyst for the HNO_3 oxidation of polysaccharides.[2,3] The chemical mechanics of this catalysis are, however, not understood. Because of its similarity to HNO_3, the use of NO_2^- decreases the possibility of contamination that would be expected through the use of metals or other compounds to charge the etch solutions. For CdTe films etched in NP containing a small amount of $NaNO_2$, bubbling began at <10s following immersion. Bubbling times decreased further with increasing $[NO_2^-]$. Literature studies have proposed various species, including N_2O_3 or NO^+, as possible candidates for the autocatalyst. Etch solutions of 0.05 – 1M $NaNO_2$ in 66% and 87% H_3PO_4:H_2O were prepared. Once the reaction between NO_2^- and the acid has subsided, the resultant solutions are blue in color. Treatment of CdTe, for 30s, in these solutions, showed immediate bubbling and the formation of Te-rich surfaces. Based on VASE measurements, the thickest Te layers were obtained for the 0.5M NO_2^- and 0.05 – 0.2M NO_2^- in 66% H_3PO_4 and 87% H_3PO_4, respectively. Higher $[NO_2^-]$ resulted in significant etching of the generated Te. The blue color and stability of the solution suggests the blue N_2O_3 as an important intermediate species during NP etching of CdTe.

The use of NO_2^- as an etchant has a number of benefits for CdTe device processing, including shorter immersion times, more efficient and controllable etching, and avoids the handling of concentrated HNO_3. Care must be taken during etch preparation as the acid decomposition of NO_2^- can be violent. Optimization of the NO_2^-- based etch solution and device processing are currently underway.

Contacts and Stability

Transparent ZnTe:Cu Contact Development

In the previous quarterly report, we discussed the galvanic solution growth of ZnTe:Cu films for use as a semi-transparent back contact and source of Cu doping. Films had been deposited, using $CuCl_2$ or $CuSO_4$ as Cu sources. Devices with $CuSO_4$ achieved 10% efficiency, but had hysteresis in the J-V retrace, slight shunting and rollover in forward bias, suggesting too much free Cu and/or formation of CuTe. In the present quarter, ZnTe; Cu films were made using tri-ethylamine (TEA) as a complexing agent to reduce the chemical reactivity of the Cu in the solution. Previously deposited films also did not show a very sharp optical band edge as would indicate a direct gap semiconductor like ZnTe. Figure 2 shows T/(1-R) measured on glass/SnO_2/ZnTe films for three different films: ZT45 and 46 with TEA and ZT30 without TEA. ZT30 and ZT45 have the same concentration of $CuSO_4$ and ZT46 had half as much. All films

were approximately the same thickness. The films with TEA have much higher transmission at wavelengths beyond the ZnTe bandgap (~560 nm), which signifies less defects and is an important consideration for tandem cell development. Only film ZT45, with TEA, has evidence of a sharp band edge. Devices have been made with the ZnTe: Cu contacts from a TEA solution and the devices are being tested. A V_{OC} of 0.82 V has been achieved with devices on CdS/CdTe from First Solar, comparable to the best values we have obtained with any contact on that material. Results will be presented in the following report.
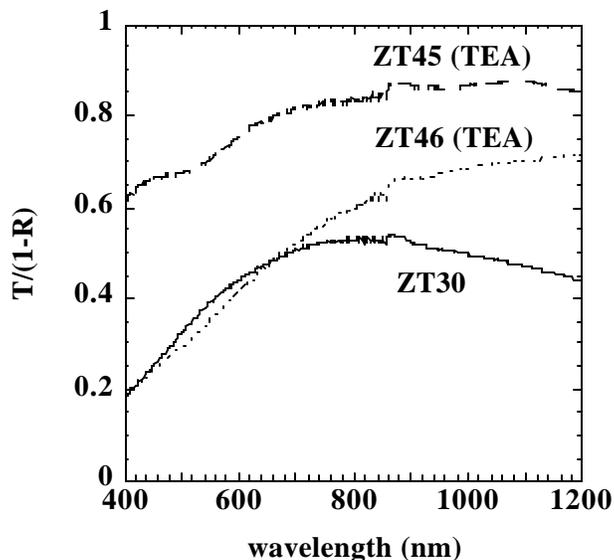

Figure 2. T/(1-R) for three ZnTe:Cu films described in the text.

High Throughput Processing

The vapor deposition system has been modified and is operational and supplying CdTe films for experiments relating to back contact development. CdTe film deposition is carried out at a substrate temperature of 550°C. Uniform films are obtained when using both pre- and post-deposition zone heaters adjacent to the source manifold, compared to depositions in which only the source manifold is heated. The original heater assemblies consisted of PBN disk heaters embedded in graphite blocks and were extremely fragile. In this reporting period, they have been replaced with heaters using a more robust tantalum filament, embedded in a milled boron nitride plate. These external heaters are an important aspect of the system design in that they prevent film deposition on the cooler areas surrounding the manifold assembly and reduce subsequent re-evaporation of CdTe deposits, resulting in higher CdTe utilization. Runs 101-104, which were deposited with a source temperature of 850°C, and with the external heaters at 650°C, exhibit very uniform films, 6-8 µm thick, deposited on a 10 cm x 10 cm translating substrate moving at 1 cm/min, giving a static equivalent growth rate of >8 µm/min. Conversion efficiencies of 10% were achieved using CdCl$_2$ treatment at 410°C for 30 minutes, Br$_2$ dichrol hydrazine (BDH) etching, and Cu/graphite contacts. Depositions performed under the same conditions but with only the pre-deposition zone heater on at 650°C were thinner, 4-5 µm thick,

and were less uniform. The effect of the post-deposition zone heater temperature on film uniformity is currently being evaluated. Next, depositions will be performed over a range of deposition rates and film thickness to determine the effects on CdTe film physiochemical and electronic properties and on CdTe/CdS device behavior. Baseline deposition conditions for 11% efficiency, with films deposited at 1-5 µm/min, will be used to evaluate different HR/TCO combinations and back contact processes.

National CdTe Team Collaboration

Under the CdTe R&D Team collaboration, IEC continued to provide support to First Solar by performing GIXRD measurements of CdTe films at different stages of processing and for different back contact processing conditions. We have also collaborated with Ceramem Corporation on development of quick application, non-vacuum back contact processes.

Sincerely,

Robert W. Birkmire

RWB/eak

Cc: Brian McCandless
        Kevin Dobson
        Steven Hegedus
        Paula Newton
        Gerri Hobbs, UD Research Office
        Carolyn Lopez, NREL

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[3] V. Kumar, T. Yang, *Carbohydrate Polymers*, 48 (2002) 403.