

Overcoming Degradation Mechanisms in CdTe Solar Cells

**Second Annual Report
August 1999–August 2000**

D. Cahen, G. Hodes, and K. Gartsman
*Weizmann Institute of Science
Rehovot, Israel*



National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

Overcoming Degradation Mechanisms in CdTe Solar Cells

**Second Annual Report
August 1999–August 2000**

D. Cahen, G. Hodes, K. Gartsman
*Weizmann Institute of Science
Rehovot, Israel*

NREL Technical Monitor: B. von Roedern

Prepared under Subcontract No. AAK-8-17619-15



National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.doe.gov/bridge>

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: reports@adonis.osti.gov

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



Table of Contents

| | |
|---|----|
| Abstract | 1 |
| Introduction | 2 |
| Task 1: Separation of Back Contact Issues from Complete Cell Problems | 3 |
| Investigation of Stressed and Unstressed Cells Supplied by NREL and First Solar.... | 3 |
| Task 2: Diffusion Processes | 5 |
| Review Paper..... | 5 |
| Diffusion Measurements | 6 |
| Model for Cu-Induced Assisted Degradation | 8 |
| Task 3: Chemical Treatments and Novel Back-Contact Materials | 13 |
| Surface Treatment of CdTe | 13 |
| Ni:P and NiTe ₂ Back-Contacts..... | 20 |
| Conclusions | 23 |
| Further Work | 24 |
| References | 25 |

Abstract

The scientific literature concerning degradation and atomic diffusion in CdTe/CdS cells has been reviewed. This led to the conclusion that there appear to be unexplained differences between module and cell stability, possibly due to the difference between encapsulated and air-exposed systems. A comprehensive model for Cu-assisted cell degradation is suggested, which should now be tested experimentally by the appropriate R&D teams.

Both LBIC and EBIC have been used to distinguish between stressed and unstressed cells. From these we conclude that decrease in charge separation efficiency is correlated with increase in electrical heterogeneity of the cell.

Cells without back contacts were treated with a series of simple organic compounds, where the dipole is varied systematically. We find, *grosso modo*, such systematics in the electronic behavior and electrical characteristics of these cells, suggesting significant porosity of the CdTe film.

NiTe₂ was found to be the product of electroless Ni:P back contact deposition from baths of low reductant concentrations. Such back contacts were further optimized and characterized, with special attention being given to cell stability considerations.

Introduction

While some outdoor tests of encapsulated modules have shown little or no degradation of CdTe modules after >4 years deployment, many experiments on individual cells, in ambient, using modestly enhancing stress conditions (e.g., exposure to 1-sun light intensity at 100°C cell temperature) have shown significant degradation.

Several causes have been proposed to explain cell instability, including junction degradation, degradation of the electrical contact to the CdTe and shunting. The most suspected cause for cell instability is the diffusion of Cu (which was found to improve contact and cell behavior) from the back contact into the CdTe/CdS cell [1]. We have reviewed the scientific literature concerning degradation and atomic diffusion in CdTe/CdS cells, and a comprehensive model for Cu-assisted cell degradation is suggested herein.

The degree and nature of degradation are dependent on the stress conditions as well as on the details of device preparation. In order to examine the effects of such details, cells supplied by different manufacturers were examined, before and after stressing under varying conditions.

The influence of surface chemical treatments on the PV behavior of the cells was examined. Such treatments are expected to affect the CdTe/back contact interface, as well as internal grain surfaces and interfaces (Grain Boundaries, GBs). It was suggested that GB diffusion is a very likely mechanism for Cu transport to the cell junction [1]. Therefore, such treatments are expected to affect the stability as well. Cells without back contacts were treated with a series of simple organic compounds, where the dipole is varied systematically, and the effects of the adsorbed molecules were characterized using Surface Photovoltage Spectroscopy (SPS) and current-voltage (IV) measurements.

Back contacts containing no Cu have been suggested in order to “bypass” the Cu effects. The use of Ni:P and NiTe₂ back contacts, deposited by electroless methods, was examined and cells made with such contacts were characterized.

Task 1: Separation of back contact issues from complete cell problems

Investigation of stressed & unstressed cells supplied by NREL & First Solar.

A set of complete cells, with NREL standard back contacts (Cu/HgTe/graphite), was received from NREL (D. Albin). These samples consisted of a number of stressed and unstressed cells. The stress conditions used included (1) operation under illumination at open circuit, short circuit and maximum power voltages, and (2) in the dark at forward and reverse bias and at open circuit (all under ambient conditions). From I-V results, the cells, which had been stressed under illumination, degraded more than those that were treated in the dark. Another set of cells was received from First Solar (D. Rose). Those cells were completed with an undisclosed back contact and the set consisted of both stressed (light-soak at ~65°C for 28 days at open circuit) and unstressed samples.

We have shown that **Front-wall** (illumination through the glass substrate) **light beam induced current (LBIC)** can be used to assist the characterization of different cells and contacts. The technique is non-destructive and can be used to determine the quality of the cell junction, and identify areas of poor current due to poor contact or mechanical damage to the cell. For example, a scratch in an NREL cell through to the glass causes a dark (low-current) area in the corresponding LBIC image, which is considerably larger than the surface scratch itself.

Front-wall LBIC of the received cells was investigated¹. The cells from each supplier (that had not been degraded) showed homogeneous current images, similar to results obtained for unstressed First Solar cells contacted at the Weizmann Institute. The LBIC images of the stressed NREL cells show a decrease in the image contrast² and varying degrees of image heterogeneity (fig. 1), but not to the extent seen for First Solar cells contacted and thermally degraded here (200°C in air, ~300 hours, uncontrolled humidity, in dark. Front-wall LBIC measurements for these cells were presented in our previous annual progress report [3]). NREL cells which had been stressed under illumination showed a greater degree of heterogeneity in the LBIC images compared to the NREL cells which had been stressed in the dark. The dark stressed samples themselves showed a varying degree of heterogeneity in

¹ Wavelength: 568nm, illuminated spot dia.: 974 nm, illumination intensity: 1 mWatt

² White = higher current, corresponding to about 10 A/cm², black = zero current.

the LBIC images, with one sample (stressed in the dark at open circuit) showing almost no difference from results of non-degraded cells. LBIC of stressed First Solar cells also showed a decrease in image contrast with respect to unstressed cells and an increase in the heterogeneity of the image.

Cross-section EBIC (electron beam induced current) measurements supported these observations by showing a decrease in the magnitude of the average junction EBIC signal with decreasing efficiency of the cells, indicating a decrease in the magnitude of the electrical field there. However, these changes were within the signal variations at various points along the cross-section. This variation might point to heterogeneity of the cell junction, as mentioned above.

We conclude that the decrease in cell efficiency with stressing is connected with a decrease in the charge separation efficiency of the junction, accompanied by an increase in the heterogeneity of the LBIC image which may be pointing to a decrease in the effective area of the cell.

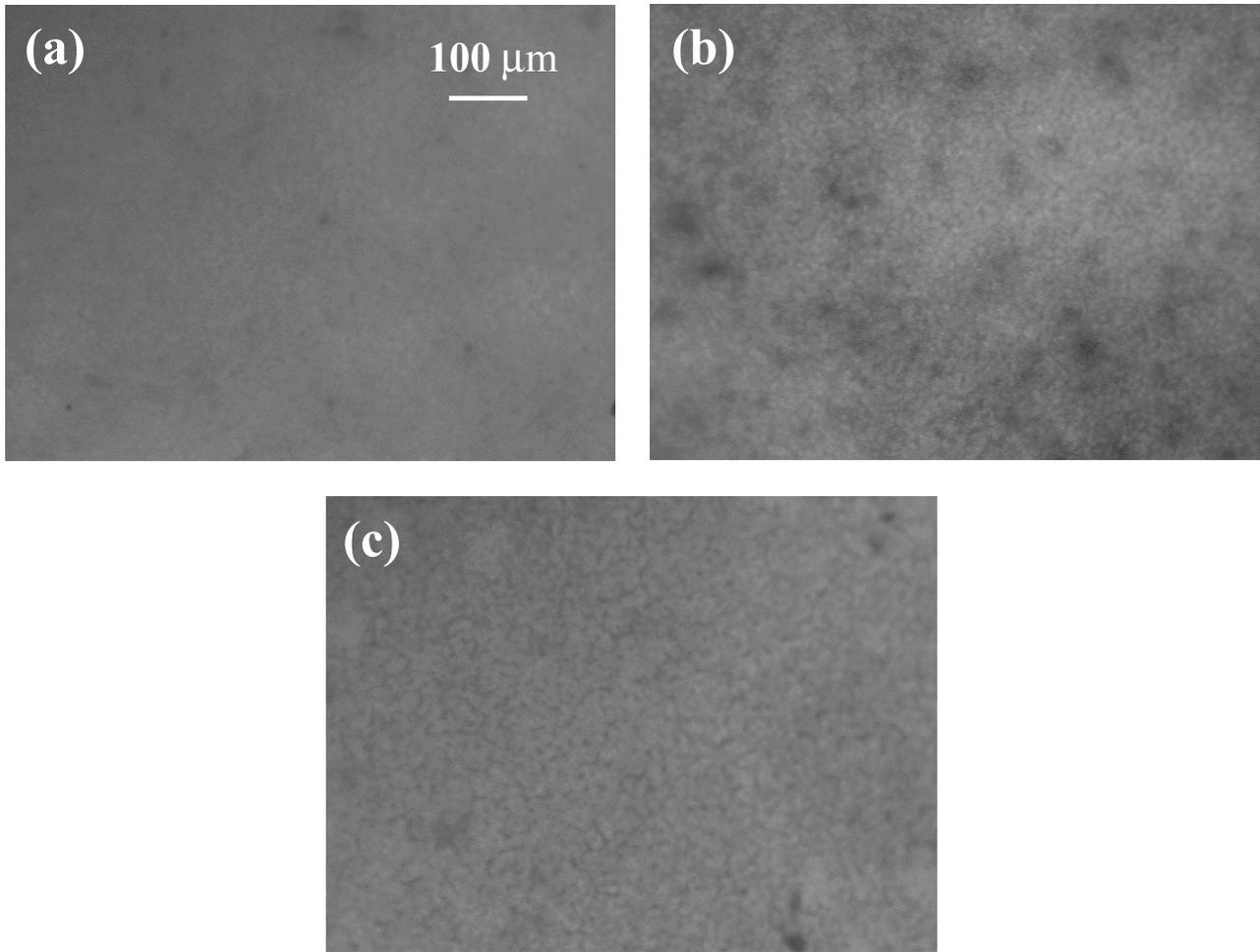


Figure 1: Front-wall LBIC images of three completed cells, supplied from NREL, recorded following; (a) no stress, (b) stressed under illumination at open circuit and (c) stressed in dark at $V > 0$. Cell (b) had exhibited increased degradation with respect to cell (c).

Task 2: Diffusion processes

Review Paper

We have prepared a paper reviewing aspects of the stability of CdTe/CdS thin-film solar cells, with particular emphasis on the possible involvement of copper in cell degradation. The manuscript was submitted to Solar Energy Materials and Solar Cells and was accepted for publication in early January 2000. Following the CdTe Team Meeting in late January, a number of points presented in the

manuscript were disputed. Following discussion, all points raised that were found to be valid, based on our scientific considerations, were addressed in the final manuscript. The paper was published in the May 15, 2000 issue of the journal [1]. As a direct result of the findings made and discussed in the review, we presented the team with a working hypothesis concerning the instability issues that often accompany back contacts (*vide infra*). We furthermore made a case for comparing, in a controlled and scientific methodological fashion, stability behavior of encapsulated modules, non-encapsulated modules, encapsulated cells and free cells.

Diffusion measurements

Investigations of degradation mechanisms in CdTe/CdS cells have continued. SIMS investigations of a number of CdTe/CdS cells (received without back contact from First Solar) of varying histories have been carried out. Cells were contacted with graphite containing Cu-doped HgTe (USF), before receiving various stress treatments (see below). Prior to measurement, the back-contacts were removed by sonication in acetone and the CdTe surface was etched with 0.1 % Br₂/methanol for 30 seconds to remove high Cu surface concentrations.

Contacting the cells shows an increase of Cu in the CdTe layer (from 1×10^{17} Cu atoms/cm³ for non-contacted samples to 3×10^{18} Cu atoms/cm³ for non-stressed cells), and an accumulation of Cu near the CdS layer of the cell (figs. 2a and 3a). Similar observations have been previously reported [2]. A similar investigation of a cell with no CdS layer (supplied from USF) found no such accumulation of Cu to occur (fig. 2b). This indicates that Cu can diffuse very rapidly throughout the cell and exhibits an affinity for the CdS layer. With stress (heating at 200°C in air, uncontrolled humidity, in dark), the concentration of Cu in the CdTe layer is only slightly increased (fig. 3a), but a notable increase in the level of Cu in CdS film is observed. Due to the low sensitivity of SIMS to Hg, its profile could not be obtained reliably.

To improve resolution of the SIMS depth data, and also remove concerns regarding the impact of various SIMS artifacts on the results obtained, investigations were carried out on the same samples with the CdTe films removed (by etching in 40% w/w aqueous FeCl₃ solution) (fig. 3b). This allowed

direct sampling of the CdS layers. Results again showed an enhancement in the concentration of Cu in the CdS film following back-contact preparation (e.g. 5×10^{17} Cu atoms/cm³ for non-contacted samples to 2.5×10^{19} Cu atoms/cm³ for contacted, non-stressed cells). No significant change, with stressing, in the amount of Cu through most of the CdS film was found, but an accumulation of Cu very near the CdS/TCO interface was observed. The amount of Cu present at this interface increases with longer stress times. A high Cu concentration at the CdS/TCO interface may be expected to affect the quality of the cell front contact, and thus affect cell behavior and performance. Interestingly, the SIMS Cu profile from the CdS film of a cell which had received 15 hours thermal stress (200°C, dark) in a clean N₂ atmosphere (not shown), was near identical to that obtained for a cell which had received 15 hours thermal stress (200°C) in air (note - we have previously shown that the degradation of cells is substantially slowed when thermal stressing is carried out in a clean-N₂ atmosphere [3]). This indicates that Cu present in the CdS film is not detrimental to the cell, but that the presence of O₂ is required for Cu-related degradation reactions to occur. Photoluminescence studies, to determine the effect and behavior of Cu within the CdS layer, are currently underway.

The profile of Cl in the CdTe/CdS cells was also monitored. Cl was found to also show an accumulation near the CdS region. However, no consistent changes or patterns in the Cl concentration of the CdTe and CdS layers were observed between the stressed and unstressed samples (with Cu containing back contact).

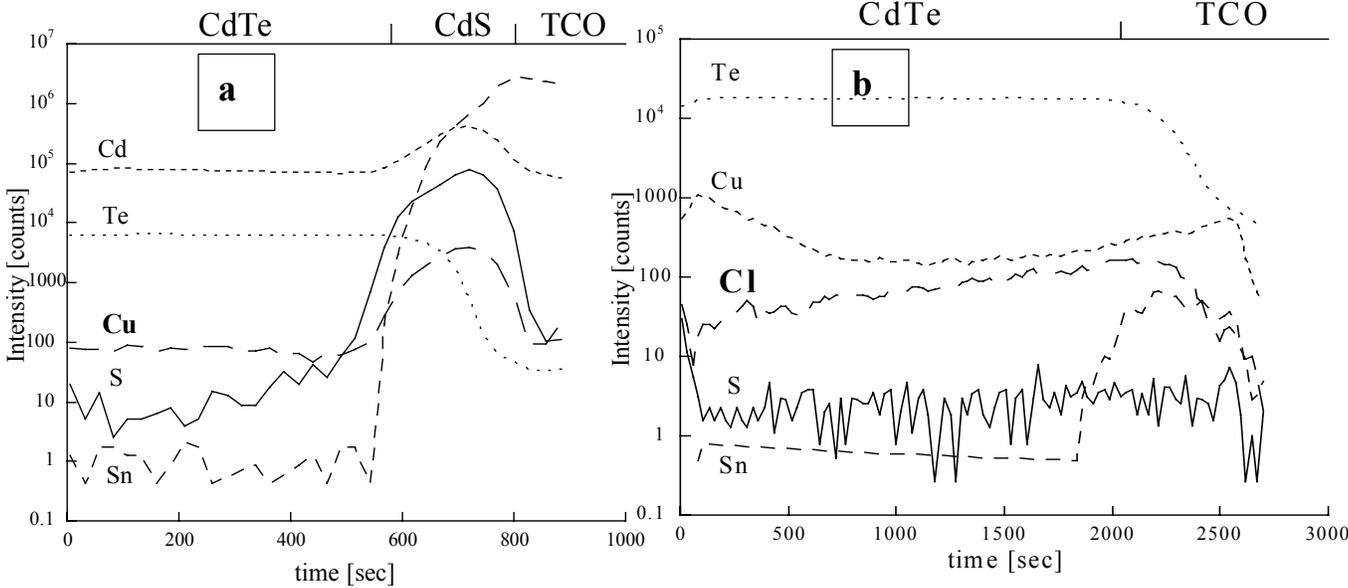


Figure 2: SIMS profiles of various elements in non-stressed cells, a. with CdS and b. without CdS

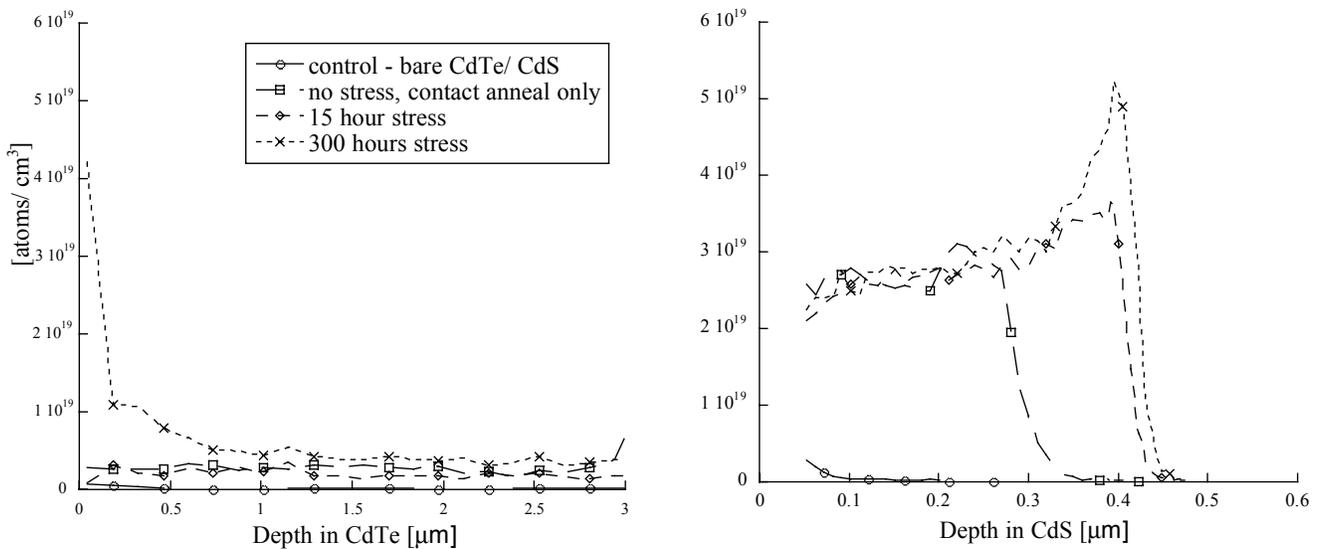


Figure 3: SIMS Cu profiles in CdTe and in CdS layers of cells with CdTe removed – with various stressing (200°C in air and in dark) times

Model for Cu-induced assisted degradation

Parts of this model were presented by DC at the Jan. 26, 2000 CdTe review meeting in Golden CO, USA.

In general the following observations are commonly accepted (for direct references see [1]):

- 1- *Adding Cu to CdTe back contacts improves the PV performance of CdTe/CdS solar cells.*
- 2- *Cu in the back contacts often also leads to poor stability of cells under working conditions.*
- 3- *Increasing [Cu] in the back contact increases the rate of cell degradation during stress testing.*

Deposition of Cu on Te-rich CdTe surfaces is found to form a Cu_2Te phase there. Increasing amounts of Cu_2Te correlate with improved cell performance. Following cell degradation the amount of Cu_2Te phase was found to decrease substantially (this correlates with the evolution of roll-over in the IV curve due to loss of the back contact). This suggests that

- 4- *Cu_2Te helps the formation of successful low resistance contacts to p-CdTe, but also acts as a source for further Cu diffusion into the cell.*

Cu uptake is found to be larger in conventional small-grain CdTe films than in larger-grained films and single crystal CdTe, under the same diffusion conditions. Hence

-5- GBs appear to be the most likely pathways for diffusion of Cu in polycrystalline CdTe (and CdS) films, and faster diffusion is expected there than in the bulk.

-6- Also Cl movement in CdTe/CdS cells, during CdCl₂ treatment is likely to occur via GB diffusion.

GBs offer low resistance pathways for diffusing species, which allow rapid transport throughout the CdTe layer and possibly further into the CdTe/CdS solar cell superstrate.

-7- Cu and Cl accumulate in, or at least near, the CdS layer of CdTe/CdS solar cells (SIMS). There is no clear evidence that this extends into the SnO₂ layer.

-8- Ion potential considerations indicate that Cu is unlikely to diffuse into the bulk CdS grains.

-9- A surface reaction of Cu with S is a possible driving force for Cu accumulation on CdS.

-10- Diffusion and accumulation of Cl and Cu may be correlated, e.g. formation of (Cu_{Cd}⁻-Cl_{Te}⁺)

-11- Enhanced (Cu_{Cd}⁻-Cl_{Te}⁺) concentrations in CdS will make the material highly resistive and photoconductive (Cu forms a deep acceptor while Cl forms a relatively shallow donor).

Schematic representation of some of the processes proposed to be involved in Cu-induced instability of CdTe/CdS solar cells is shown in figure 4. These include formation of Cu₂Te following deposition of Cu-containing back contacts, fast GB diffusion of Cu from the surface telluride (resulting in depletion of the Cu₂Te with cell degradation) and accumulation of Cu and Cl in GBs in or near the alloy and/or CdS regions. Although not further discussed here, Cu GB diffusion to the TCO interface, with the suggestion of reaction at the oxide surface or penetration of this interface, is also indicated as a possible cell degradation mechanism [1].

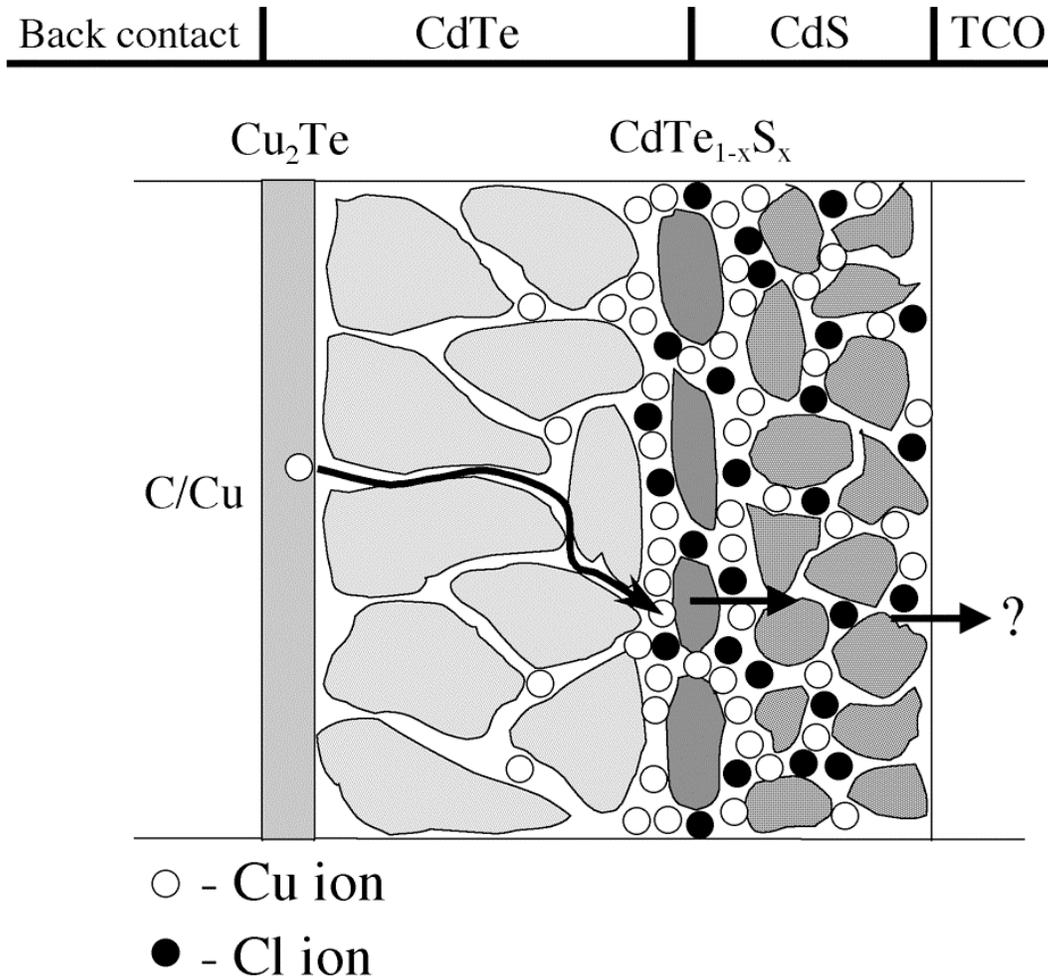


Figure 4: Schematic representation of processes involved in Cu-induced instability of CdTe/CdS solar cells.

Cu accumulation in /on CdS

Ion potential diagrams suggest that there is no thermodynamic driving force for Cu^+ to enter CdS. Further experimental work on this is in progress at the ENSC de Paris. Therefore, the Cu accumulation must have another explanation. We can make the following suggestions:

(1) Originally, during contacting, the Cu accumulates mainly at the CdS grain surface, driven by the concentration (activity) gradient of free Cu^+ , due to the relatively high Cu-S (or the even higher Cu-O) bond energy as compared to the Cu-Te one. This difference can be appreciated by comparing the enthalpies and free energies of formations of Cu sulfides (oxides) and Cu telluride [4]. The $\Delta\mu_{\text{Cu}}$ has to

be sufficient to overcome the electric potential difference, $\Delta\phi$, which exists at the PV junction and which opposes the drift of positively charged species across the junction in the CdS direction.

(2) Because we assume GB diffusion to dominate, the relative grain size of CdTe and CdS can provide a driving force for what may be in part a stochastic process, because CdS grains which tend to be (much) smaller than CdTe ones, can provide more binding sites for Cu.

(3) The ion diagrams consider only pure CdS and not Cl-doped CdS. According to P.L. Kukk and M.E. Altosaar [5] Cu solubility in CdS increases with increasing Cl content. Thus $\mu_{\text{Cu}}^{\text{CdS(Cl)}}$ may well be more negative (with respect to the reference level of Cu° in CdS) than $\mu_{\text{Cu}}^{\text{CdS}}$. Naturally, also here the resulting $\Delta\mu_{\text{Cu}}$ has to be sufficient to overcome the $\Delta\phi$, mentioned above.

Cl accumulation in / on / near CdS

Cl is known to dope Cd-chalcogenides, esp. CdS, CdSe and their alloys. Based on size considerations Cl (crystal radius 167 pm) is expected to prefer to substitute for S (170 pm) in CdS over Te (207 pm) in CdTe (Radii from [6]).

How come cells degrade only upon stress and do not show poor efficiencies immediately after preparation with Cu-containing back contact, at least in those cases where we find the Cu in/on/near the CdS?

(Here and in the following CdS stands for CdS and Cd(S,Te).)

We propose that the Cu ions that are ON the CdS grains do not adversely affect the material, possibly because they create only shallow surface states or only surface resonances. Also the Cl that, contrary to the Cu, HAS penetrated into the CdS grain forms only shallow (donor) levels. As such it is not detrimental to the electronic and optical properties of the CdS (this is in contrast to what is the case for Cu, which also without Cl can make the CdS resistive and photoconductive).

Upon stressing, the Cu will now enter the CdS grains and create the above-mentioned complex with Cl, which will lead to high resistive CdS³. As Cu leaves the surface, more Cu, hitherto stored on the

³ If we form CdS that is highly resistive, but NOT photoconductive, then we will have lost part of our photovoltage (the increase in $|E_{\text{CB}}-E_{\text{F}}|$), i.e. V_{oc} decreases. In this case both in the dark and in the light a high resistance will be measured. If we form CdS that is photoconductive, then the photovoltage may not be affected at all, because under illumination the quasi- E_{F} shifts back to its original position close to E_{CB} . In this case there will be a marked difference in resistance at forward bias under illumination and in the dark. This effect is similar to what is seen in dye-sensitized solar cells where ALL of the photovoltage comes from an (in that case indirect) light-induced shift in the quasi E_{F} .

CdTe or more probably in the contact/Cu_xTe, will arrive to take its place. At some point all of the Cl will be complexed with the Cu and additional Cu that will arrive will be present in other forms. These other forms will decrease the carrier mobility-lifetime product (diffusion length) and increase recombination. This will decrease V_{OC} and FF and ultimately also the I_{SC}. Taking a bulk diffusion coefficient of 10⁻¹² cm²/sec and a 1 μm grain this will take a day or two. However, this assumes diffusion of Cu already in the CdS or possibly from a Cu^o source. In our case, we need to break the Cu-S (Cu-O) bond, which can significantly retard the process.

I_{sc} vs. V_{oc} stressing

Stressing has the strongest effect when done at V_{oc} (OC) or forward bias [1]. This follows directly from the analyses by Lubomirski and Cahen on p/n junction stability ([7], [8]). Cu moves as a positive species. The built-in potential at the CdTe/CdS junction is such that it opposes the Cu movement i.e. diffusion and drift are opposing each other. At OC / under forward bias this field is cancelled, or even reversed. The effect becomes significant beyond the max power point.

At SC the field is there in full strength, something that will slow down the transfer of Cu to the CdS region. Stressing at SC we get (initially, at least) only changes in the dark I-V, not in the photo I-V. Even if we get resistive CdS, we maintain good back contact and will not get a second junction. This is in contrast to what happens at OC, where the increased outflux of Cu can lead to loss of back contact (if there is not sufficient Cu reserve at the back contact) and the evolution of roll-over in the IV curves.

Na

Possibly Na can take the place of Cu ON the CdS and thus retard the arrival of Cu during contact formation or later, during stress. This can limit or slow down the degradation of cell performance.

O₂/N₂

Several reports exist showing that stress in O₂ brings about faster degradation than stress in inert atmospheres [3]. In an (extra) O₂-containing environment (because there will always be some present; even at 10⁻⁶ torr a monolayer can form in seconds) the CdTe surface will oxygenate (bulk oxidation; cf. eq. (1)) more readily than CdS. Let us consider the effect of O₂ on the surface band bending and on the bulk doping of CdS and CdTe grains. Because of the general surface reaction



the positive surface charge is decreased. The reaction of O_2 with the surface will take free electrons from the bulk, i.e., oxidize the bulk, but will reduce the surface. For CdTe (*CdS*) this means that the doping level of the grains is increased (*decreased*) and that the barrier for electron transport across the grain boundaries is decreased (*increased*).

Most of the junction band bending is thought to be in the CdTe. Therefore, the effect there can dominate. Then, in analogy to what has been worked out for CIGS, the decrease in surface barrier for CdTe implies not just improved carrier collection, but also a decrease in the junction band-bending and in the V_{oc} .

Another factor will be enhanced diffusion due to increased oxidation of the CdTe and CdS grain surfaces, which is expected to decrease activation energies along these surfaces.

However, it appears to be likely that a more trivial effect may be involved or even dominate, viz. loss of back contact, electrically and /or mechanically (loss of adhesion due to oxidation). This would appear to be worthwhile to investigate further.

Task 3: Chemical treatments and novel back-contact materials

Surface Treatment of CdTe

Purpose: To control CdTe grain boundary chemistry and through this, GB electronic behavior.

Organic molecules were deposited on the CdTe back surface prior to contact deposition. The molecules used were benzoic and tartaric acid derivatives, with (di)carboxylic acids as the binding elements and aromatic substituents as auxiliary elements (fig. 5). Such molecules were shown to affect the electron affinity and the band bending of n-CdTe surfaces in a controllable manner [9], and their

adsorption in Cu(In, Ga)Se₂/CdS junctions was shown by our group to affect charge transport properties of that cell [10].

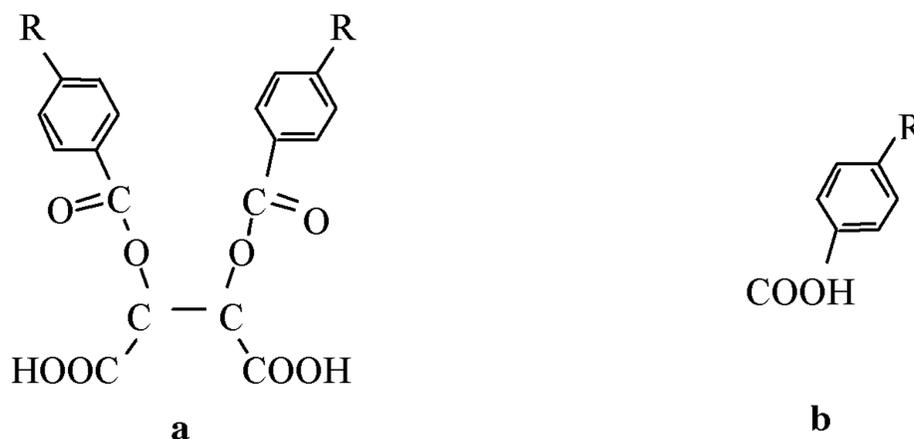


Figure 5: Schematic representation of the structure of: a. the dicarboxylic acid derivatives. R = H, CF₃, CN (electron acceptor groups, dipole moment pointing away from the surface), b. benzoic acid derivatives. R= OCH₃ (anisic acid) or N(CH₃)₂ (DMA) (dipole moment pointing towards the surface), CN, Br, NO₂ (electron acceptor groups, dipole moment pointing away from the surface).

The cells (received from USF and First Solar, LLC) to be measured were etched in 0.1% Br₂/methanol (v/v) for 10 sec, then soaked overnight in a 2 mM acetonitrile solutions of each carboxylic acid. The cells were washed in acetonitrile prior to the contact potential difference (CPD) measurements in order to remove excess (non-adsorbed) molecules. The same procedure was followed for 5 mM solutions of the benzoic acid derivatives in acetonitrile.

Dark CPD measurements show a change in the work function of the CdTe surface after molecule adsorption, which scales with the direction (as well as the relative magnitude) of the dipole moment: A decrease in the CPD (more negative) when the dipole points towards the surface and an increase in the CPD when the dipole moment is pointing away from the surface) (fig. 6).

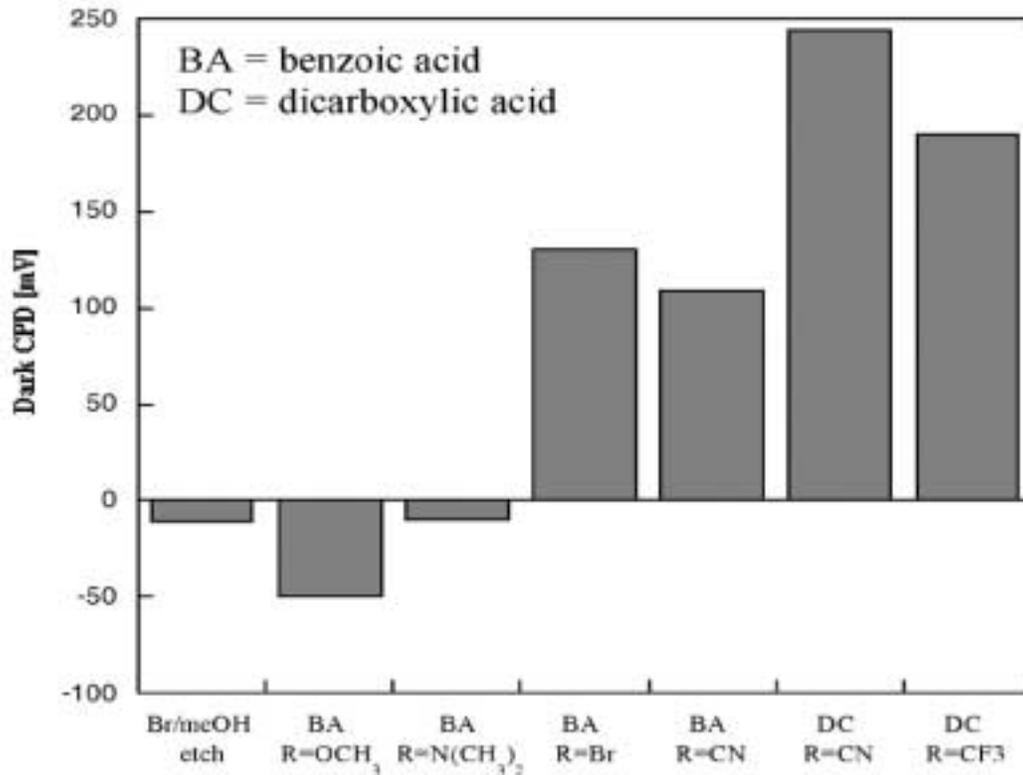


Figure 6: Changes in CPD of the CdTe back surface, as a function of the surface treatment

Surface Photovoltage Spectroscopy (SPS) measures the CPD under illumination at different wavelengths. Typical curves showing the CPD as a function of the wavelength are shown in figure 7. The samples were illuminated through the back CdTe surface.

The CPD decrease at wavelengths longer than 830 nm might be due to band flattening at the cell junction, as the CdTe is transparent to these photons (flattening of the surface band-bending in the p-CdTe would result in an increase of the CPD). The increase in the CPD from 830 nm is due to band flattening at the surface combined with return of the band bending at the junction, as most photons are now absorbed at the surface.

Certain adsorbed molecules push the onset of the photo-response (the beginning of the drop in the CPD) to shorter wavelengths, possibly indicating that the molecules reached the junction area (via GBs) and changed the absorption properties there.

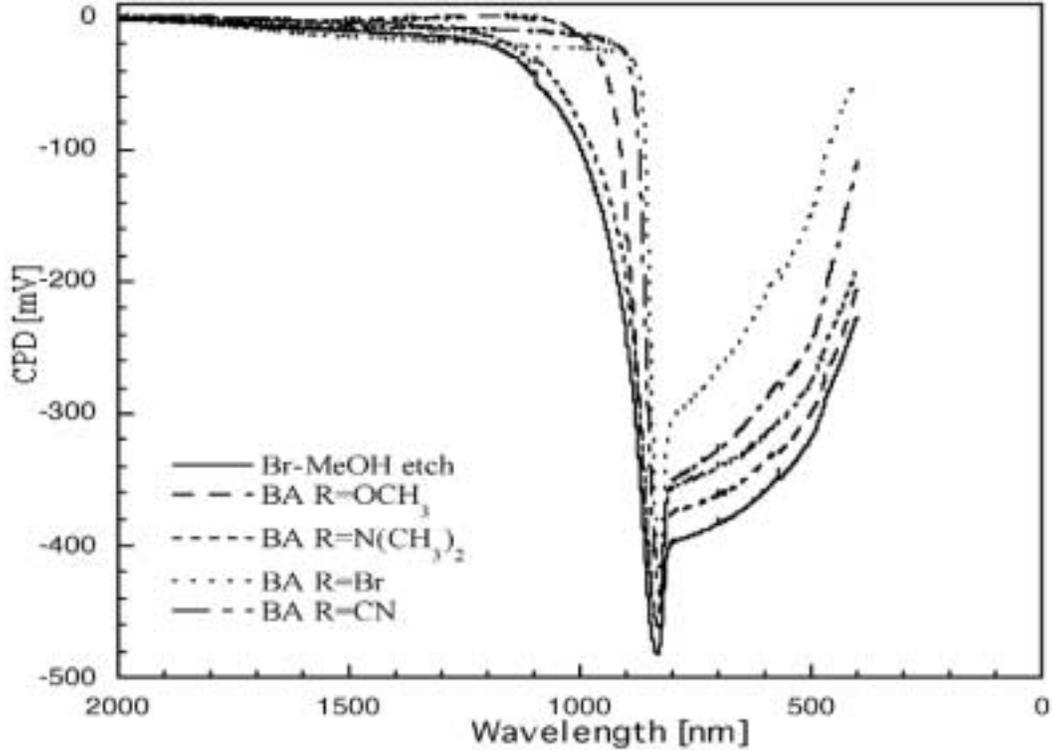


Figure 7: SPS of CdTe in CdTe/CdS cells. Illumination was through the CdTe back surface. (All plots have been offset to the same dark value)

Adsorbed molecules with $R=CF_3$, Br or CN usually pushed the onset of the photo-response to shorter wavelengths. In samples with adsorbed OCH_3 -BA and $N(CH_3)_2$ -BA, the onset occurred at longer wavelengths compared to that in samples with dipole moments pointing away from the surface (the onset of photoresponse in etched and solvent-soaked only samples might depend on the oxide layer). Similar behavior has been observed in USF and in FS cells.

SPS measured with illumination through the glass (the front cell contact) showed that the dark CPD value, as well as the general shape of the curve, is kept at wavelengths longer than the E_g (830 nm) (fig. 8). The onset of the photoresponse shifts to longer wavelengths when illuminated through the glass, but the trend of molecule-induced shifts according to the direction of the dipole moment, is preserved. The drop in the CPD might again reflect the flattening of the junction band-bending due to absorption by junction in-gap states in the CdTe (or by $CdTe_xS_{1-x}$?). When the CdTe starts absorbing, the light is still absorbed near the junction. Therefore, there is no return of the band bending and the CPD value remains almost unchanged till ~ 540 nm (2.3 eV - a little lower in energy than $E_g(CdS)=2.4$ eV,

eV, maybe due to in-gap states in the CdS-SnO₂ interface) where the CdS starts absorbing and the junction band bending returns. The difference observed between the illumination directions at wavelengths shorter than 830 nm is explained by the absorption at the CdTe-CdS interface instead of the CdTe surface, when the CdTe is no longer transparent.

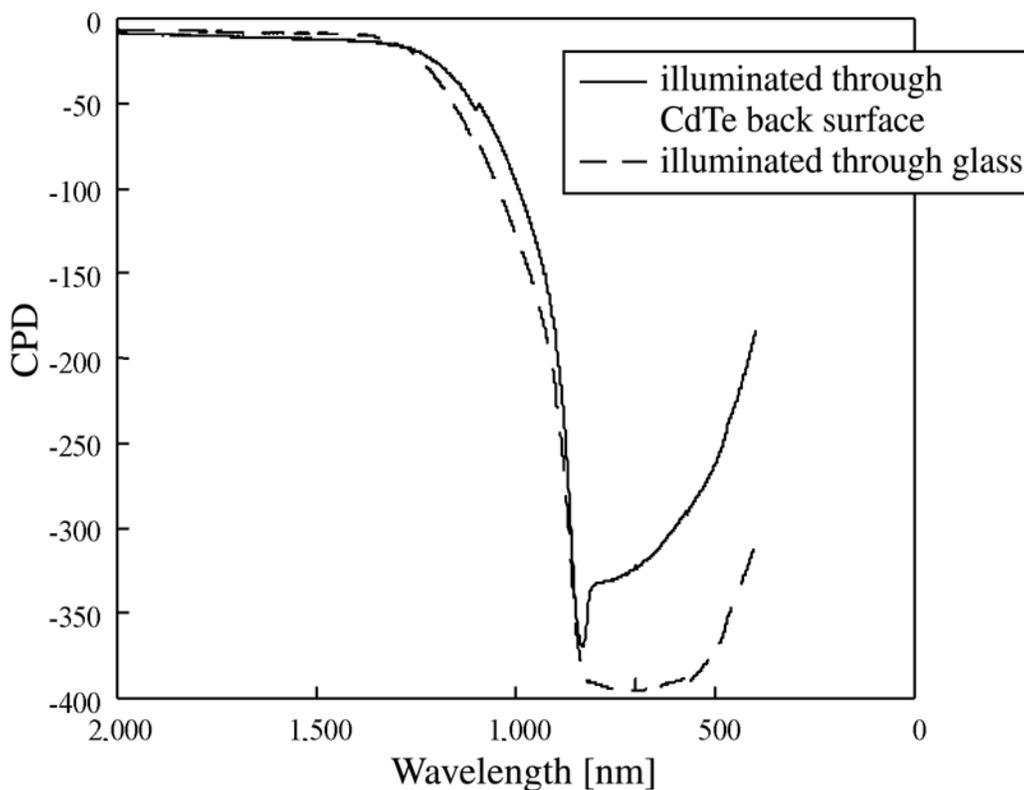


Figure 8: Comparison of SPS with different direction of illumination (USF cell, non-contacted, treated with BA R=OCH₃).

Preliminary **I-V measurements** of these cells (after application of Cu/HgTe doped graphite contact, received from USF) show an effect of the presence of molecules on the photovoltaic behavior. The slope of dark IV curve close to V=0 changes after adsorption of different molecules, which indicates that the molecules do affect the junction (figure 8, top). In dark, molecules with dipole moments pointing towards the surface "improve" diode characteristics of the junction (better FF), while those with dipole moments pointing away from the surface produced little change in the IV characteristics. In light, however, molecules with dipole moments pointing away from the surface worsened the

photovoltaic behavior of the cell (worse FF, lower J_{sc}), while those with dipole moments pointing towards the surface produced little change in the IV characteristics (figure 9, bottom). The behavior under illumination is influenced by generation and separation of charge carriers in a large SCL. Therefore, this probably reflects the influence of the molecules on the junction as well as on the CdTe layer and on the back contact/ CdTe interface. The behavior in dark (close to zero) reflects mostly the properties of the junction area only. Most of the cells with adsorbed molecules showed a "bending" of the curve near open circuit conditions ($I=0$). This is where the junction band bending is minimal and therefore it probably reflects recombination in the junction region or a series resistance in the back contact ("roll-over").

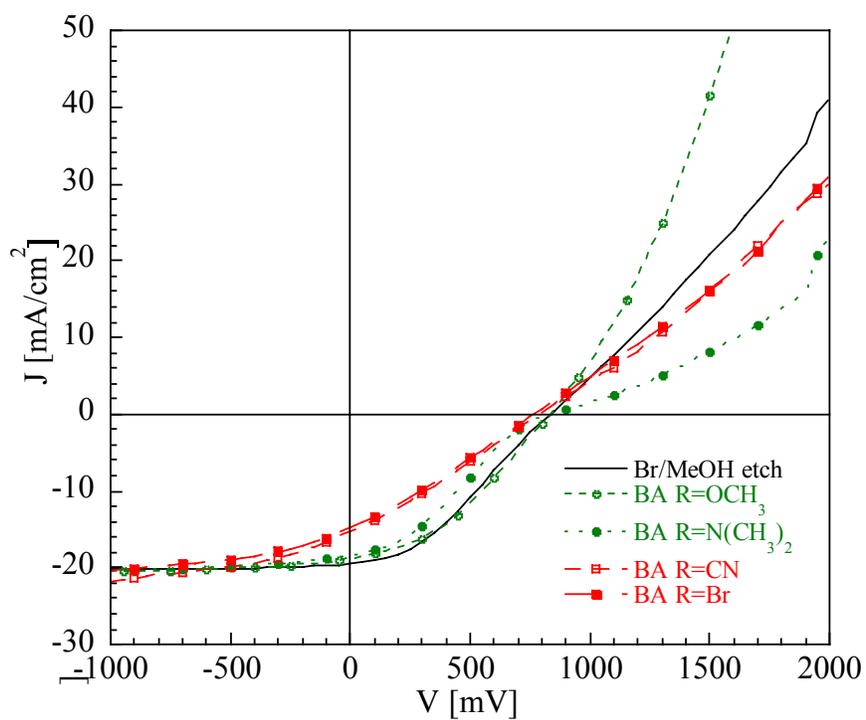
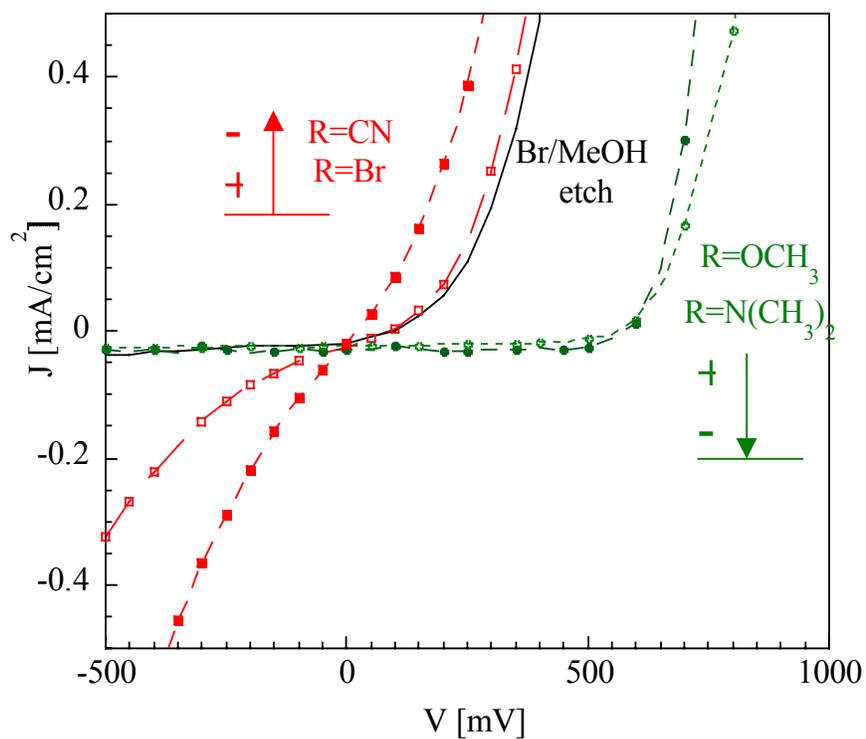


Figure 9: Representative IV curves of (USF) cells with adsorbed molecules; top: dark, bottom: light

In samples received from First Solar, LLC, the molecules decreased the efficiency, mainly due to decrease of FF. Molecules with dipole moments pointing towards the surface produced a smaller effect on the efficiency. The trend is not as clear in USF samples. Results up till now show that adsorption of organic molecules influences the electronic behavior of these cells. Further work is needed to optimize this interface treatment, to see if also it can improve the cell performance and to understand these effects.

Ni:P and NiTe₂ back-contacts

The studies of the electroless-Ni:P back contacts have continued. In our first annual report [3] it was shown that CdTe/CdS cells of superior performance were obtained when the Ni:P back-contacts were deposited from baths of lower hypophosphite (HP) (reductant), concentration (giving dull-brown contacts as opposed to the shiny contacts obtained from baths of higher reductant concentration).

Both materials are deposited on CdTe from aqueous baths, containing NiCl₂.6H₂O, sodium citrate and NH₄Cl, of pH = 8-9 (NH₄OH) at 90 – 95°C. Electroless Ni:P (shiny contact) is deposited on CdTe from baths which also contain > ~0.2 mol dm⁻³ HP. Ni:P deposition proceeds with copious evolution of H₂(g), while the dull-brown contacts, prepared in baths with no added HP or of low [HP], form with little H₂ evolution. During formation of the dull-brown contact, a gray surface deposit forms a short time after sample immersion, with the product itself only beginning to form (growing from the cell edges) after ~30 minutes immersion. The reaction reaches completion within 60 minutes of sample immersion. Both contacts receive anneal treatments at 200°C for 90 minutes in air.

X-ray diffraction (XRD) studies have been carried out on both contact materials. Fig. 10(a) shows the XRD patterns of a shiny Ni:P contact, before and after anneal. The spectra are dominated by the CdTe pattern and a single, broad peak at 44.5°, due to the Ni(111) plane, which becomes stronger with annealing. The width of the Ni peak may be indicative of small crystal size or strain in the film. Fig. 10(b) shows the XRD patterns of a bare CdTe/CdS solar cell, the dull-brown contact and the gray product formed initially in the chemical bath. The spectrum of the gray region indicates the presence of elemental Te. The pattern of the dull-contact contains two new peaks at 32° and 34°. These features

correlate to the (101) and (002) planes of NiTe₂ (or melonite, PDF #08-0004) No metallic-Ni is observed in either area.

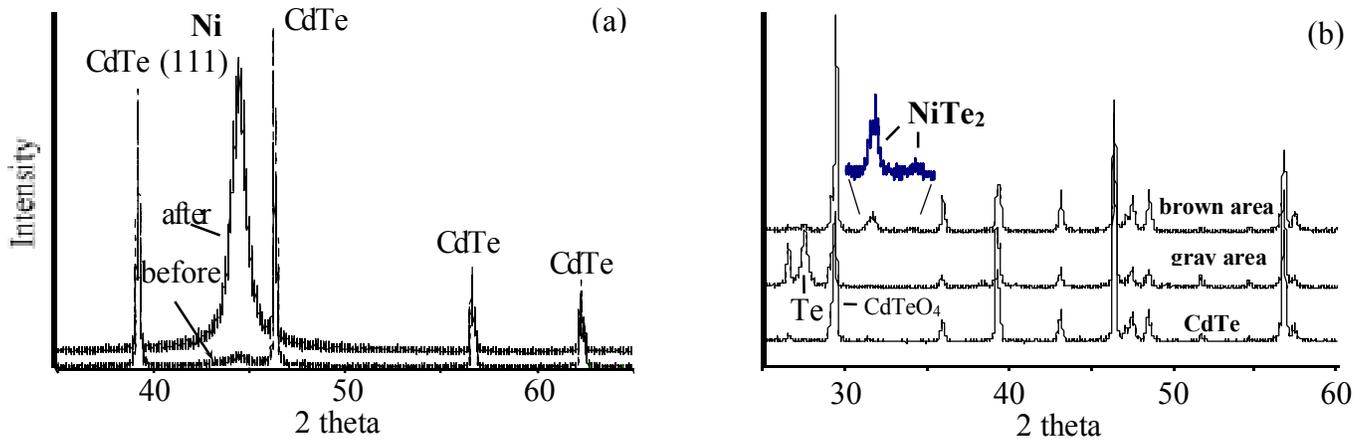


Figure 10: XRD patterns of (a) electroless Ni back-contact, before and after anneal, deposited on a CdTe/CdS solar cell and of (b) bare CdTe and the ‘brown’ and ‘gray’ areas formed during NiTe₂ deposition on CdTe/CdS solar cells.

X-ray photoelectron spectroscopic measurements of electroless Ni:P contacts (not shown), showed up to 10% P (originating from HP) at the surface. Little change in composition was observed following contact anneal. Fig. 11 shows the Ni 2p and Te 3d core level regions from XPS spectra of the NiTe₂ deposit, recorded at increasing sputter depths. The spectra confirm that Ni is present in the form of Ni²⁺ (d⁸) (e.g. Ni²⁺Te₂²⁻). The NiTe₂ was found to be ~0.1μm thick. The gray deposit was found to be Te-rich, but containing no Ni. No P was found in either the NiTe₂ or the gray product, even when HP had been present in the chemical bath. In the early stages of deposition, the bath appears to act as an etchant solution, forming the gray Te-rich CdTe surface. In time, NiTe₂ is formed, possibly via a surface-replacement reaction with Ni²⁺ ions.

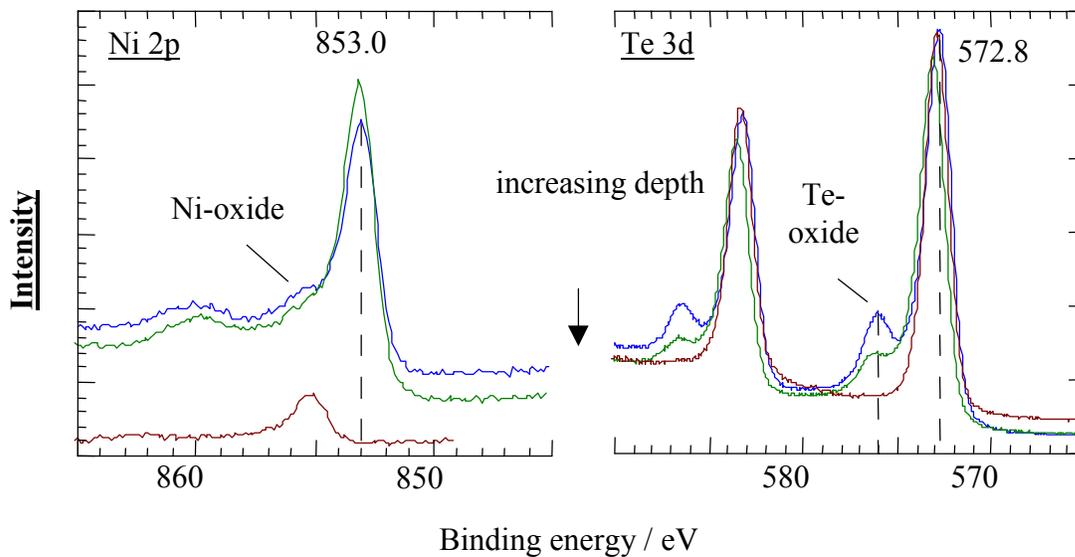


Figure 11: XPS spectra of Ni 2p and Te 3p core levels of the brown NiTe₂ deposit.

Preparation of the dull-brown NiTe₂ contacts has been found to be not reproducible between different samples of the NiCl₂·6H₂O starting material. In each case the CdTe receives the surface etch (forming the gray deposit), but formation of the NiTe₂ product does not always occur. Our observations indicate that NiTe₂ is more likely to form as the NiCl₂·6H₂O samples age. This behavior is indicative of the presence of an, as yet, unidentified contaminant (however, preliminary results indicate that Al may be present in the starting material and may act as a catalyst for NiTe₂ formation).

Cell stability is an important consideration for determining the success of a new back contact. Diffusion of species from back-contacts has been proposed to be a possible degradation mechanism of CdTe/CdS cells [1],[11]. SIMS investigations of NiTe₂ contacted cells (not shown), have found that following thermal stress (200°C in air for 20 hours), there is no Ni movement or accumulation in the cell, as has been previously seen for Cu from Cu-containing back contacts [1],[11]. This may be an important observation for future stability considerations of cells contacted with NiTe₂ and similar materials.

While NiTe₂-contacted cells may be expected to exhibit reasonable stability, in our previous report [3] we highlighted an observation of a decrease in cell behavior with storage in ambient conditions. However, no such effect was noted when cells were stored in dry air, indicating a susceptibility of the contact material to H₂O vapor. This degradation effect has been found to be reversible, with restoration

of cell performance occurring within a few days of returning cells to dry air conditions. This indicates that no chemical changes occur within either the contact material or the cell itself on exposure to water vapor, but that the observed effects must be due to physical processes. We note that any such degradation could be overcome in the field by encapsulation.

Preliminary results have been collected in the form of a short paper on the Ni:P and NiTe₂ work; submitted to 'Thin Solid Films' as part of the Proceedings of the E-MRS 2000 Spring Meeting in Strasbourg, France.

Conclusions

Front wall LBIC has been found to be useful to monitor the condition and quality of the cell junction. It can also be used to identify areas of low current or contact as a result of mechanical damage to cells. Front-wall LBIC is non-destructive and results can be rapidly obtained.

Complete cells, supplied by NREL and First Solar, have produced front-wall LBIC results analogous to those obtained for First Solar cells contacted here. The stressed cells show a higher degree of heterogeneity in the LBIC images than unstressed cells. NREL cells stressed under illumination showed, from I-V curves, a greater degree of degradation and, from LBIC, a greater degree of heterogeneity in the current images, than unstressed cells.

Contacting the cells with graphite containing Cu-doped HgTe results in an increase of Cu concentration in the CdTe layer and an accumulation of Cu near the CdS layer of the cell. With stress a notable increase in the level of Cu in the CdS part is observed. With stressing, an accumulation of Cu very near the CdS/TCO interface was observed, which increases with longer stress times. A high Cu concentration at the CdS/TCO interface may be expected to affect the quality of the cell front contact, and thus affect cell behavior and performance. Stressing cells in different environments indicates that Cu present in the CdS film is not detrimental to the cell, but that the presence of O₂ is required for Cu-related degradation reactions to occur. Also Cl was found to accumulate near the CdS region.

A model is proposed for Cu-related degradation mechanisms. It includes formation of Cu_2Te following deposition of Cu-containing back contacts, fast GB diffusion of Cu from the surface telluride (resulting in depletion of the Cu_2Te , with cell degradation) and accumulation of Cu and Cl in GBs in or near the alloy and/or CdS regions, which makes it photoconductive. The model suggest an explanation for the observation that cells degrade only upon stress and do not show poor efficiencies immediately after preparation with Cu-containing back contact, and to the differences between cells stressed at forward- and reverse-bias. The explanation is based on the diffusion of Cu as a positively charged ion. The effect of surface oxidation on the doping levels is also discussed.

Adsorption of organic molecules influences the electronic behavior of the back CdTe surface, as well as the GB properties. This chemical treatment affects the PV behavior of the CdTe/CdS cell, which may also be explained by a change in the junction electronic properties as well as a change in the optical absorption of the CdTe in the vicinity of the junction. The nature of these effects depends on the direction of the molecules' dipole moment.

Electroless Ni-P contacts, deposited under conditions which give good PV behavior, appear to be predominantly NiTe_2 rather than metallic Ni. No P was found. In the early stages of deposition, the bath appears to act as an etchant solution, forming a gray Te-rich CdTe surface. In time, NiTe_2 is formed, possibly via a surface-replacement reaction with Ni^{2+} ions. SIMS investigations of NiTe_2 contacted cells show that, following thermal stress, there is no Ni movement or accumulation in the cell. The degradation effects resulting from storage in ambient conditions were found to be reversible.

Further Work

Further measurements are planned to detect the diffusion of other contact-related species, such as Hg. Photoluminescence studies, to determine the effect and behavior of Cu within the CdS layer, are currently underway. Stressed and unstressed cells will again be used for comparison in order to have a better understanding of diffusion-related degradation.

Back-wall LBIC studies have previously shown a junction around 30-50 μm from the edge of Cu/HgTe/graphite back contacts of non-stressed cells. This phenomenon may be related to fast diffusion of ionic species from the back contact. SIMS analysis of the junction region is underway (S. Asher, NREL).

Work is underway to enable electrical measurements of a single grain and a single grain boundary. These include the use of electron microscopy for using a manipulated probe with sub-micrometer resolution, as well as the use of scanning probe microscopy techniques (as explained in [3]). Such measurements can assist in checking some of the ideas suggested in the “model for Cu-assisted degradation” section, as well as characterizing the effect of chemical treatments (see in “task 3” section) on the grain bulk and surface.

Further investigation of the influence of adsorption of organic molecules on the CdTe surface will be done, in order to better understand it and, eventually, use it to improve cell efficiency and stability. Such investigations include adsorption of a wider variety of molecules, characterization of the effect of molecule adsorption on the electronic properties of single-crystal p-CdTe, and further characterization of treated cells. Inorganic chemical treatments of CdTe may also be examined.

Further characterization of the NiTe₂ back contact is planned, especially the identification of contaminants in the NiCl₂·6H₂O solution which affect the behavior of the deposited contact. Co will also be studied in place of Ni.

References

1. K. D. Dobson, I. Visoly-Fisher, G. Hodes and D. Cahen, *Sol. Energy Mater. Sol. Cells*, 62 (2000), 295.
2. C. Narayanswamy, T.A. Gessert, and S.E. Asher. in *15th NCPV Photovoltaics Program Review Meeting (AIP CP462)* (1998), 248.
3. D. Cahen, K. Gartsman, G. Hodes, O. Rotlevi, I. Visoly-Fisher and K. D. Dobson, *First Annual Report*, (1999) Weizmann Institute of Science.

4. D. Cahen and R. Noufi, *J. Phys. Chem. Solids*, **52** (1991), 947.
5. P. L. Kukk and M.E. Altosaar, *J. Solid State Chem.*, **48** (1983), 1.
6. R. D. Shannon, *Structure and Bonding in Crystals*, ed. M. O'Keefe and A. Navrotsky. Vol. 2. (1981), New York: Academic.
7. I. Lubomirsky and D. Cahen. *Electrochem. Solid State Lett.*, **2**(3) (1999), 154.
8. I. Lubomirsky and D. Cahen, *Sol. State Ionics*, (2000), in press.
9. R. Cohen, S. Bastide, D. Cahen, J. Libman, A. Shanzer and Y. Rosenwaks, *Advanced Materials*, **9** (1997), 746.
10. D. Gal, E. Sone, R. Cohen, G. Hodes, J. Libman, A. Shanzer, H-W. Schock and D. Cahen, *Proc. Ind. Acad. Sci. Chem. Sci.*, **109** (1997), 487.
11. H. C. Chou, A. Rohatgi, N. M. Jokerst, E. W. Thomas and S. Kamra., *J. Electron. Mater.*, **25**(7) (1996), 1093.

| REPORT DOCUMENTATION PAGE | | | Form Approved OMB NO. 0704-0188 | |
|---|---|---|--|--|
| Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503. | | | | |
| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE January 2001 | 3. REPORT TYPE AND DATES COVERED Second Annual Report August 1999 – August 2000 | | |
| 4. TITLE AND SUBTITLE Overcoming Degradation Mechanisms in CdTe Solar Cells; Second Annual Report, August 1999 – August 2000 | | | 5. FUNDING NUMBERS C: AAK-8-17619-15 TA: PVP1.5003 | |
| 6. AUTHOR(S) D. Cahen, G. Hodes, K. Gartsman | | | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Weizmann Institute of Science Rehovot, Israel | | | 8. PERFORMING ORGANIZATION REPORT NUMBER | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393 | | | 10. SPONSORING/MONITORING AGENCY REPORT NUMBER NREL/SR-520-29416 | |
| 11. SUPPLEMENTARY NOTES NREL Technical Monitor: B. von Roedern | | | | |
| 12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161 | | | 12b. DISTRIBUTION CODE | |
| 13. ABSTRACT (<i>Maximum 200 words</i>) The scientific literature concerning degradation and atomic diffusion in CdTe/CdS cells has been reviewed. This led to the conclusion that there appear to be unexplained differences between module and cell stability, possibly due to the difference between encapsulated and air-exposed systems. A comprehensive model for Cu-assisted cell degradation is suggested, which should now be tested experimentally by the appropriate R&D teams. Both LBIC and EBIC have been used to distinguish between stressed and unstressed cells. From these we conclude that decrease in charge separation efficiency is correlated with increase in electrical heterogeneity of the cell. Cells without back contacts were treated with a series of simple organic compounds, where the dipole is varied systematically. We find, <i>grosso modo</i> , such systematics in the electronic behavior and electrical characteristics of these cells, suggesting significant porosity of the CdTe film. NiTe ₂ was found to be the product of electroless Ni:P back contact deposition from baths of low reductant concentrations. Such back contacts were further optimized and characterized, with special attention being given to cell stability considerations. | | | | |
| 14. SUBJECT TERMS photovoltaics; degradation; atomic diffusion; CdTe/CdS cells; module and cell stability; electrical heterogeneity; back contacts; CdTe film | | | 15. NUMBER OF PAGES | |
| | | | 16. PRICE CODE | |
| 17. SECURITY CLASSIFICATION OF REPORT Unclassified | 18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified | 19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified | 20. LIMITATION OF ABSTRACT UL | |