Subcontractor Report

Overcoming Degradation Mechanisms in CdTe Solar Cells

First Annual Report
August 1998 — August 1999

D. Cahen, K. Gartsman, G. Hodes, O. Rotlevy, I. Visoly-Fisher, and K. Dobson
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NOTICE

Project Title: **Overcoming Degradation Mechanisms in CdTe Solar Cells**

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Subcontractor: Weizmann Institute of Science, Rehovot 76100, Israel.

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ABSTRACT
The importance of chemical processes for the stability of CdTe solar cells, in particular diffusion in the ohmic contact/ absorber junction regions, is studied. Both whole cells and test systems containing only the ohmic contact and the absorber are used. We found several experimental methods to be useable tools to follow effects of impurity diffusion on the CdTe GBs, grain bulk and surface. In addition we have explored alternative contacting schemes.
Our first year of activities lead to the following tentative conclusions:
- GBs in CdTe/CdS cells are NOT fully passivated and are expected to be electrically active.
- There appears to be fast ionic diffusion in the vicinity of the Cu/HgTe/graphite back contact, possibly enhanced by GB diffusion.
- The macroscopic response to stress is different for cells, with identical back contact but from different manufacturers. Possibly different factors, and/ or different reactions to identical factors are at work here.
- Ni-P appears to be a promising back-contact material.

[#] **Several figures are collected in the appendix. These are marked as A1 - A4**. The other figures (from 5 onwards) appear embedded in the text.

Objectives
To investigate the back 'ohmic' contact to the p-CdTe with the aim of improving the stability of this contact while maintaining performance. Several strategies are involved in this study.
1. Separate back contact lifetime performance from overall cell lifetime performance.
2. Investigate new back contact materials.
3. Explore use of surface treatment of the CdTe to modify the contact.

1st year Milestones
-1- Establish experimental capabilities to measure diffusion of species in CdTe solar cells at temperatures at which the bias stressing experiments are carried out.
-2- Complete experiments aimed at separating degradation effects of the back contact region from those in the absorber layer and in the front junction regions in devices with currently used back-contacting schemes.

1st year problems
(Very) late availability of sets of stressed vs. unstressed samples

TASK 1:   Diffusion processes
-A- *Is cell degradation connected only with back contact degradation or are other factors involved?*

Our approach is to effect chemical changes of the films, grain boundaries (GBs), grain bulk and surface, and to examine how these changes influence the material's electrical properties and the overall PV cell performance. In addition, we characterize the (opto)electronic properties of the different parts of the material: the grain bulk, the grain surface and the GBs.

-B- *How can we measure experimentally the diffusion of impurities in CdTe cells or appropriate test structures?*

Our approach is to characterize the effect of diffusion of impurities on the CdTe GBs, grain bulk and surface. In particular, we are looking for differences in that effect between GBs and grain bulk/ surface, that might indicate preferential diffusion paths and/or differences in the electronic activity of impurities in the different parts of the material. For that purpose we have put in place the following spatially controlled electrical measurement methods.

METHODS
Use of high-resolution microscopy with accurately manipulated probes will enable placing two probes across a single GB/ single grain, or along a single GB. As a first step we use one probe, accurately positioned on the CdTe back surface, to measure across the film with the conductive substrate as the opposite contact.
IV curves are used for conduction mechanism characterization (see, for example, Fig. A1).

Scanning probe techniques:
SSR (scanning spreading resistance)– A small bias is applied between a sharp conducting AFM tip and the sample, and the resulting current is measured during scanning in contact mode. If a constant contact area is assumed, SSR can resolve areas of different conductivity, indicating possible differences in carrier concentration, type and mobility (see, for example, Fig. A2).

STS & CITS –STS (scanning tunneling spectroscopy) provides a curve of the tunneling current as a function of the bias voltage between an STM tip and the sample surface at a designated point. Such curve can provide information about the local density of states distribution and the energy gap. In continuous imaging tunneling spectroscopy (CITS) an STS curve is measured at each selected point, at a constant tip-surface separation. The current corresponding to a chosen bias is plotted as a function of tip position. In this way local differences in electronic properties can be observed. Up till now we have been able to obtain reliable results only by STS, and then in isolated cases.

SKP (Scanning Kelvin Probe) (+SSPV; Scanning Surface PhotoVoltage): Uses a conductive AFM tip as a Kelvin probe to measure the surface potential. At a constant tip-surface separation, an oscillating voltage with amplitude V_{ac} is applied to the tip. This creates an oscillating force on the tip cantilever, at the same frequency, with amplitude $F = \dfrac{dC}{dZ}V_{dc}V_{ac}$, where dC/dZ is the vertical derivative of the tip/sample capacitance, and V_{dc} is the dc voltage difference between the tip and the sample. When the tip and the sample surface are at the same potential (V_{dc}=0), the cantilever feels no oscillating force. The tip potential is then plotted as a function of tip position, creating a surface potential map (see, for example, Fig.A3). The measurement can be performed in the dark or under illumination, which changes the surface potential due to free carrier generation. Using laser illumination at fixed wavelengths, focused on the scanned area through an optical fiber, allows one to perform spectroscopy of local surface photovoltage changes ("SKP+SSPV"). This can be used to detect differences in the band bending and/ or surface states distribution in the vicinity of GBs, and to probe changes in the local surface potential, induced by chemical treatments.

EBIC & LBIC (electron- beam-induced current & light beam induced current):   Absorption   of   an electron or optical (laser) beam of photons with energy larger than the band gap energy (hν>E_g) by the sample material generates electron-hole pairs. If these are generated near an internal electric field, the charge carriers can be separated to produce an electric current. The direction of the current depends on the field direction. Scanning the surface by an electron/ laser beam enables creating an image corresponding to the relative magnitude of the current in a given direction, as a function of the beam position, revealing the location and direction of internal fields. Current in the opposite direction will appear as dark (zero current) area. EBIC may also be used to measure carrier diffusion length/ effective lifetime. Both methods are commonly performed by scanning a thin Schottky contact on the sample surface which collects the induced currents (the substrate of the sample is grounded) (see, for example, Fig. A4). Remote EBIC (LBIC) is done by scanning the area between remote contacts, which collect the induced currents.

RESULTS
Several of the characterization techniques were tested for applicability. The samples were solar cell quality CdTe films on SnO$_2$:F substrates.

EBIC showed contrast between GBs and grain bulk, when mapped under a Schottky (evaporated Au) contact (Fig. A4). Such contrast indicates a variation in the space charge layer (SCL), induced by the Au contact near the GBs. This phenomenon may be caused by a GB SCL, which affects the Schottky contact SCL at its intersection, or by different doping concentrations. EBIC mapping of the cross-section revealed the electric field at the heterojunction, and a weaker electric field at the CdTe/ back contact interface, indicating its Schottky nature. Contrast was also seen at the GBs. The EBIC signal was seen throughout the entire film thickness, but only within the back contact limits, indicating a

longer diffusion length perpendicular to the film plane than parallel to it. Some EBIC contrast may be induced by sharp topography differences. In order to overcome that, samples were polished before metal (Schottky) contact deposition, which indeed reduced the GB contrast, but under certain conditions this contrast persists [1]. These will be used to compare samples before and after impurity diffusion.

SSR plots follow the topography closely, with highest conductivity at the GBs. Topography effects are strong in SSR because they can change the tip-surface contact area. The small dark areas (low current) do not follow the topography and are probably related to non-uniformity of the oxide layer on the CdTe (fig. A2).

In the following scanning probe methods (except EBIC & LBIC) the probe scanned the back CdTe surface (planar configuration). The second electrical contact was a permanent contact to the conductive substrate.

Spatially resolved I-V measurements of CdTe samples were performed at varying distances from a GB, using AFM topography mapping. The curves resemble a diode characteristic, probably due to the sample set-up: p-CdTe on n-type SnO_2. The forward-bias currents measured closest to the GB were the highest, and decreased with increasing distance from the GB (the currents at reverse-bias were always below the detection limit) (fig. A1). Since the current was measured between a probe on the (front) surface and back contact, the higher conductivity might be explained by enhanced conductivity along the GB, possibly explained by higher carrier concentration and/ or lower E_g at the GB. If so, this might be a dominant mechanism of current collection in such cells. (Interestingly, similar measurements performed on CIS films showed negligible differences between measurements at different distances from the GB, and lower (forward bias) currents. Thus, the GB-related mechanisms dominating the PV performance of CdTe and CIS thin film cells might be different).

SKP mapping of vapor-$CdCl_2$ (followed by wash in de-ionized water) treated CdTe was sensitive to a fine sub-structure of particles on the scale of 50-100 nm on top of larger grains (Fig. A3). The origin of this sub-structure is not clear, since previous works reported its disappearance after $CdCl_2$ (solution) treatment [2]. The differences in surface potential related to the boundaries between these particles were explored further, using SKP + SPV, using a 488 nm laser. The plots reveal larger differences in surface potential of GBs and grain surfaces in the dark than under illumination. This can be explained by straightening of the formerly larger GB band-bending, or by differences in optical absorption between GBs and grain surfaces. It may indicate differences in mid-gap states distribution and/or in the band gap between the GB's and the grain surfaces.

In SKP mapping of GBs it is necessary to eliminate possible geometry effects and after encouraging first results more work will be done in that direction.

LBIC mapping was performed using a scanning laser microscope in the visible range. An electric field of a Schottky contact generated an LBIC contrast between CdTe coated by a thin evaporated Au layer and uncoated CdTe. The LBIC signal under the Au pad was not uniform, and further investigation is needed to determine if the non-uniformity relates to the CdTe PX structure or to a larger-scale phenomenon.

Macroscopic electrical measurements were performed for future comparison with microscopic measurements. Measurements on CdTe/CdS cells showed dark IV curves typical of a p-n junction, influenced by the back contact material (see below). Capacitance measurements of the CdTe/CdS cells showed a transient capacitance when subjected to constant bias. The capacitance-time curves neither fit perfectly to a model of electronic processes (deep traps in the energy gap), nor to a model of ion drift in the SCL. The mechanism causing the transient is probably a mixture of these processes, and might also involve chemical reactions. Experiments at different temperatures are needed to separate the effects of different processes. This phenomenon may affect the interpretation of further capacitance measurements.

MEASUREMENTS of CELL DEGRADATION

Cu/HgTe/graphite back contact fabrication.
Early attempts to fabricate cells using USF and First Solar samples (conducting glass/CdS/CdTe) using Cu/HgTe/graphite paste obtained from USF resulted in poor results. It took a considerable amount of optimization of contact application, together with new graphite-paste samples, to make cells good enough to carry out meaningful degradation measurements. In the last months of year 1, the typical cell efficiencies have increased from <5% to ca. 10%. Solar efficiencies between 8 - 10.5% and 9 - 11.5% can easily be obtained with the graphite paste contacts on First Solar and USF samples respectively. A maximum efficiency of 11.5% has been obtained for both sample types [a].

Figs. 5 and 6 show the I-V behavior of cells prepared on First Solar and USF substrates. In contrast to cells contacted on First Solar substrates, USF ones prepared by the above procedure often show a roll-over in the I-V plots recorded under illumination (see Fig 6). Further heating of USF samples resulted in the loss of the roll-over, but it never returns after accelerated degradation tests. Comparatively, after a period of heating a roll-over appears in the illuminated I-V plots on cells contacted on First Solar samples. The physical/chemical reasons for this are not yet clear.

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[a]   The contact is applied, following a bromine/methanol etch, as a thick graphite paste to a masked CdTe sample. The cell is annealed in scrubbed N_2 at 250°C for around 25 minutes. The graphite contact is completely coated with Ag paint and isolated by scribing around the contact edge. The conducting glass is cleaned by, prior to the etching, removing a strip of CdTe along one edge of the sample and the underlying CdS is removed by the etch. Contact to the conducting glass is made with Ag paint.

Voc = 804 mV
Isc = -5.8 mA
Jsc = 22.1 mA cm-2
Fill Factor = 64.6%
Pmax = 3.0 mW
Efficiency = 11.5%
Cell Size = 0.260 cm2
R-d = 7.6 ohm cm2
R-l = 5.1 ohm cm2
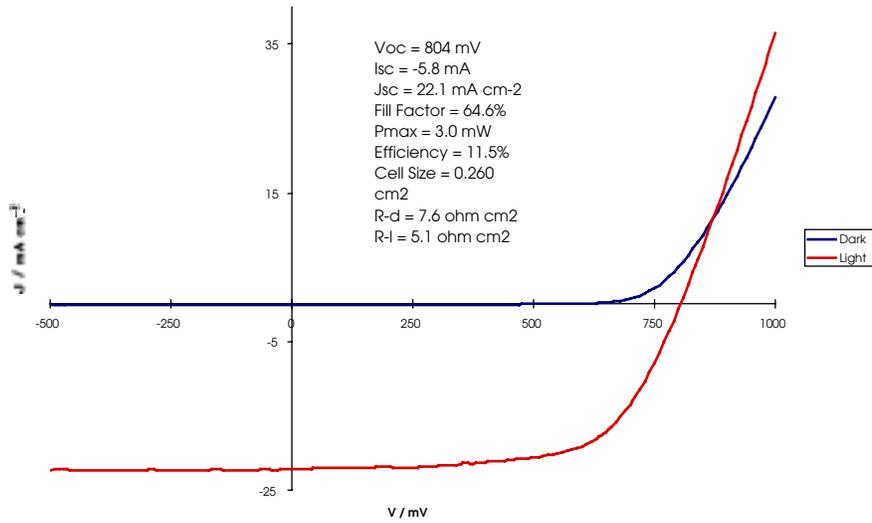
Fig. 5 Light and dark I-V plots of CdS/CdTe solar cell with Cu/HgTe/graphite back contact prepared on First Solar sample. A typical cell has a $V_{oc} \sim 800$ mV, $J_{sc} \sim 21$-22 mA cm^{-2}, fill factor of 60-65% and series resistance (under illumination) of 4-6 Ω cm^2. Cells of 11.5% showed improved J_{sc} (>26 mA cm^{-2}) or fill factor (~65%).

Voc = 799 mV
Isc = -5.3 mA
Jsc = -26.3 mA cm-2
Fill Factor = 54.3%
Pmax = 2.3 mW
Efficiency = 11.4%
Cell Size = 0.2 cm2
R-d = 23.8 ohm cm2
R-l=11.3 ohm cm2
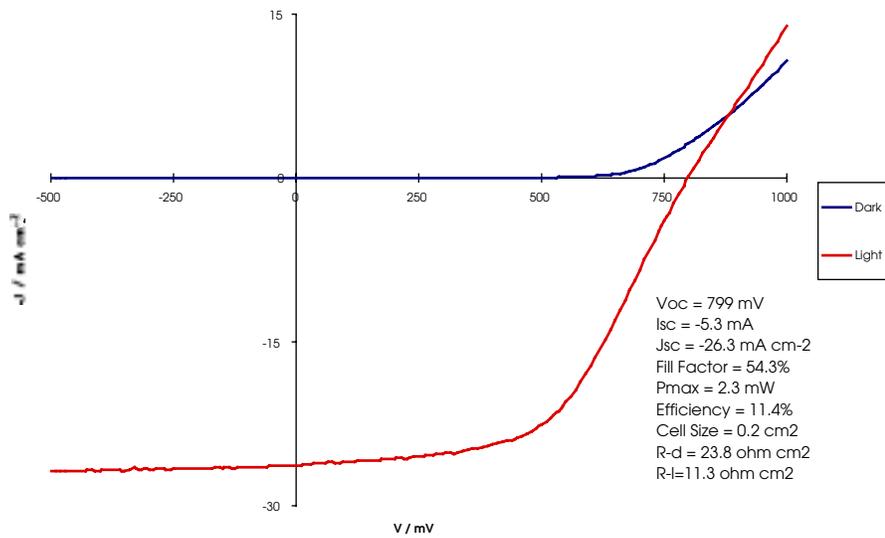
Fig. 6   Light and dark I-V plots of CdS/CdTe solar cell with Cu/HgTe/graphite back contact prepared on USF sample.

Cell Degradation Studies

Accelerated lifetime tests have been carried out on cells with reasonable (9-11%) solar efficiencies [b]. *The immediate goal was to see which cell parameters were affected in which manner by the tests*. It should be noted that cells in the field are encapsulated and rarely experience temperatures above 70 °C. Thus, the 200 °C-in-air stress may introduce failure mechanisms that may not normally occur in field-devices. However, higher-temperature stress testing is useful for understanding changes that can occur for CdTe/CdS cells and their behavior.

Fig. 7 bottom (top) shows the illuminated (dark) I-V plots, recorded at various times, of a First Solar CdTe/CdS samples contacted by ourselves with a graphite paste contact (prepared in USF) which had been heated at 200° C in air at open circuit without illumination. The initial illuminated and dark plots, recorded after no or short heat times, show typical IV curves for such samples. After some time, usually heating overnight, roll-over in the illuminated I-V curve occurs. This parallels a significant drop in the solar efficiency, V_{oc}, J_{sc} and fill factor of the cell. The appearance of the roll-over in the illuminated IV curves corresponds with a significant drop in the slope of the dark forward I-V characteristic. This slope also continues to decrease and becomes more or less constant following 70-100 hours heat treatment. A control cell (Cu/HgTe/graphite back contact on First Solar CdTe/CdS samples), which was stored in the dark and did not receive any heat treatment, showed constant behavior over the period of the experiment. No changes in the I-V characteristics occurred.

 The cells contacted to USF samples behaved differently. Fig 8 shows the illuminated I-V plots of a USF cell, heated at 200° C in air. The earlier mentioned roll-over effect can been seen in the initial plot. After heating the roll-over disappears from the illuminated I-V curves. With the loss of the roll-over, only cell efficiency and fill factor increase (to 10% and 55% respectively).

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[b] Degradation was carried out by heating at 200° C in air at open circuit and in the absence of light. Cells were removed at various times and I-V and LBIC recorded.. Two cells have also been heat-treated at 200° C in a scrubbed N_2 atmosphere (at open circuit and in the absence of light) for around 36 hours.
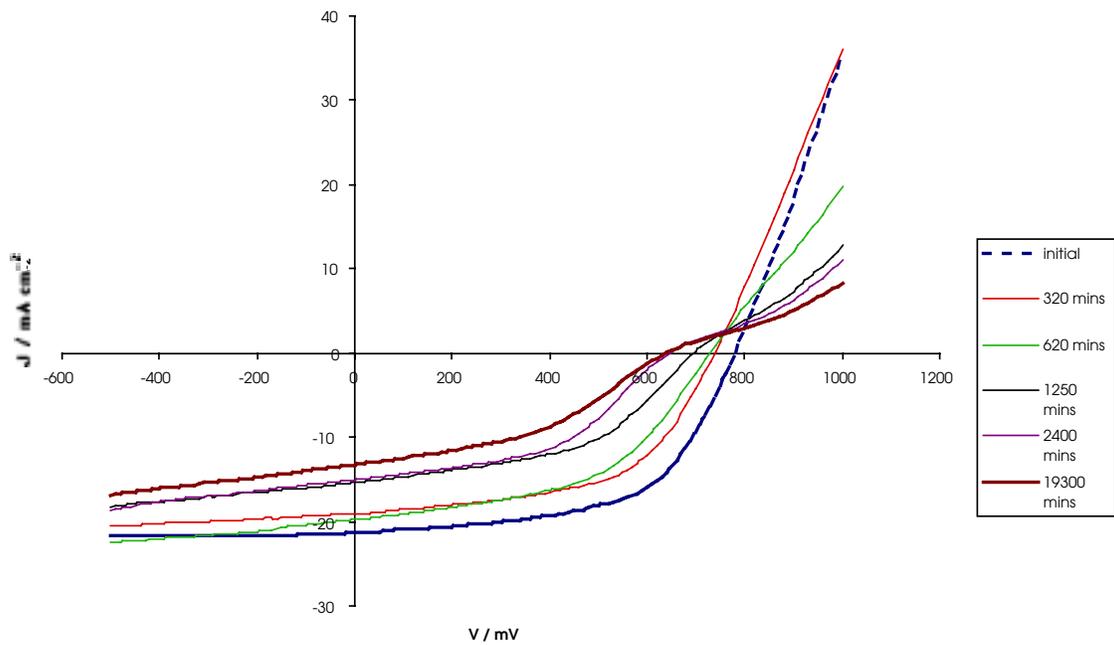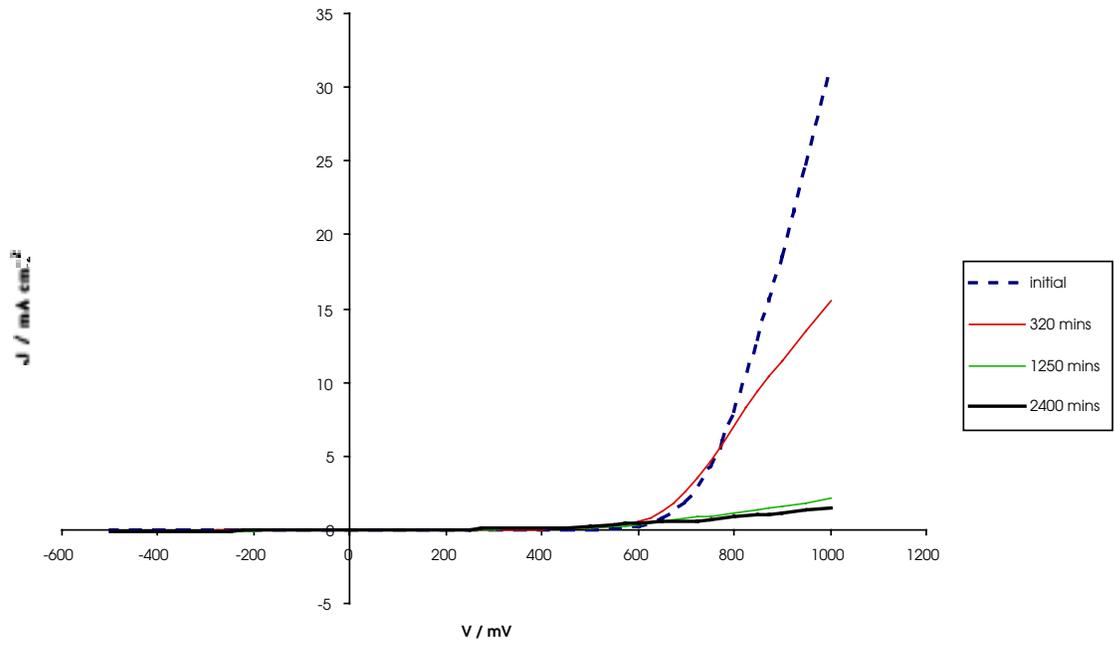
Fig. 7. Light (bottom) and dark (top) I-V plots of CdS/CdTe solar cell with Cu/HgTe/graphite back contact prepared on First Solar sample recorded following heat treatment over time. Prior to treatment cell parameters were: efficiency 9.6%, fill factor 60%, V_{oc} 760 mV and J_{sc} -21 mA cm^{-2}. At the conclusion of the experiment cell parameters were: 4%, 40%, 620 mV and -14 mA cm^{-2}, respectively.
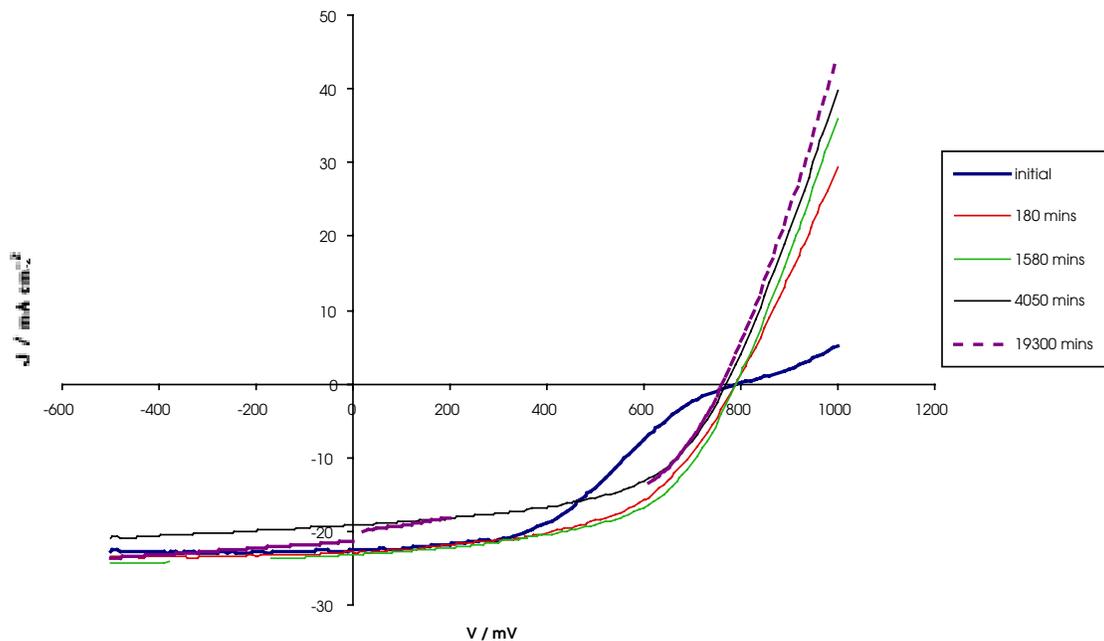
Fig. 8. Light I-V plots of CdS/CdTe solar cell with Cu/HgTe/graphite back contact prepared with USF sample recorded following 200 °C treatment over time. Prior to treatment cell parameters were: efficiency 7.6% , fill factor 42% , $V_{oc} \sim 800$ mV and J_{sc} -23 mA cm^{-2}. At the conclusion of the experiment cell parameters were 7%, 50%, 740 mV and -18 mA cm^{-2}, respectively.

The decrease in parameters of cells contacted on USF samples during heat treatment is not as large as seen for cells contacted on First Solar CdTe/CdS samples. The dark I-V curves (not shown) for the USF cell initially show a constant slope of the forward characteristic with heating. The loss of the roll-over corresponds to a significant increase in the slope of the dark I-V. The slope continues to increase, reaching a maximum following 26 hours heat treatment. Further treatment then results in a steady decrease of the dark I-V slope, without change in any other parameters.

Heat treatment in a scrubbed $N_2(g)$ atmosphere of cells contacted with Cu/HgTe/graphite back contact on both First Solar and USF CdTe/CdS samples was also investigated. The USF cell showed the initial roll-over effect in the illuminated I-V plot. As for air treated USF samples, after a short heat treatment time the roll-over had gone. Heating (up to 36 hours) resulted in no further change in the IV behavior of either cell. For cells heat-stressed in air, a significant decrease in behavior is already noted after 36 hours treatment.

Front-Wall Light Beam Induced Current (LBIC)

Initial LBIC investigations were 'back-wall' ones, i.e., the CdTe/contact side of the cell is illuminated by the laser. Such LBIC (and EBIC) investigations of unstressed cells with Cu/HgTe/graphite back-contacts show a junction approximately 30-40 μm from the contact edge. In unstressed cells this

junction is continuous and sharp. Degradation of the cell resulted in an increase in the distance of the junction from the contact with heating time. The increasing contact-junction distance corresponds with the decreasing cell efficiency. As the cell degrades, the appearance of the junction also becomes less defined. *These observations may be interpreted as the result of fast ionic diffusion of species away from the back-contact.*

We modified the experimental set-up for front-wall LBIC, with laser illumination through the glass as would occur during solar illumination. By comparing stressed and unstressed cells we monitor effects of heat degradation on the current images of the CdTe cells. This provides current images of the cell contact, to investigate the homogeneity of contacts, and indicate areas of low current.

Fig. 9a shows the front-wall LBIC image of an unstressed cell contacted to First Solar CdTe/CdS samples. It shows a bright contrast, indicating high current, and is reasonably homogeneous. Generally there are a number of isolated dark areas present in the images of non-degraded cells which are probably due to areas of poor contact between the CdTe or mechanical damage to the contact and/or CdTe. There may be a relation between 'poor' behaving cells and the extent of dark areas, but further monitoring is required to confirm this. The optical images of this, and subsequent samples were all featureless. They were taken by focusing through the glass and imaging the back side of the CdS film.

The above cell was degraded by heat treatment (200° C in air) and was removed at various times to record I-V and LBIC. A second (identical) cell was used as control. The control cell was stored in the dark for the period of the experiment and had initial parameters of: efficiency ~ 9.5%, fill factor ~ 63%, V_{oc} ~ 800 mV and J_{sc} ~ -20 mA cm^{-2}. The initial LBIC image was very similar to Fig 9a.

Figs 9b and c show the LBIC images of the degraded cell after 18 hours heat treatment (before roll-over) and 35 hours heat (after roll-over). A major increase in the heterogeneity of the current images occurred after heat treatment. In each case the recorded image was indicative of the current image over the whole contact. Longer heating times increased the degree of heterogeneity even more (not shown here). The LBIC images of the control sample showed no change over the period of the experiment.

The brightness of the LBIC image also decreases in general with degradation. These brightness results are only semi-quantitative at present since variations in contrast affect the apparent results. Recent experiments with careful control of contrast indicates that this loss in brightness (current collection) does really occur. Particular care will be taken in future to ensure images are recorded with as similar contrast settings as possible.

Cells that were heated in scrubbed $N_2(g)$ were investigated using front-wall LBIC. The images obtained were very similar to those seen for non-degraded cells, confirming that these cells had shown no degradation throughout the experiment.

These studies show that the current degradation can be divided into two components: severe loss of current in localized regions (from the heterogeneity of the LBIC images) and overall loss in current over the entire sample area. Reasons for the loss in current may be electronic (such as increased recombination due to chemical changes in the cells) and/or mechanical (poor contact between the CdTe and carbon).

Future studies will aim to understand the cause of the degradation (both overall and heterogeneous) and to extend the LBIC to maximum power and LBIC spectroscopic measurements (to see if fill factor and V_{oc} change in the same way as $I_s)_c$.
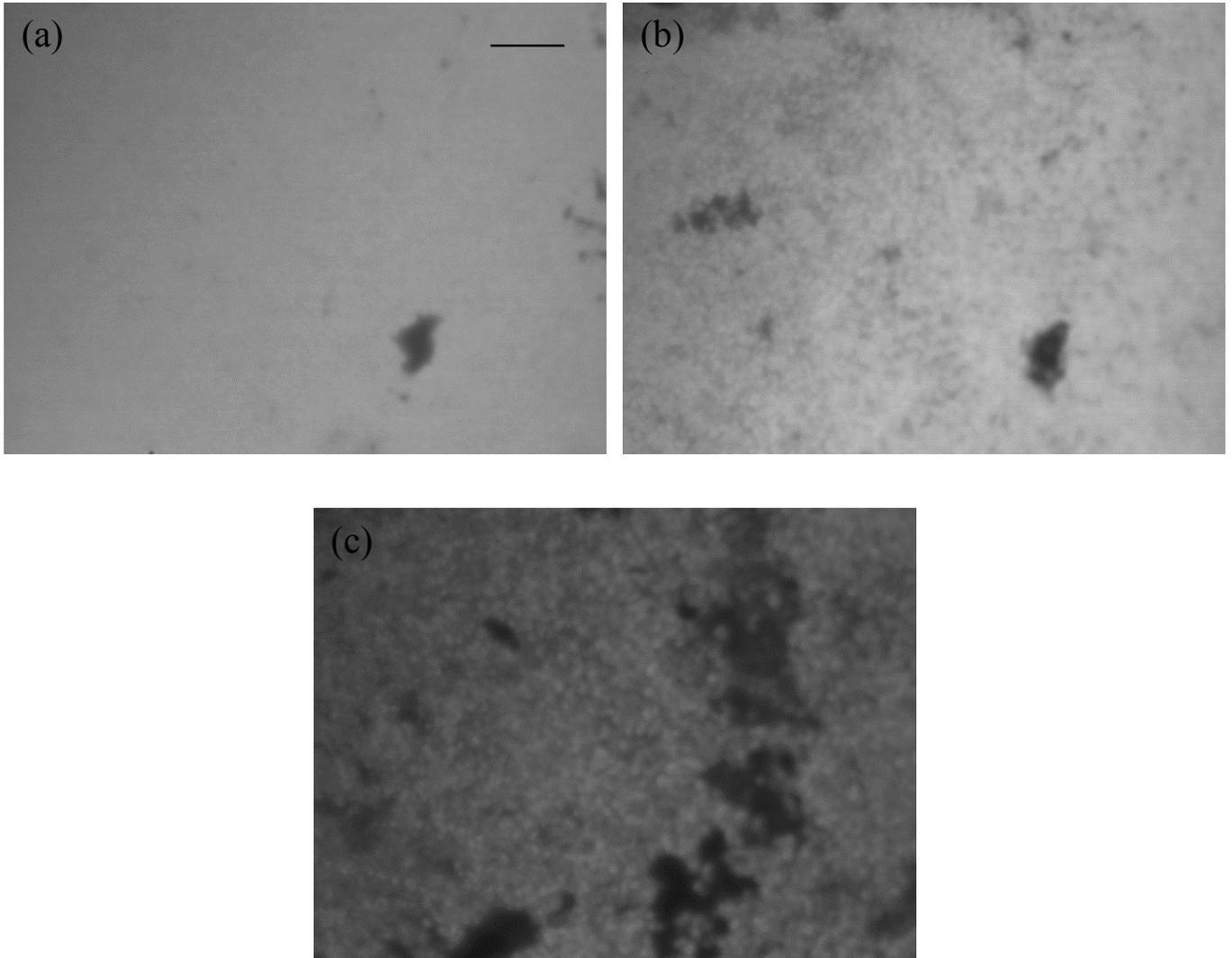
Fig 9. Front-wall LBIC images of a cell with Cu/HgTe/graphite back-contact prepared with First Solar CdTe/CdS samples following (a) 0, (b) 18 and (c) 35 hours treatment at 200°C in air in the dark. Bar = 100 μm.

TASK 2: Novel back-contacting schemes

We investigate Ni-P contacts to p-CdTe. Ni-P is a well-known electrically conducting material which can be deposited by electroless deposition. It is only recently, however, that it has been used for contacts to semiconductors [3,4]. Since the deposit contains P, a known p-type dopant for CdTe, it appears a good choice as a contact material as a p^+ tunneling layer of CdTe may form at the interface. Regarding the stability of the contact, the conditions of preparation of this contact on CdTe (up to 250°C for 90 min in air) strongly suggest that it will be stable. Our investigation of this material is largely based on this latter point. Ni-P can be deposited from both acidic and alkaline baths. Since the CdTe was not very stable under the conditions of the acid bath, we have concentrated on the latter.

Electroless Ni-P is normally deposited using a standard double activation treatment of Sn followed by Pd treatments. The Ni-P is deposited from an alkaline bath, using hypophosphite as a reducing agent for Ni ions onto First Solar CdTe/CdS samples. On the basis that the presence of Sn and, more likely, Pd at the interface may be detrimental to the cell, we have deposited the Ni-P without an activation treatment, hoping that the CdTe itself may act in this role. Use of such activation actually resulted in inferior contacts. Also, etching the CdTe was not found to be necessary.
As a final forming step these cells are heated at 200°C in air for ca. 90 min. It was found that oxygen is crucial in this annealing step. Cells, which were annealed in a nitrogen atmosphere, were inferior to those annealed in air.

The best cells have somewhat matt and 'dirty' looking Ni-P contacts, compared to the normal shiny deposits. The lateral resistance of these contacts are poorer (by up to an order of magnitude), yet I_{sc} and V_{oc} are better. Fig. 10a shows the illuminated I-V behavior of 4 cells (not heat treated) fabricated using different concentrations of hypophosphite (shown in the figure). There is a major improvement in the characteristics when the concentration is reduced from 0.2 M to 0.1 M. Heat treatment (as described above) improves both sets of cells (fig. 10b), but the low hypophosphite cells are still much better, in particular V_{oc} (and through the larger V_{oc}, also better FF). The cell parameters of these 4 cells (after annealing) are summarized in Table I.
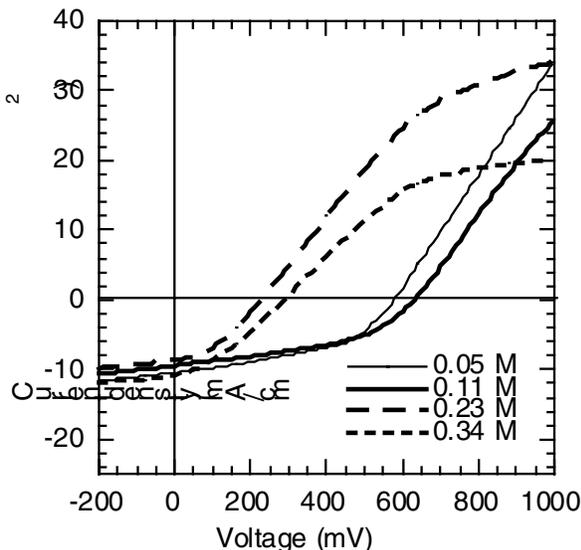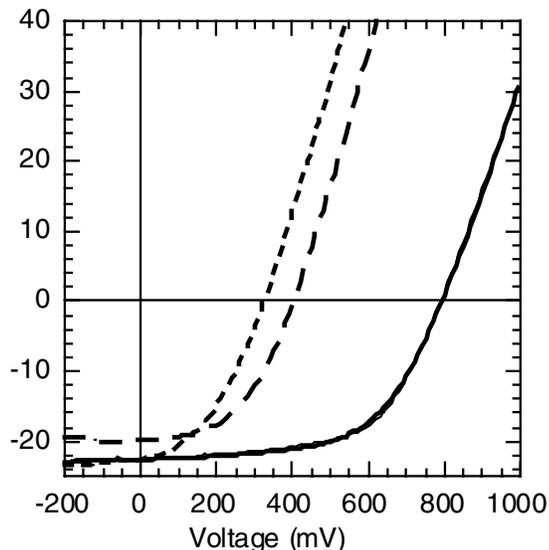
| Fig. 10a | Fig. 10b |

	0.056M	0.113M	0.227M	0.340M
Voc(mV)	791	793	402	323
Isc(mA)	2.02	2.04	1.78	2.02
ff (%)	60	58.3	35	40.9
η	10.7	10.5	3.9	2.9
cell size (cm^2)	0.09	0.09	0.09	0.09

Table 1: Upper row indicates [H$_2$PO$_2^-$]

The change from high hypophosphite (poor cells) to low hypophosphite (good cells) corresponds to the visual change in the Ni-P layer from shiny to matt black. This provides a clue to the effect of the hypophosphite concentration. It may be that the high hypophosphite concentration reduces the Ni^{2+} all the way to Ni metal, while the low concentrations can only partially reduce the deposition solution. Chemical analyses of the "Ni-P" layers are being carried out and the results should clarify this effect.

It was necessary to study the optimum annealing conditions for these contacts since these conditions are clearly very different than those using graphite paste contacts. Fig. 11a shows the effect of annealing (in air) temperature while that of annealing time (at 200°C) is given in fig. 11b.
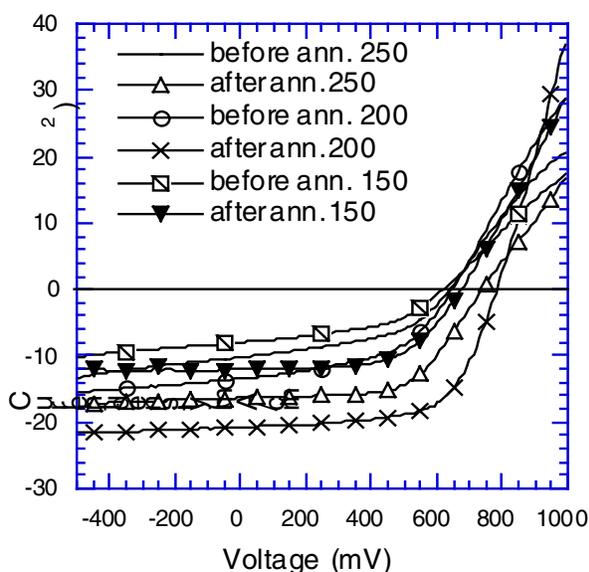
Fig. 11a
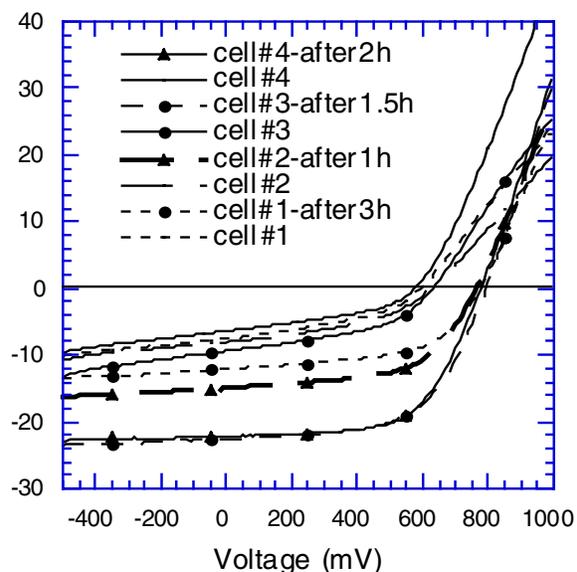
Fig. 11b

From these two sets of data, the optimum annealing conditions were set at 200°C for 90 min as described above. Higher temperature (250°C) results in a drop of V$_{oc}$ (and I$_{sc}$) while more-than-optimum heating duration causes a drop in current but only a small drop in V$_{oc}$. This suggests that the effects of higher-than-optimum temperatures and annealing durations are different.

Annealing in air (oxygen) is necessary to obtain good cells, as can be seen from fig. 12. Two cells, with essentially identical as-deposited cell characteristics, were annealed, one in air and one in nitrogen. The air-annealed cell is much superior, particularly in I_{sc}. Furthermore, when the cell, which had been annealed in nitrogen, was re-annealed in air, the cell improved almost to the level of the only air-annealed cell. Elucidation of the cause of the effect of the oxygen in the annealing step will constitute one of the next steps in the study of these contacts.
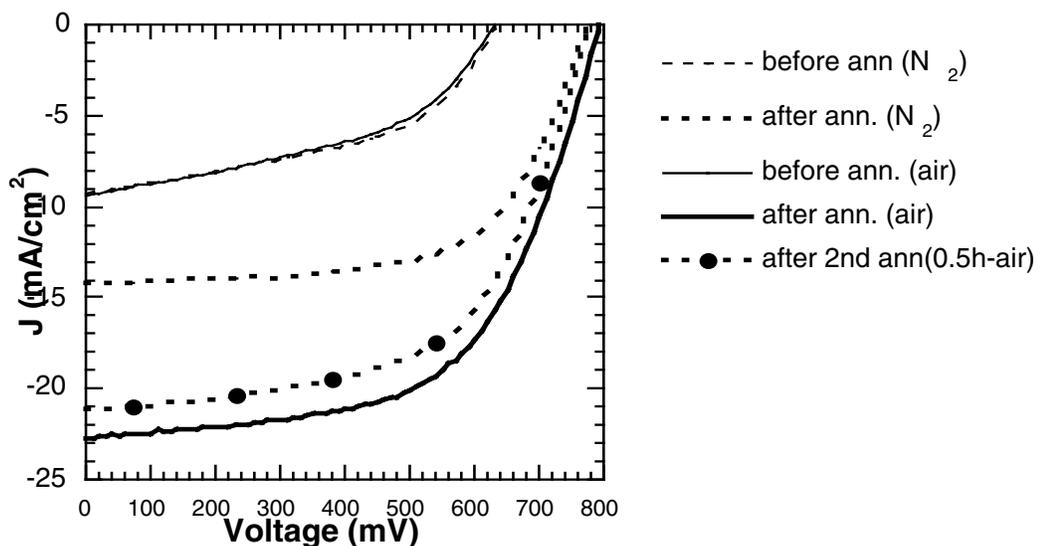
Fig. 12

While oxygen does not lead to cell degradation (and in fact is necessary for good cells), water vapor in the atmosphere does cause degradation (mainly decreasing J_{sc}) under normal dark storage conditions. Cells exposed to normal atmosphere degraded considerably even after one day, while those kept in a dessicator were stable (fig. 13). This is somewhat surprising since the contacts are prepared in aqueous solution at ca. 90°C for ca. 1 hr. It may be that the reducing environment in the solution plays a role.
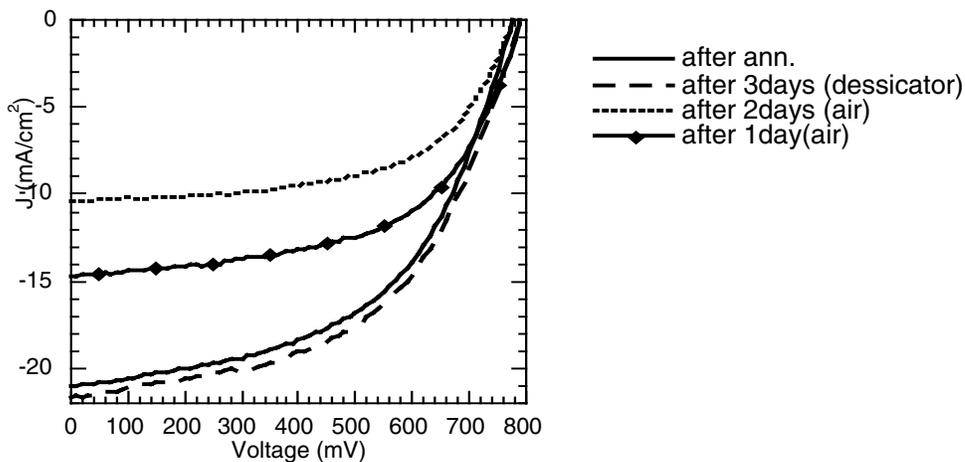
Fig. 13

FUTURE RESEARCH

Scanning probe measurements of CdTe in complete cells will be compared with those in the $CdTe/SnO_2$ configuration. Analysis of the high-resolution measurements will be combined with that of macroscopic measurements of the cells. The scanning probe techniques will be further used to characterize the influence of chemical and/ or thermal treatments on the various parts of the CdTe: GBs, grain surface and grain bulk. Examples of such treatments are surface treatments, that affect the back contact interface, and thermal treatments recently developed in our lab that affect CdTe doping concentration [5]. Controlled changes in the GB states (type and density) can be achieved by treatments that affect the GBs faster than the bulk, or by enhanced GB diffusion. The techniques we developed should be useful for following such changes, in order to characterize the role that the different parts of the polycrystalline material play in the cell performance.

Cells of reasonable efficiencies needed in this project, are now being produced from First Solar and USF structures (and now also being supplied from other sources), and cell degradation has been characterized using IV and front-wall LBIC. The next step is to try to determine the role of Cu and/or Cu ions in the degradation of these cells. Possible techniques that will be considered to measure levels of Cu include chemical analysis, EPR, Rutherford Back-scattering Spectrometry and SIMS. Cross-section EBIC of degraded and non-degraded cells will be carried out.

Degradation studies, especially with the observation that no degradation occurred when heated in N_2, require further investigation. Ideas include heating cells in atmospheres of various N_2-air and N_2-O_2 mixes. Stress testing at different conditions, for example under illumination at open circuit and maximum power voltages, are planned.

Some other etch techniques will be re-checked now that better cells are being produced. These include HNO_3-H_3PO_4 etch (etch used for NREL cells) and hypophosphite (based from treatments used to produce Ni:P contact.)

LBIC studies will continue to be used to assist characterization of various cells and contacts and to understand and see what further information can be obtained from the technique.

We plan to emphasize understanding the "Ni-P" contact in the near future. This will involve various analyses of the contact (and devices) as-deposited, after annealing and after degradation by moisture, as well as trying to identify any new phases, that may contain one or more of the following elements Ni, P, O, Cd , Te.

CONCLUSIONS

1) GBs in CdTe thin films have shown differences in electrical behavior compared to grain bulk/ surface, indicating that the CdTe GBs are NOT fully passivated and are expected to be electrically active. It should be noted that CdTe/CdS intermixing was shown to be enhanced in the GBs [6] and is therefore expected to affect that conclusion.

2) Capacitance and LBIC results may be interpreted as fast ionic diffusion in the vicinity of the Cu/HgTe/graphite back contact, possibly enhanced by GB diffusion.

3) Surface modification of the CdTe was shown to affect the interface with the back contact, and might be used to improve its characteristics.

4) Several methods were shown to be applicable for the characterization of the effect of diffusion of impurities on the CdTe GBs, grain bulk and surface.

5) The macroscopic response to stress is different for cells, with identical back contact but from different manufacturers. Possibly different factors, and/ or different reactions to identical factors are at work here.

6) Heat-stressing of cells in an oxygen-containing atmosphere enhances the rate of cell degradation compared to cells stressed in oxygen-free atmospheres. The formation of 'roll-over' in First Solar cells may be attributable to the formation of CdTe surface oxides.

7) Degradation of the junction can be monitored using front-wall LBIC. An increase in heterogeneity of the current image is observed in degraded cells compared to unstressed cells.

8) Ni-P appears to be a promising back-contact material. While oxygen does not lead to cell degradation, water vapor in the atmosphere does causes degradation under normal dark storage conditions.

REFERENCES

1. S. A. Galloway, P. R. Edwards and K. Durose, Sol. Energy Mater. Sol. Cells, **57**, 61 (1999)
2. D. H. Levi, H. R. Moutinho, F. S. Hasoon, B. M. Keyes, R. K. Ehrenkiel, M. Al-Jassim, L. L. Kazmerski and R. W. Birkmire, Sol. Energy Mater. Sol. Cells, **41/42,** 381 (1996).
3. B. Ghosh, S. Purakayastha, P. K. Datta, R. W. Miles, M. J. Carter, and R. Hill, Semicond. Sci. Tech., **10**, 71 (1995).
4. R. W. Miles, B. Ghosh, S. Duke, J. R. Bates, M. J. Carter, P. K. Datta, and R. Hill, J. Crystal Growth **161**, 148 (1996).
5. V. Lyahovitskaya, L. Chernyak, J. Greenberg, L. Kaplan and D. Cahen, to be published in J. Cryst. Growth.
6. V. Kaydanov and T. R. Ohno, Quart. Tech. Status Rprt., Sub Contract No. XAK-8-17619-28, NREL, Golden, Co, Sep. 1999.
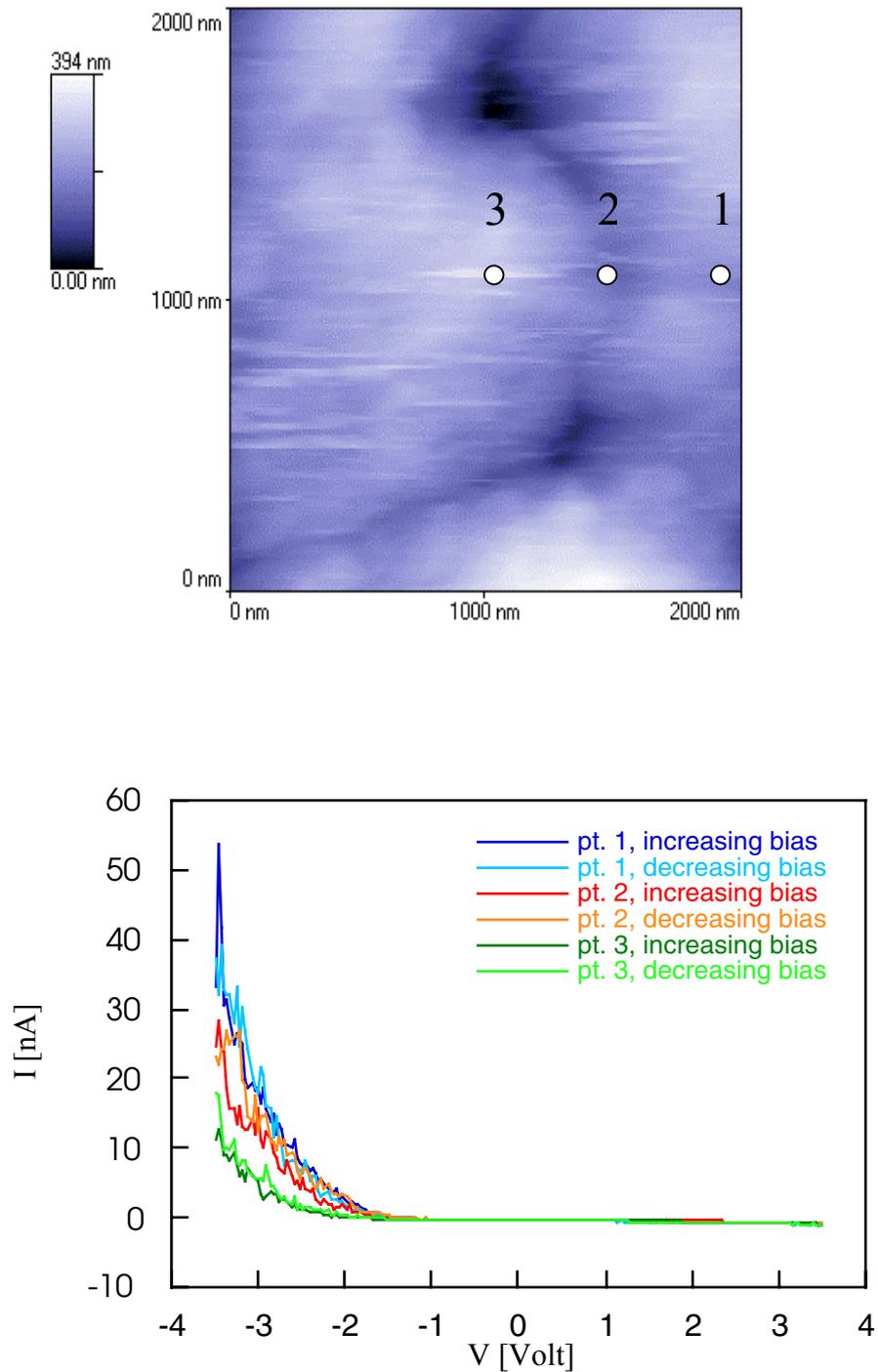
Fig. A1 Spatially resolved IV measurements of CdTe film, using a conductive AFM tip: top. Locations of the tip (the counter-contact is the SnO$_2$ substrate), bottom. IV spectroscopy in the respective locations
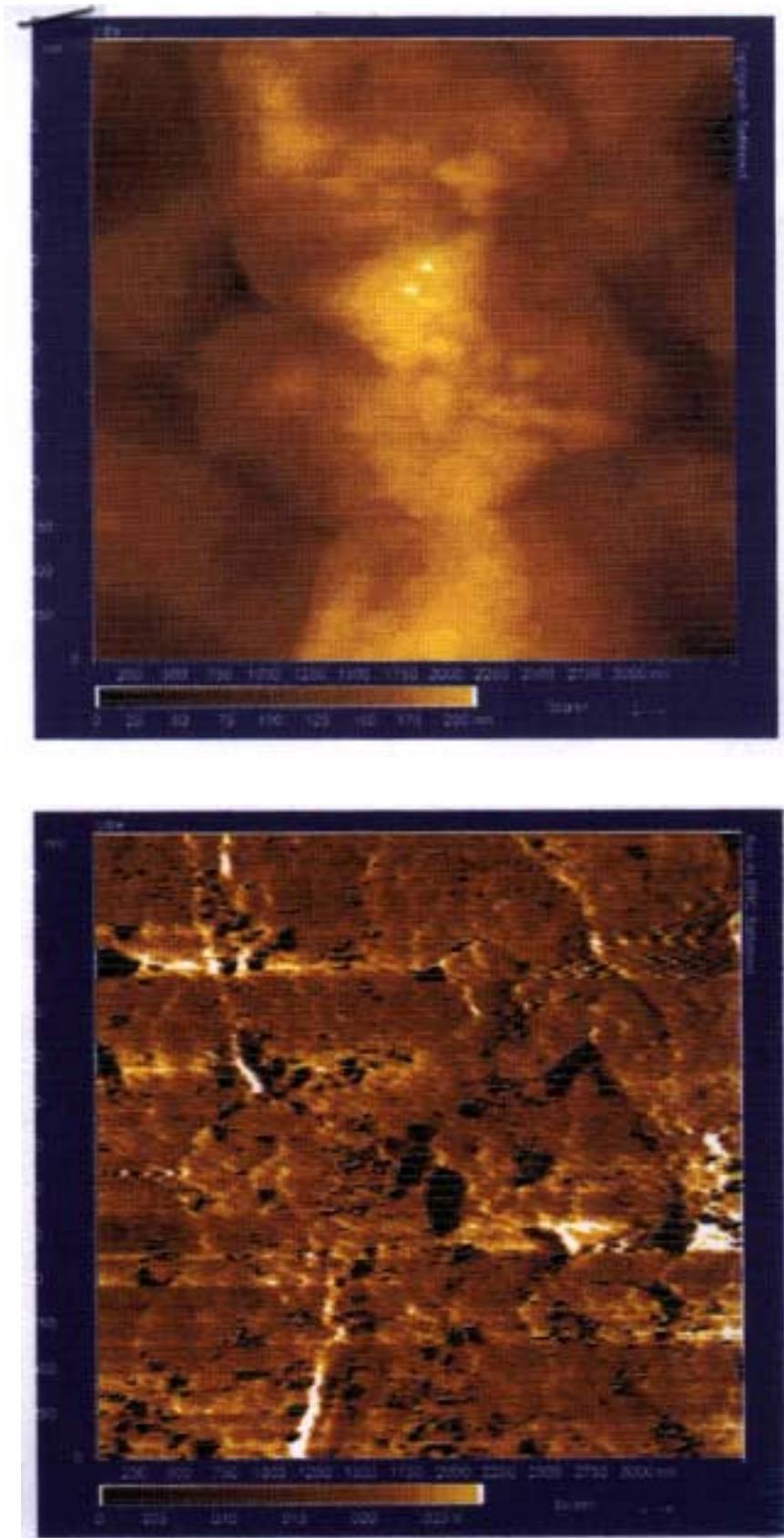
Fig. A2 CdTe film surface plots, using AFM in contact mode (3500x3500 nm^2): top: topography, bottom: SSR
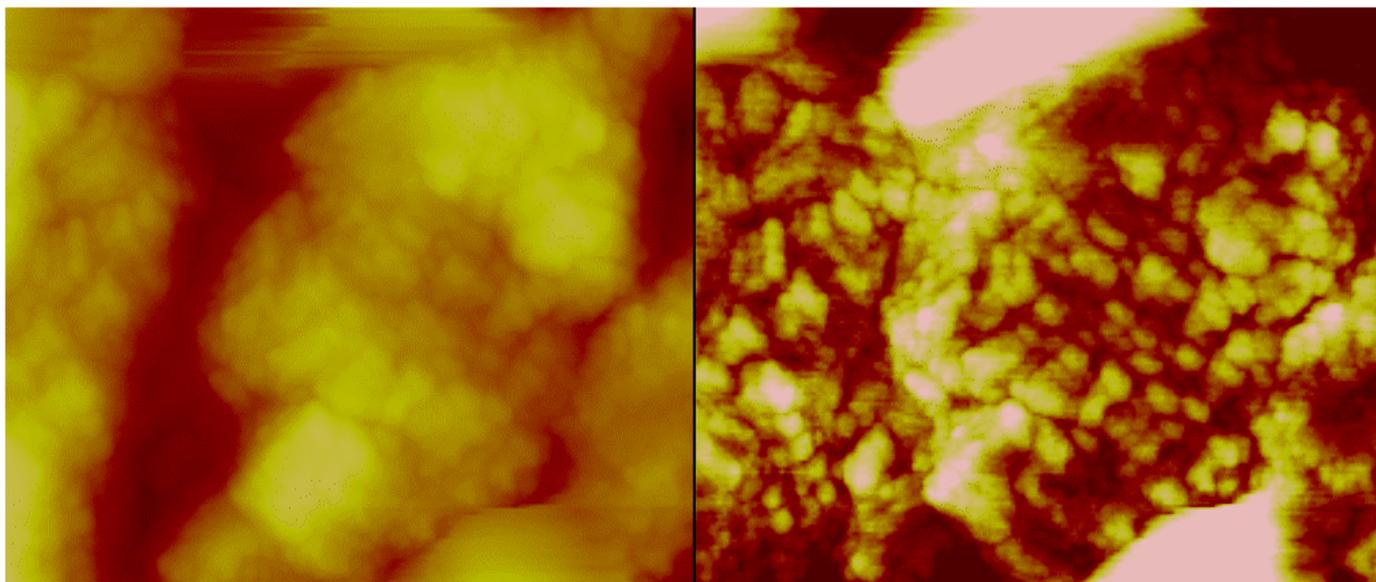
| Data type | Height | | Data type | Potential |
| Z range | 400 nm | | Z range | 0.200 V |

3.00 µм

3.00 µм

Fig. A3 AFM plots of CdTe film surface: left: topography, obtained in tapping mode, right: SKP
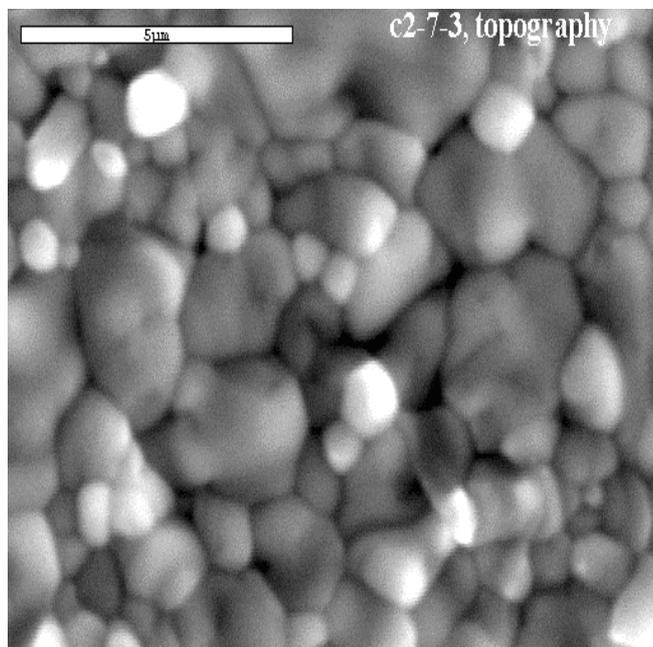
a
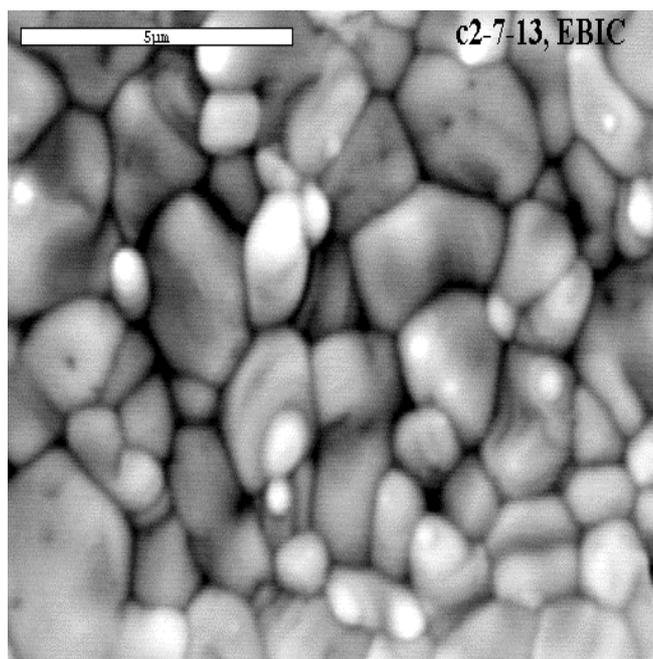
b

Fig. A4 CdTe film surface SEM micrographs: a. topography, b. EBIC

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13. ABSTRACT *(Maximum 200 words)*
We have studied the importance of chemical processes for the stability of CdTe solar cells, in particular, diffusion in the ohmic contact/absorber junction regions. Both whole cells and test systems containing only the ohmic contact and the absorber are used. We found several experimental methods to be useable tools to follow the effects of impurity diffusion on the CdTe grain boundaries, grain bulk, and surface. In addition, we have explored alternative contacting schemes.
Our first year of activities led to the following tentative conclusions:
- Grain boundaries in CdTe/CdS cells are NOT fully passivated and are expected to be electrically active.
- There appears to be fast ionic diffusion in the vicinity of the Cu/HgTe/graphite back-contact, possibly enhanced by grain boundary diffusion.
- The macroscopic response to stress is different for cells with identical back-contact, but from different manufacturers. Different factors and/or different reactions to identical factors are possibly at work here.
- Ni-P appears to be a promising back-contact material.

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