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Solar Energy Materials & Solar Cells 62 (2000) 295–325

Solar Energy Materials  
& Solar Cells

www.elsevier.com/locate/solmat

# Stability of CdTe/CdS thin-film solar cells

Kevin D. Dobson\*, Iris Visoly-Fisher, Gary Hodes, David Cahen

*Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel*

## Abstract

The recent literature regarding the stability of CdTe/CdS photovoltaic *cells* (as distinguished from *modules*) is reviewed. Particular emphasis is given to the role of Cu as a major factor that can limit the stability of these devices. Cu is often added to improve the ohmic contact to p-CdTe and the overall cell photovoltaic performance. This may be due to the formation of a Cu<sub>2</sub>Te/CdTe back contact. Excess Cu also enhances the instability of devices when under stress. The Cu, as Cu<sup>+</sup>, from either Cu<sub>2</sub>Te or other sources, diffuses via grain boundaries to the CdTe/CdS active junction. Recent experimental data indicate that Cu, Cl and other diffusing species reach (and accumulate at) the CdS layer, which may not be expected on the basis of bulk diffusion. These observations may be factors in cell behavior and degradation, for which new mechanisms are suggested and areas for future study are highlighted. Other possible Cu-related degradation mechanisms, as well as some non-Cu-related issues for cell stability are discussed. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** CdTe; CdS; Solar cell; Cu diffusion; Photovoltaics; Thin films; Stability; Migration; Contact; Drift

## 1. Introduction

Thin films of CdTe receive much attention as absorber materials for efficient, low-cost solar cells. Their advantages include high absorption coefficient, direct band-gap with nearly optimum values for solar photovoltaics and good match of their electron affinity to CdS as a window material. Cell efficiencies as high as 16% have been reported, and the maximum theoretical efficiency was estimated to be over 29% [1,2].

\* Corresponding author. Fax: 00-972-8-9344137.

E-mail address: kevin.dobson@weizmann.ac.il (K.D. Dobson)

Commonly cells are based on an n-CdS/p-CdTe heterojunction because of the difficulty in doping CdTe to create a shallow homojunction with a high conductivity layer. In spite of the 9.7% lattice mismatch between hexagonal CdS and cubic CdTe high efficiency devices result with this junction, probably due to interdiffusion at the CdS/CdTe interface. Such interdiffusion is enhanced by a post-deposition  $\text{CdCl}_2$  heat treatment [3,4], which was found to significantly enhance the cell efficiency. No consensus exists about the exact role(s) played by the  $\text{CdCl}_2$  treatment. It is thought to enhance CdTe grain growth, help grain recrystallization [3] and improve p-doping (possibly by creating a shallow acceptor complex,  $V_{\text{Cd}}-\text{Cl}_{\text{Te}}$  [5]).  $\text{CdCl}_2$  heat treatment of the CdS layer, prior to CdTe deposition, was also found to improve cell characteristics [6].

The CdS layer is usually prepared by chemical bath deposition (CBD) or close space sublimation (CSS) on conductive glass. CdTe films have been deposited in a variety of ways, including electrodeposition and screen printing, but the best CdTe-based cells are made using the CSS method [1,7].

While encapsulated modules have shown several year stability in the field [8], high efficiency CdTe cells often show a decrease in conversion efficiency under accelerated stress conditions (cf. Section 1.3). Because of such variations in stability, this review will deal only with degradation phenomena in single cells.

Several causes have been proposed to explain cell degradation, such as junction degradation, degradation of the electrical contact to the CdTe and shunting. The onset of degradation of CdS/CdTe solar cells is frequently represented by perturbation of the current-voltage characteristics, and in particular the development of 'roll-over' at high forward bias, a decrease in open circuit voltage ( $V_{\text{oc}}$ ), an increase in the series resistance and a decrease in the fill factor (FF) (see Section 1.3 and, for example, Fig. 1). The short circuit current ( $I_{\text{sc}}$ ) of the cells is generally less affected [22,39].

The extent and effects of cell degradation can vary with cell properties and method of stress, with different characteristics often reported for similar device types. This indicates that a variety of degradation mechanisms may be occurring in CdS/CdTe

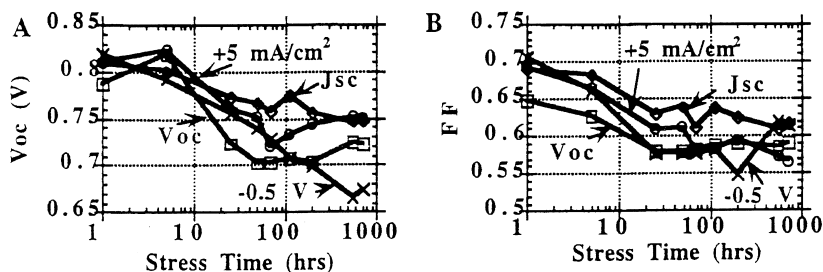


Fig. 1. The effect of the onset of degradation on  $I$ - $V$  parameters of CdTe/CdS thin film (prepared by vapor transport deposition) solar cells completed using 'diffused Cu' back contact processing, followed by deposition of Mo [87]. (A)  $V_{\text{oc}}$  and (B) FF vs. hours under stress, for devices held at the indicated voltage bias at  $92^\circ\text{C}$  and  $70 \text{ mW}/\text{cm}^2$ . (Reprinted with permission from Meyers et al. [87]).

solar cells. The most suspected cause for cell instability is the diffusion of Cu from the back contact into the CdS region. A small amount of Cu is often added to back contacts to effectively p<sup>+</sup>-dope the CdTe surface, to allow the formation of better ohmic contacts to CdTe. Contact to p-CdTe is a long standing problem for CdTe-based technologies in general and for CdTe solar cells in particular [9,10]. Several groups demonstrated improved initial cell efficiencies using Cu-containing back contacts [11–13].

Cu is known to be a fast diffuser in CdTe. It was suggested that grain boundary (GB) diffusion is a very likely mechanism for Cu transport to the cell junction [14]. Because Cu<sup>+</sup> and Cd<sup>2+</sup> ions were taken to be similar in size (based on classical Pauling radii), Cu<sup>+</sup> was thought to substitute readily for Cd<sup>2+</sup> in CdTe [12].<sup>1</sup> Then Cu-doping of CdTe should occur throughout the entire CdTe layer and, indeed, diffused Cu has been detected at the CdTe/CdS interface or alloy region of cells [16]. At the cell junction Cu was proposed to form recombination centers and shunt pathways, limiting the lifetime of the cell.

Back contacts containing no Cu have been used to overcome these effects (for example Ni:P [18–20], Sb<sub>2</sub>Te<sub>3</sub> [21] and HgTe [22]). While such devices may show improved lifetimes, generally they are limited by low initial conversion efficiencies, though Romeo et al. [21] have recently reported Sb<sub>2</sub>Te<sub>3</sub> back contacted cells with conversion efficiencies as high as 14.6%. To date, cells with pure graphite contacts showed lower conversion efficiencies, but mostly better stability, than those with Cu-containing graphite contacts. Their accelerated laboratory lifetimes (for cell conversion efficiency to decrease by 10%, at 100°C, open circuit conditions) were > 1000 hours (corresponding to estimated field lifetimes > 100 years for a 10% drop in conversion efficiency) [23]. By comparison, Cu-containing contacts under the same conditions had accelerated laboratory lifetimes of up to only 250 hours (estimated field lifetime up to 20 years). We note that devices completed with HgTe-doped graphite back contacts have shown better stability than those made with Cu-doped contacts (accelerated laboratory lifetime of > 600 hours, estimated field lifetime > 50 years) but exhibit poorer photovoltaic behavior [23]. Contacts prepared without Cu (or other dopants) may, however, be more susceptible to effects of uncontrolled contaminants [23].

Determining the behavior of Cu in polycrystalline CdTe and its effect on both improving the initial performance of CdS/CdTe solar cells and its proposed roles in the limited stability of these devices is thus a subject of much interest. Here we present a review of the recent literature regarding the effect and behavior of Cu in CdS/CdTe solar cells with respect to device performance and lifetime. To put things in perspective, effects of some pre-treatments on device stability, the behavior of various metals in CdTe and other proposed degradation mechanisms are also discussed.

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<sup>1</sup> In reality, when the more appropriate sulfide crystal radii are used [15], Cu<sup>+</sup> in tetrahedral coordination is found to be 25% smaller than Cd<sup>2+</sup>.

### 1.1. Short background on defects and diffusion in CdTe

The electrical properties of II–VI compound semiconductors are often determined by a departure from 1:1 stoichiometry, which leads to the presence of intrinsic defects, in addition to that of extrinsic ones. Such defects may introduce doping levels in the band-gap, act as compensating species to the major dopant or introduce deep levels that can enhance carrier recombination [23]. Intrinsic (native) point defects may be introduced as a result of the preparation conditions, as well as by post-growth treatments [23,24]. Examples of such defects are Cd vacancies ( $V_{\text{Cd}}$ ) and interstitials ( $\text{Cd}_i$ ) as acceptors and Te interstitials ( $\text{Te}_i$ ) and vacancies ( $V_{\text{Te}}$ ) as donors [25]. Extrinsic dopants will influence the material's electrical properties if they are present as single ionized impurities in the lattice or as part of complexes with a native defect [23,26]. A prominent example is the ( $V_{\text{Cd}}\text{--Cl}_{\text{Te}}$ ) complex, identified as an acceptor [26]. Extrinsic impurities may be introduced in the semiconductor lattice during growth, or by post-growth diffusion.

Extrinsic dopant diffusion, as well as self-diffusion of the compound semiconductor elements, can strongly affect the electronic properties of the semiconductor and of devices made of it, and is especially relevant to devices that contain p–n junctions [27]. Quantification of such a phenomenon requires knowledge of the diffusion coefficient  $D$  of the mobile species at the device operation conditions, which determines the diffusion rate. The driving force for diffusion is a gradient of the electrochemical potential,  $\Delta\eta_i$  of species  $i$ .  $D$  is usually calculated from a fit of the experimental concentration profile to the theoretical one, after a known time period. The theoretical profile can be obtained from the generalized Fick's law, calculating  $J_i$ , the flux of species  $i$ , resulting from the electrochemical potential gradient [28]:

$$J_i = - \frac{DC}{kT} \frac{\partial \Delta\eta_i}{\partial x} \quad (1)$$

Here  $C_i$  is the concentration of species  $i$ ,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature and  $x$  is a spatial coordinate perpendicular to the plane across which the flux is measured (for a general discussion of defects and diffusion see Ref. [29]). If the mobile species is charged and an electric field ( $E$ ) is present (as in a p–n junction region), then Eq. (1) will read,

$$J_i = -D \frac{\partial C_i}{\partial x} + \mu C_i E \quad (1a)$$

where  $\mu = Dzq/kT$  is the zero-field mobility of species  $i$  [29], with  $zq$  the effective electrical charge of the ion ( $z > 0$ ).

### 1.2. Ohmic contacts

Ohmic contacts are often the Achilles heel of devices based on non-classical (i.e., different from Si or common III–V) semiconductors, something that holds especially for p–CdTe-based ones (cf. [30]). There are several ways to make contacts that are

ohmic or pseudo-ohmic (i.e., with such a low contact resistance that its influence on device performance is negligible). Here we mention briefly two of the less complicated ones [31,32]. The first is to eliminate the metal/semiconductor barrier height according to the classical Anderson model (which, for a p-type material means that the semiconductor work function should be less than that of the contact material). If that is not possible, the barrier height can be minimized to yield at least a low-resistance contact. Another way is to dope the semiconductor surface to such a high level that the barrier width becomes small enough to make tunneling through it significant. Because the work function of p-CdTe, doped sufficiently to allow its use in solar cells, is so large ( $\sim 5.7$  eV, cf. [9]), there are no metals known for making contact that can reduce the barrier height sufficiently to make the contact quasi-ohmic, let alone, to make ideal ohmic contact (still, highly conducting materials, such as p-HgTe, were tried to minimize the barrier height [21]). Therefore efforts to make low-resistance contact to p-CdTe concentrate on the second approach. (In general p-absorbers, rather than n-ones are preferred for heterojunction cells. The reason is that one wants to take advantage of the fact that, in most semiconductors the electron mobility is significantly higher than the hole one. For CdTe, representative values are 1050 and  $100 \text{ cm}^2/\text{V s}$ , respectively [33]).

One way to make highly doped surface layers (levels  $\geq 10^{19} \text{ cm}^{-3}$  are often used) is to apply a suitable surface treatment before contact deposition. To save a manufacturing step, a metallic contacting material can be used that will react with the semiconductor to form the highly doped layer. Examples include metallic contacts containing a layer of a diffusing metal (e.g., Au/Cu) and graphite paste doped with Cu, Au or Hg salts. The dopants are reported to readily form interlayers, e.g.,  $\text{Cu}_2\text{Te}$ ,  $\text{Au}_2\text{Te}$  and  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ , at the back contact/CdTe interface [17,34]. Cells contacted with these materials have exhibited the best reported conversion efficiencies for CdTe/CdS devices; for example 15.8% for graphite paste contact containing a Hg compound [7], 16% for Ag/carbon contact [1a] and  $> 15\%$  for Au/Cu [35]. A variation is to form an interlayer of another semiconductor which has a suitable valence band match with CdTe, and is able to be doped highly p-type at the interface with the metal contact, such as ZnTe [36,37].

### 1.3. *Testing of cells: stressing of cells*

To investigate (in)stability, estimate lifetimes and identify degradation mechanisms of CdTe/CdS solar cells, testing is carried out in the laboratory under a variety of conditions, including ones that can enhance degradation. Such tests (and conditions) are commonly referred to as stress (conditions). The conditions that are specified generally include temperature (often  $50\text{--}200^\circ\text{C}$ ), whether the test is done under illumination (and under which illumination conditions) or in the dark, the electrical bias (open or short circuit or maximum power under illumination; forward, zero or reverse bias in the dark), the atmosphere (air, vacuum, etc.) and the duration of the test. Cell condition is monitored using the  $I$ - $V$  technique. This approach allows a fast and simple comparison of behavior of different types of cells, for which variations may include back contact material, preparation method, age and history. Stressing under

illumination at open circuit voltage generally produces the fastest performance degradation of working cells [22,38]. A decrease in  $V_{oc}$ , as result of stress, is ascribed to degradation of the PV junction, while a decrease in FF is considered a result of contact degradation [38]. A decrease in  $I_{sc}$  during stress is believed to be due to an increase in cell series resistance. Perturbation of the  $I$ – $V$  plot at forward bias following stress, also called ‘roll-over’ or ‘blocking’ behavior, is typical of the formation of a barrier at or near the back contact, which acts as a second diode which opposes the main cell junction [39].

#### 1.4. Effects of CdTe etching on cell stability

Treatment of the CdTe surface, prior to applying the contact material, has been explored to achieve a  $p^+$ -surface layer and, thus, low resistance contacts on CdTe (see Section 1.2). Excess surface Te results in Fermi level pinning. Metal/CdTe junctions formed on such surfaces show low barriers and no dependence on the metal work function [9,43]. This might be explained by a high density of  $V_{Cd}$ , which act as acceptors (perhaps in complexes with other defects) to dope a layer close to the CdTe surface  $p^+$ .

Te-rich surfaces are commonly produced using either  $Br_2$ -methanol or  $HNO_3$ – $H_3PO_4$  (NP) etch treatments [40–43]. Chromate etches ( $K_2Cr_2O_7$ · $H_2SO_4$ ) form Te-enriched surfaces with a large proportion of  $TeO_2$ . Te-rich surfaces are susceptible to oxidation, forming  $TeO_2$  [40,43],  $CdTeO_3$  [44] or, more likely, a mixture of these. Oxidation of Te and of CdTe beneath back contacts has been shown to be a degradation mechanism of unencapsulated CdS/CdTe cells [44]. McCandless and Birkmire [45] and Chou et al. [12,46] describe the use of bromine-methanol treatment of CdTe following deposition and anneal of Au/Cu contacts. The etching treatment removes residual surface oxides from beneath the Au/Cu contact (see below) and increases the cell's  $V_{oc}$ . Etching also removed curvature seen in the forward bias part of the  $I$ – $V$  curves of cells without treatment, which is consistent with oxide removal. It was proposed that this results in Te-enrichment, which forms  $Cu_2Te$  on reaction with Cu, and improves contact properties (see also Section 2.2.1). The rapid effect of this treatment suggests interactions are occurring within the GBs [12,45]. It should be noted that Te-rich surfaces have also been obtained by depositing a Te layer on CdTe prior to contact preparation (see Section 3.1).

Few studies of the effect of pre-treatments on cell stability have been reported. The stability of CdTe/CdS cells after cell pre-treatments with vapor or solution of  $CdCl_2$  treatments or both, with and without a further NP etch, has been investigated [47]. Samples that were subjected only to solution or vapor  $CdCl_2$  treatments were found to have oxide-coated and clean CdTe surfaces, respectively. After etching, however, both samples had thick Te surface layers. Devices were completed with Cu:HgTe doped graphite contacts and stressed ( $100^\circ C$  under 1.5–2 suns illumination for 100 h at  $V_{oc}$ ). Device stability was found to be a strong function of sample pretreatment. The etched cells showed superior photovoltaic (PV) stability, but developed contact blocking behavior with increased stressing. The  $V_{oc}$ , FF and cell efficiency of

non-etched cells decreased with stress, but without formation of blocking behavior. Other researchers have also shown that cells etched (with  $\text{Br}_2$ -dichloro-hydrazine which forms a Te-rich surface on CdTe) before deposition of Cu-free carbon showed improved stability, with less roll-over and FF loss, compared to cells that had not been etched [48].

#### *1.4.1. Other etching effects*

While the preparation of Te-rich CdTe surfaces, usually by wet chemical methods, prior to contact deposition is a generally accepted procedure for the formation of low-resistance contacts [40,42], improvements in cell performance have also been shown with post-metallization etches [12,45]. Such treatments appear to be capable of removing oxides from the contact itself or even CdTe surface oxides from beneath the contact. The latter possibility can be explained if the thin (50 nm) contacts are porous, something that is expected for thin films on rough surfaces. The rapid effect of the post-contact etch suggested that treatment proceeds within the CdTe via GBs.

Cells completed on Te-rich CdTe surfaces, using back contacts with or without Cu, show stability that is superior to that of cells which had received no etch treatment prior to contacting [47]. We suggest that the improved performance of cells completed with Cu-containing back contacts to Te-rich CdTe may be related to an increased amount of  $\text{Cu}_2\text{Te}$  phase formed at the back contact/CdTe surface (see Section 2.2.1). This may also account for the improved lifetimes of these cells by slowing further diffusion. Note, however, that cells contacted on Te-rich CdTe still exhibited significant, though slower, degradation. Therefore,  $\text{Cu}_2\text{Te}$  can also be considered as a source for Cu diffusion (see Section 2.2.1).

## **2. Diffusion and role of Cu in cell degradation**

A dual role has been proposed for the behavior of Cu in CdTe/CdS solar cells when used as an additive to the back contacts [12]. It is generally accepted that Cu aids the formation of better ohmic contacts by increasing the p-doping of CdTe near/at the back contact interface. It is, however, at the same time considered to be the principal component responsible for the degradation of these cells, something that is ascribed to its ability to diffuse through the polycrystalline CdTe film to the cell junction. However, the nature of the involvement of Cu in these processes is not well understood. Early studies of the use of graphite paste as a back contact material to CdS/CdTe solar cells showed a remarkable improvement in the cell conversion efficiency when an impurity species, and in particular Cu, was added to the contact material [11,49].

### *2.1. Diffusion of Cu in single crystal CdTe*

Cu is considered to be a fast diffuser in single crystal CdTe ( $D \sim 3 \times 10^{-12} \text{ cm}^2/\text{s}$ ) [50,51]. In CdTe, Cu has been reported [51–54] to exist as an interstitial ion ( $\text{Cu}_i^+$ ), giving rise to a shallow donor state or to substitute for a Cd atom to form a deep

acceptor state. It is also thought to be able to form complexes of the types  $(\text{Cu}_i^+ - \text{Cu}_{\text{Cd}})$  and  $(\text{Cu}_i^+ - \text{V}_{\text{Cd}}^{2-})^2$ . Investigators have identified slow and fast components for the diffusion of Cu in single crystal CdTe [50,55]. The fast diffusion component has been assigned to  $\text{Cu}_i^+$ , thought to be the only species mobile at room temperature [51,55], while the slower component has been assigned to complexes.

The evidence for actual fast *bulk* diffusion at room temperature for Ag (and, by analogy, for Cu) in CdTe, has been questioned [51]. Those authors argue that high diffusion coefficients are due to Te precipitates, or, more generally, to extended defects present in (defective) crystals. We note that this implies a minor role for bulk vs. grain surface and GB diffusion of Cu in CdTe at low (near room-) temperature.

A SEM-cathodoluminescence study of Cu-doped CdTe crystals observed, following heat-treatment at 200°C, that Cu diffuses preferentially along GBs and crystal defects [56] (The Cu source was a Cu electrode evaporated on the CdTe; heating was carried out for 1 h under  $\text{N}_2$ – $\text{H}_2$  mixture). Treatment at higher temperatures (250–300°C for 1 h) resulted in the appearance of black dots in the image due to supersaturation of Cu near the defects. Bright areas around the supersaturated Cu were dominated by CdTe:Cu luminescence. After removal of the Cu electrode, further high temperature treatment (800°C in Te atmosphere for 2 h) resulted in dissolution of the black dots and the formation of bright areas in the images, which were found to be dominated by Cu acceptor-related radiative transitions. Points outside the bright areas contained Cu acceptor-bound complexes. A later investigation [57], however, found no evidence for the presence of Cu precipitates or supersaturated areas at crystal defects following diffusion of Cu (325°C for 170 hours in vacuum) in single crystal CdTe, but found that changes in the photoluminescence (PL) spectra were dominated by the annealing process rather than by Cu diffusion.

## 2.2. Diffusion of Cu in polycrystalline CdTe and CdTe/CdS solar cells

Diffusion of Cu in polycrystalline CdTe may be expected to be faster than in single crystals, with GBs proposed to be suitable pathways for rapid diffusion [12,14]. Generally, diffusion along GBs is more facile than through the bulk of a grain (surface bonds are weaker than bulk ones due to incomplete coordination). In many cases GB diffusion is also easier than diffusion along grain surfaces, because at GBs, two surfaces are available for temporary coordination of the diffusing species, rather than one, along grain surfaces. The ability of Cu to move under the influence of electric fields, for example like that present at a p–n junction [51], may also enhance Cu diffusion within CdS/CdTe cells.

Park et al. [58] studied the effect of  $\text{CuCl}_2$ -doping of polycrystalline CdTe films and graphite paste contacts on the PV behavior of CdS/CdTe cells. Best cell behavior was obtained when only the contact itself had been doped. However, at concentrations of  $> 25$  ppm  $\text{CuCl}_2$  in the paste, cell performance decreased. Heat stressing

<sup>2</sup> As explained in Ref. [51], Ag and Cu in (Hg, Cd)Te act as negatively charged (with respect to the lattice) acceptors, while moving as positively charged species. This is a form of interstitial-substitutional diffusion that leads to a modified form of Eq. (1a), viz.  $J_i = -D \partial C_i / \partial x - \mu C_i E$ .



(350°C in N<sub>2</sub> for 40 min) of cells with contacts containing varying amounts of added CuCl<sub>2</sub> (from 0–500 ppm CuCl<sub>2</sub>) showed that the degree of degradation was greater for cells with doped contacts and degradation was further enhanced at higher CuCl<sub>2</sub> concentrations. It was proposed that the degradation for CuCl<sub>2</sub>-containing cells was due to a decrease in optical transmission and increase in resistivity of the CdS layer as a result of excessive Cu-doping.

Birkmire et al. [38] described the effects of stressing cells (at 100°C, in the dark or under 1.5 suns illumination at  $V_{oc}$  for 6 d), following various back contact processing steps, on the cell performance. The Cu-contacted cells showed an enhanced rate of degradation when stressed under illumination. Stressed cells showed a decrease in  $V_{oc}$ , which the authors suggested was due to degradation of the junction. Following this, cells were completed with a carbon ink contact, deposited on the evaporated Cu layer, and received further stressing. The second stress resulted in roll-over behavior at forward bias. Interestingly, if the contact was removed, the cell etched and re-contacted with a new carbon ink contact, the roll-over was eliminated but with no change in  $V_{oc}$ .

Studies of the stability of carbon paste contacts prepared with and without underlying Cu have also been carried out [48]. The CdTe surface of both cells received the Br<sub>2</sub>-dichloro-hydrazine etch leaving a Te layer for contacting. Cells without Cu had much poorer performance initially ( $V_{oc} \sim 0.72$  V and FF  $\sim 60\%$ ) than cells with 0.2–0.5 nm Cu ( $V_{oc} \sim 0.8$  V and FF  $\sim 70\%$ ). After stress (100°C at  $V_{oc}$  for 6 d), cells without Cu showed  $V_{oc} \sim 0.68$  V and FF  $\sim 50\%$ , compared to cells with Cu, which had  $V_{oc} \sim 0.60$  V and FF  $\sim 60\%$ . Thus, cells without Cu exhibit a smaller  $V_{oc}$  loss (junction degradation) but comparable FF loss (contact degradation). After stress the light and dark  $I$ – $V$  curves of cells without Cu showed less roll-over at forward bias compared to cells with Cu. Cells which were rested (in dark at room temperature for 6–12 months) showed some recovery in behavior (increase in  $V_{oc}$  and loss of  $I$ – $V$  roll-over), but cells without Cu exhibited less recovery in storage. This suggests that under certain circumstances Cu can return to the CdTe surface/back contact interface.

The effect of varying the Cu content in the back contact of CdTe/CdS cells has been investigated [59]. During stressing (under illumination at 100°C for 1000 h), decreases in  $V_{oc}$  and FF occurred progressively faster when the Cu content was increased, while the onset of ‘roll-over’ in the  $I$ – $V$  characteristic was faster for cells with lower Cu content. We note that these observations suggest that roll-over is indeed an indication of low Cu (acceptor) density near the back contact and that excessive Cu near the junction, or front (CdS side) of the cell, results in degradation of cell performance [59].

### 2.2.1. $Cu_2Te$

Crystalline phases present at the CdTe surface have been monitored at various stages of back contact processing using glancing angle incidence X-ray diffraction (GIXRD) [60] with an incident beam angle of 0.5°. Following deposition of a 10 nm Cu layer on a Te-rich CdTe surface, Cu<sub>2</sub>Te and elemental Cu phases were detected, and following reaction in Br<sub>2</sub>/methanol, Cu<sub>2</sub>Te and CuTe phases were detected. Surfaces were found to be richer in Cu<sub>2</sub>Te when thicker (10–50 nm) Cu layers were deposited. Thicker contacts gave cells with higher  $V_{oc}$  ( $> 800$  mV) and a linear

forward bias characteristic, as opposed to cells with thinner Cu contacts ( $< 10$  nm), which gave lower  $V_{oc}$  and diode-like curvature at forward bias. Stressing (at  $150^{\circ}\text{C}$ , under 1.5 suns illumination, for 80 h, at open circuit) of cells with 10–50 nm Cu, some of which were completed with a carbon conductor, showed a decrease in the amount of surface  $\text{Cu}_2\text{Te}$  phase, with near-elimination of the phase for regions which were under the carbon conductor during stressing. The post-stressing  $I$ – $V$  behavior showed a reduction in  $V_{oc}$  and development of curvature in the forward bias characteristic.

The  $\text{Cu}_2\text{Te}$  phase may be formed by a simple reaction between the Cu and Te (formed by etching) or by the diffusion of Cu into  $V_{Cd}$  sites of the Te-rich CdTe surface. We suggest that the correlation between the amount of the  $\text{Cu}_2\text{Te}$  phase present at the back contact and cell performance indicates that  $\text{Cu}_2\text{Te}$  may act as/promote formation of a low resistance contact to CdTe. However the degradation of cell performance and the corresponding decrease in the level of  $\text{Cu}_2\text{Te}$  at the back contact, indicates that  $\text{Cu}_2\text{Te}$  is also a good source for diffusion of Cu deeper into the cell. These observations also suggest that cell degradation is related to a deterioration of favorable back-contact characteristics.

Uda et al. [61] investigated the stability of CdS/CdTe solar cells completed with Au– $\text{Cu}_2\text{Te}$  contacts. Auger profiles obtained by sputtering of as-deposited Au– $\text{Cu}_2\text{Te}$  layers on CdTe (by vacuum evaporation at room temperature) showed a Cu diffusion region approximately 500 nm into the CdTe. This was expected to form a ‘heavily p-type doped layer’. The cells were stored in air at room temperature for 120 d. After this period the cells exhibited an increase in series resistance, which corresponded to a  $\sim 10\%$  decrease in conversion efficiency. Auger profiles showed; (1) out-diffusion of Cu and Te through the Au layer with accumulation of both at the Au surface; (2) a decrease in the Cu signal at the  $\text{Cu}_2\text{Te}$  contact; (3) a decrease in the amount of Cu in the CdTe, but no change in the Cu penetration depth. The compositional change at the Au– $\text{Cu}_2\text{Te}$ /CdTe interface was suggested to lead to an increase of the contact resistance and concomitant degradation of cell performance.

### 2.2.2. PL studies of Cu diffusion

PL measurements are widely used to characterize the electronic character of Cu in CdTe. Levi et al. [62] investigated the effects of Cu distribution through polycrystalline CdTe, prepared on CdS-coated  $\text{SnO}_2$ , from evaporated Cu contacts. Using Secondary Ion Mass Spectrometry (SIMS), Cu was found to have penetrated around  $1\text{ }\mu\text{m}$  into the CdTe following contact deposition and was distributed throughout the  $4\text{ }\mu\text{m}$  thick film (0.01–0.1 at. % concentration) after annealing (at  $300^{\circ}\text{C}$  for 30 min in a flowing He atmosphere). The presence of Cu in CdTe was found to produce no change in the junction PL spectrum (excitation through the  $\text{SnO}_2$  glass). Due to its relatively high mobility in CdTe, Cu was proposed to dope grains and GBs equally, as indicated by the high concentrations from SIMS. Other metals which were suggested to diffuse only via the CdTe GBs produced significant changes in the junction PL spectra (see Section 3.4). The authors ascribe this to band-bending produced at the heterojunction by ‘connecting it to the back contact via GB’s’. It was proposed that the high and homogeneous Cu-doping of CdTe does not produce such surface band

bending, and therefore shows no effect on the PL spectrum. However, currently no other evidence supporting this model is available and it appears difficult at this stage to suggest experiments to test it.

The effect of Cu diffusion in highly efficient CdS/CdTe/Cu-doped graphite cells was recently investigated by Okamoto et al. [63]. While  $V_{oc}$  and  $I_{sc}$  of cells decreased with increasing temperature of post-contact heat treatments, lower temperatures produced cells with poor FFs (high cell series resistance), probably due to low incorporation of Cu in the CdTe. PL spectra of cells following treatment at increasing temperatures were obtained. Following treatment at 350°C and 365°C (for 15 min), a sharp peak appeared which was assigned to a 'neutral acceptor-bound exciton' line (at 1.590 eV), due to Cu acceptors incorporated onto the Cd sites of CdTe (which would appear to mean that the line is due to a  $Cu_{Cd}$  acceptor-bound exciton). Following treatments at lower (335°C for 15 min) or higher temperatures (380°C and 395°C for 15 min), the PL spectra of the cells reverted to their original form, with a broad peak at a slightly lower energy (Fig. 2). The change was assigned to the low (at lower temperature) or excessive Cu doping (at higher temperatures) of the CdTe film. The same group also reported a PL depth profile of Cu-doped CdTe, measured the same way [64]. Following annealing of a 13  $\mu m$  CdTe film, contacted with a Cu-doped graphite electrode, at 365°C for 15 min, the bound exciton line was observed in the PL spectrum (Fig. 3). After polishing to a film thickness of 12  $\mu m$ , the bound exciton line was absent from the PL spectrum and was replaced again with the broad emission, very similar to the PL spectrum obtained prior to film anneal (Fig. 3). At subsequent depths similar, but weaker, PL spectra were obtained. It was proposed that this result indicated that 'heat treatment for Cu diffusion facilitates the formation of a low resistance contact to CdTe through the formation of a heavily doped ( $p^+$ ) region in the CdTe adjacent to the back electrode, but Cu atoms do not act as effective acceptors in the CdTe layer except in the region near the back electrode'. This, therefore, suggests a role of  $Cu_2Te$  in the formation of successful back contacts to CdTe.

Grecu and Compaan [16] have compared the room-temperature PL spectra of single-crystal CdTe and of the interface region (confirmed to be  $CdS_{0.05}Te_{0.95}$ ), excited through the glass, of glass/SnO<sub>2</sub>/CdS/CdTe/Cu solar cells following Cu diffusion. Diffusion was carried out following thermal evaporation of Cu and annealing at 150°C in air for 60 min, using single crystal samples and at 250°C for 180 min, using the cells. Similar results were obtained in each case. The most significant changes in the spectra following diffusion of Cu was a loss of the donor-acceptor pair (DA) transition, at 1.55 and 1.52 eV for single- and poly-crystal CdTe, respectively, associated with Cd vacancies, probably due to the formation of  $(Cu_i^+ - V_{Cd}^{2-})$  complexes or  $Cu_{Cd}$  states. Another change was an increase in intensity of lower energy bands due to deep acceptor sites. The difference in DA transition energy between the two types of samples was ascribed to alloy formation at the CdTe/CdS interface of the solar cells.

Comparing the different PL measurements we note that the spectra of samples with high Cu content in polycrystalline-CdTe are similar to those with low Cu-content (assuming Cu exists always in CdTe as an impurity even before Cu-contacting [51]), on both CdTe surfaces [62,63]. Intermediate Cu quantities show a distinct exciton

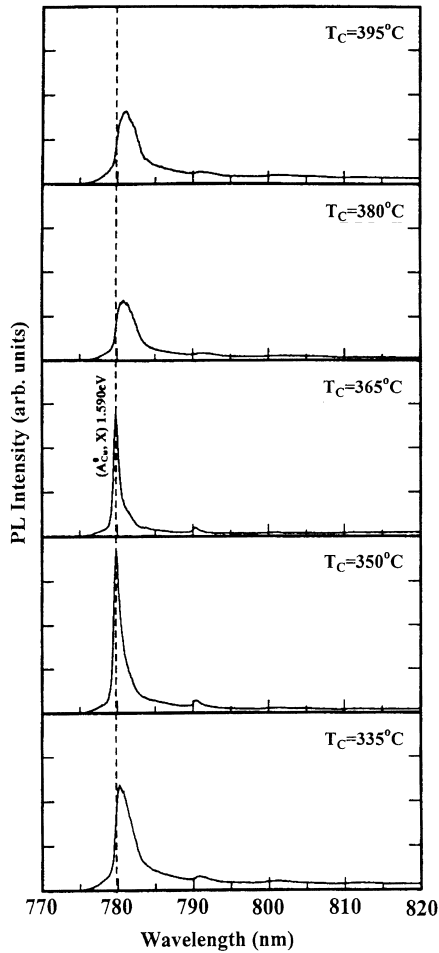


Fig. 2. PL spectra of thin film polycrystalline CdTe layers (prepared by the CSS method) at various temperatures as a function of heat treatment after screen printing of the Cu-doped graphite electrode. The bound exciton line (1.590 eV) is present following treatment at 350°C and 360°C (for 15 min). Different spectra were obtained following lower and higher temperature treatments (also for 15 min), due to very low and excessive Cu-doping, respectively. (Reprinted with permission from Okamoto et al. [63]).

peak (assigned to  $\text{Cu}_{\text{Cd}}$ ), only close to the Cu-containing back contact interface [63,64].

The results of the two junction-PL measurements are contradictory [16,62]. This contradiction might be explained by the differences in the annealing processes and the PL measurement conditions. We note that, from a number of SIMS investigations, Cu has been shown to diffuse throughout the entire CdTe layer, and it is reasonable to assume it is also electronically active there (at least in part). This may not have been evident in the PL results due to the measurement conditions.

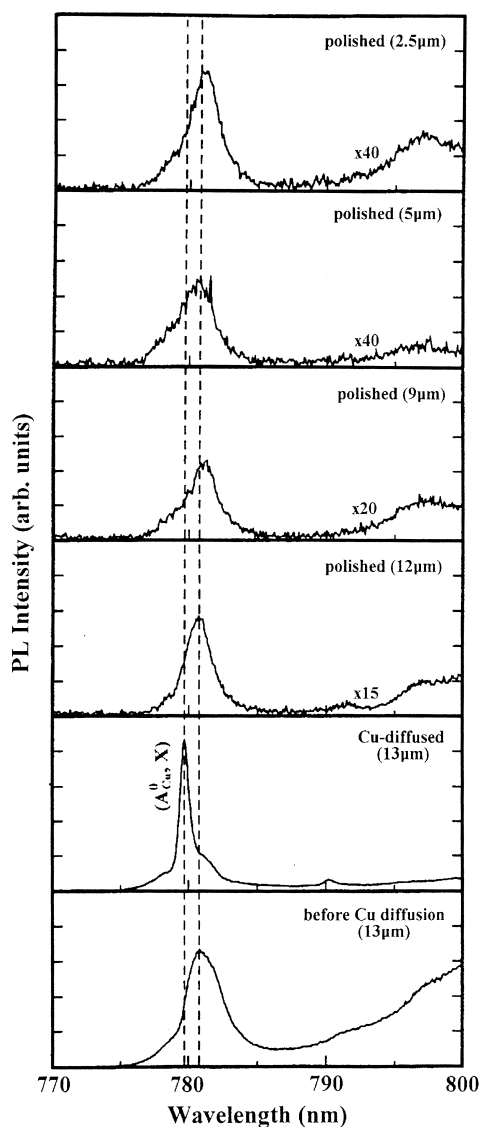


Fig. 3. Depth profiles of PL spectrum of a polycrystalline CdTe film (prepared by the CSS method) heat-treated ( $365^{\circ}\text{C}$  for 15 min) after screen printing of the Cu-doped graphite electrode, as a function of the thickness of the CdTe films remaining after polishing. The bound exciton line (1.590 eV) can be seen only in spectra recorded within in the first micron of the sample. This suggests that Cu atoms act as effective acceptors only in the region immediately below the back contact and may therefore indicate a role of  $\text{Cu}_2\text{Te}$  in the formation of successful back contacts to CdTe. (Reprinted with permission from Okamoto et al. [64]).

### 2.2.3. SIMS studies of Cu diffusion

The effects of stressing on Cu-containing cells were also examined from both the diffusion and the electronic points of view. Chou et al. [12] confirmed from SIMS

measurements the incorporation of Cu into the CdTe film from Au/Cu back contacts during the metallization process (including annealing at 150°C in Ar ambient for 90 min). The SIMS results exhibited a diffusion-like profile through the CdTe with a non-negligible concentration of Cu near the CdTe/CdS interface. No significant change in the Cu profile in CdTe was observed before and after the post-contact anneal. In an attempt to determine the involvement of GBs, the same group prepared CdTe films with different grain size [14]. Thus, single-crystal CdTe was prepared directly on GaAs, and CdTe films containing large ( $\sim 10\text{ }\mu\text{m}$ ) grains were prepared on a CdS/GaAs substrate. To investigate Cu diffusion, cells were contacted with Au/Cu, separated from the GaAs by selective etch with NaOH–H<sub>2</sub>O<sub>2</sub> solution and completed as ITO/CdTe/Cu/Au/glass (for single crystal CdTe, a Schottky junction cell) and ITO/CdS/CdTe/Cu/Au/glass (for large grain CdTe, a p–n junction cell) cells. These cells were compared to the conventional small grain polycrystalline Au/Cu/CdTe/CdS/SnO<sub>2</sub>/glass cell. SIMS measurements showed that the incorporation of Cu into the CdTe film of the conventional cells was more than an order of magnitude greater than what was observed for the larger grain devices, while Cu was undetectable in the single-crystal CdTe device (Fig. 4). This led the authors to suggest that GBs are the main conduits for Cu diffusion in CdTe films (see Section 2.6). A significant amount of Ga was also found incorporated into the large grain CdTe film during substrate preparation. Both the large grain CdTe and single crystal CdTe cells exhibited low conversion efficiencies, suggested to be due to junction degradation by diffused Ga or poor contact bonding.

Tang et al. [65] have recently compared the degradation behavior of ZnTe/Au, ZnTe:Cu/Au and Cu/Au back contacted cells (with ZnTe, Cu:ZnTe and Cu in contact with the CdTe, respectively). It was shown that the Cu dopant plays a significant role

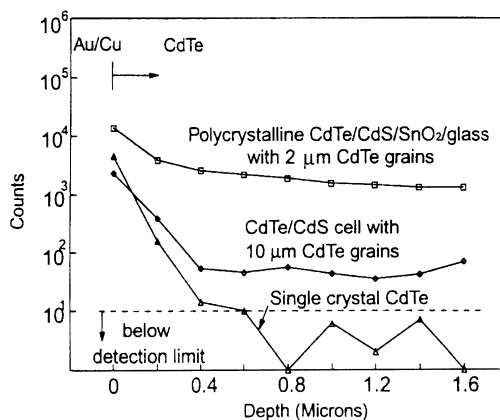


Fig. 4. Comparison of Cu SIMS profiles in thin films of polycrystalline CdTe for samples with different degrees of crystallinity (for details of sample preparation, see text and Ref. [15]). The figure shows high Cu uptake for small-grained CdTe films (following contact deposition and 90 min anneal at 150°C in Ar), but decreases with increasing grain size. This suggests that GBs are the main conduits for Cu diffusion in polycrystalline CdTe. (Reprinted with permission from Chou et al. [15]).

not only in cell performance, but also influences the degradation process. Interestingly, the degradation, which in this case was due to an increase in series resistance and not to a drop in  $I_{sc}$  and  $V_{oc}$ , was less for cells using contacts with higher Cu content. The formation of a back contact barrier following stress testing, was suggested to arise because of a decrease in the CdTe doping level near the contact interface. After anneal of ZnTe:Cu/Au back contacts (140°C for 165 hours in vacuum), Auger Electron- and X-ray Photoelectron Spectroscopies (AES and XPS, respectively) showed that significant interdiffusion of Cu into Au had occurred, as well as the formation of small islands of Te on the Au surface. However, comparative studies of Ni metallization layers showed that no interdiffusion occurred for ZnTe:Cu/Ni back contacts. Interdiffusion of Cu into the Au layer limits the amount of Cu available to diffuse to the CdTe/CdS interface and thus can lead to cells of increased stability due to Cu–Au alloying.

Compaan et al. [66,67] also showed effects of aging on the PL spectra of CdS/CdTe solar cells. With storage under ambient light, the PL lines (including the DA and bound exciton lines) present in the freshly Cu-diffused samples are diminished or eliminated altogether. A decrease of the cell  $V_{oc}$  also occurs during this time. They proposed that aging effects occur as a result of the instability of substitutional  $Cu_{Cd}$  and  $(V_{Cd}^{2-} - Cu_i^+)$  states, leading to the formation of Cu- and Te-rich areas which could act as non-radiative recombination centers. They found that the PL spectrum is partially restored following re-anneal (200°C in air for 40 h). This was also coupled with the restoration of cell  $V_{oc}$ . Hall measurements confirmed, following 7 d storage, a drop in carrier concentration by a factor of 5–10, which was restored to the initial level by re-annealing. To explain these observations they forwarded the following hypothesis [66,67].

- (1) Following diffusion at 200°C,  $Cu_{Cd}$  and/or  $(V_{Cd}^{2-} - Cu_i^+)$  type complexes form (increase in DA PL signal).
- (2) With time/aging these defect complexes decompose into  $Cu_i^+ + V_{Cd}^{2-}$  (due to instability of  $Cu_{Cd}$  and  $(V_{Cd}^{2-} - Cu_i^+)$  complexes) and/or react with another Cu to form a neutral  $(V_{Cd}^{2-} - 2Cu_i^+)$  complex. The authors then postulate the formation of Cu clusters, about which they speculate that these are due to dissociated  $V_{Cd}^{2-}$  being ‘dragged along by the migrating positively charged Cu ions and leading to the formation of Cu- and Te- rich regions’. They suggest that these reactions correspond to reduced (hole) carrier concentration, the formation of traps and recombination centers, and a reduction of the DA PL transition. This process can be accelerated by, for example, light-soaking or application of an electric field.
- (3) Re-annealing the cells (thermal restoration) restores the  $Cu_{Cd}$  and/or  $(V_{Cd}^{2-} - Cu_i^+)$  type complexes, which corresponds to the observed recovery of the DA PL signal.

The PL behavior of Cu in CdTe for aged and thermally restored cells described above is similar to effects reported for Ag-doped single crystal CdTe [52,68]. Chamonal et al. [52] showed that, following storage at room temperature, p-doped samples exhibited a drastic decrease in doping level. Fresh samples showed a DA line in the PL spectrum, but all Ag-related lines disappeared from the spectrum with aging.

The effect was found to be reversible by redistribution of Ag following an 800°C anneal in a Te atmosphere. Yang et al. [68] also showed similar aging effects of Ag-, Li- and Na-doped CdTe, due to the instability of these impurities occupying substitutional defects (on Cd-sites).<sup>3</sup>

### 2.3. Impurity accumulation near the CdS interface

#### 2.3.1. Cu accumulation

Results of SIMS investigations of Cu in CdS/CdTe solar cells, contacted with Cu-doped p-ZnTe, deposited on undoped ZnTe and completed with either Ni or Ti metal were reported [69,70]. Contact deposition was carried out at 300°C. Data obtained from cells without metallization showed some accumulation of Cu near the CdTe/CdS interface. The thickness of the ZnTe and ZnTe:Cu contacts was shown to affect the amount of Cu reaching the CdTe/CdS interface, e.g., thinner undoped ZnTe and thicker Cu-doped ZnTe layers correspond to a greater amount of Cu near the CdS/CdTe interface [69,70]. Cells completed with Ti exhibited enhanced PV stability over cells contacted with Ni [69]. This difference was reflected in the SIMS data, with Ni-contacted cells showing a significant Cu depletion in the ZnTe/Cu layer (corresponding to the very left of the SIMS profiles in Fig. 5a). For cells completed with each metal, a slight increase in Cu concentration, compared to an as-received (non-contacted) device, was detected in the CdTe layer. However, a significant accumulation of Cu was found to occur in or near the CdS layer for each type of cell (Fig. 5a). This observation is consistent with recent PL results which, with excitation by a 2.71 eV laser line, have detected Cu in the CdS layer (and maybe also in the CdTe<sub>1-x</sub>S<sub>x</sub> layer adjacent to it) following annealing of Cu contacts (200°C for 40 min) [66]. A possible explanation for the enhancement of Cu accumulation at the CdS interface with metallization, is that contact metallization affects band bending, and hence the electric field, which may assist Cu<sup>+</sup> diffusion.

The effects of Cu-doping of CdS on device performance and stability have not been previously explored. Cu is well known as a dopant that imparts photosensitivity to CdS [71–73]. Thus we can expect that increased or excessive Cu-doping of n-CdS will be detrimental to the cells' electrical performance. Studies of polycrystalline CdS films doped with Cu during growth showed the films to be actually p-type [74]. Changes in crystal structure, in conductivity and a decrease in band-gap with increasing Cu concentration were also observed [74]. Fahrenbruch and Bube noted that Cu, Ag and Au introduce deep acceptor states into CdS [75])

#### 2.3.2. Cl accumulation

Recently investigations of the effect of CdCl<sub>2</sub> treatment on CdTe/CdS solar cells performance have been reported [76, cf. also ref [77] below]. Pre-contacting CdCl<sub>2</sub>

<sup>3</sup> If this interpretation is correct, then any substitutional defect on the Cd site appears to be unstable, whether larger (Ag<sup>+</sup>) or smaller (Cu<sup>+</sup>, Li<sup>+</sup>) than Cd<sup>2+</sup> (the instability of Na<sup>+</sup> is probably first and foremost due to the instability of tetrahedrally coordinated Na<sup>+</sup> in chalcogen environments).



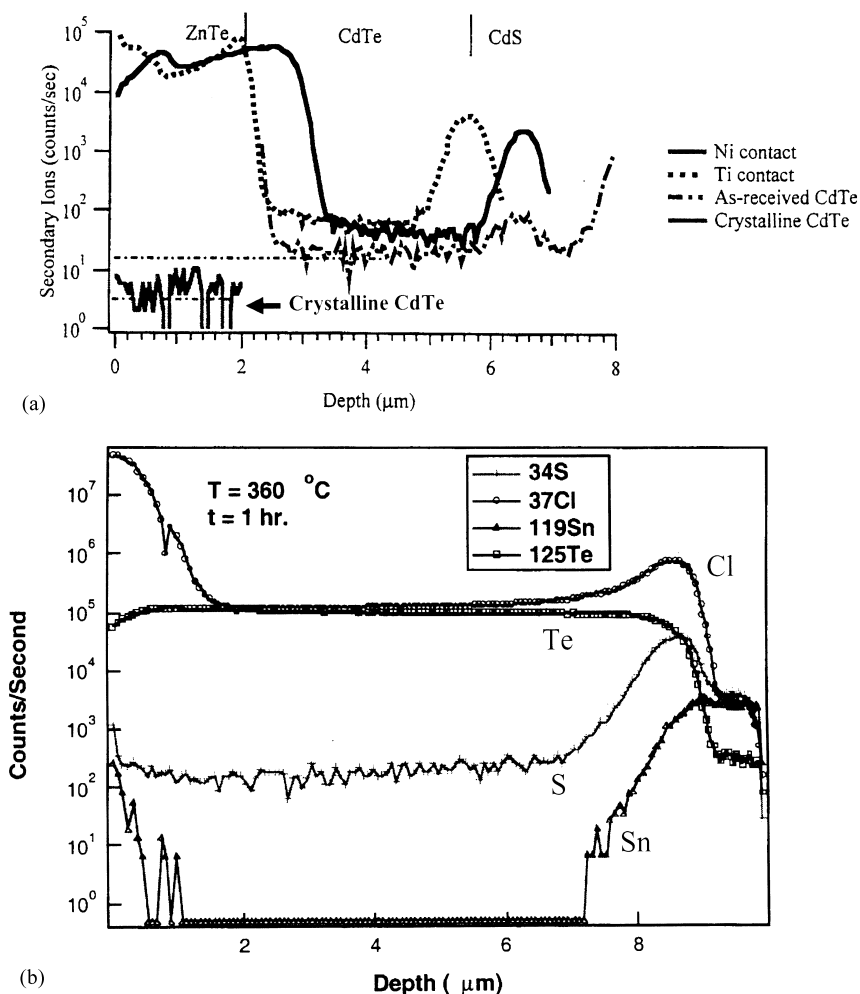


Fig. 5. (a) High-mass resolution SIMS profiles comparing the effect of Ni and Ti metallizations on Cu diffusion from the Cu:ZnTe contact into thin polycrystalline CdTe film (CdTe prepared by the CSS method, back contacts deposited by r. f. magnetron sputtering at  $\sim 300^\circ\text{C}$ ). The figure also shows the SIMS-measured Cu concentration for a non-contacted CdTe device and a single crystal CdTe substrate. (Note that the locations of the interfaces are only approximate, especially for the polycrystalline sample). Cu-depletion in the back contact is noted with Ni, but not with Ti metallization (corresponding to the very left of the profile). An accumulation of Cu near the CdS interface can be seen for both back-contacted cells. (Reprinted with permission from Narayanswamy et al. [69]). (b) SIMS profiles for  $^{37}\text{Cl}$ ,  $^{34}\text{S}$ ,  $^{119}\text{Sn}$  and  $^{125}\text{Te}$  in a polycrystalline CdTe/CdS/SnO<sub>2</sub>:F structure (CdTe prepared by the CSS method) following vapor-CdCl<sub>2</sub> treatment at  $360^\circ\text{C}$  for 1 h (CdCl<sub>2</sub> source temperature was  $400^\circ\text{C}$ ). Profiles have not been normalized. An accumulation of Cl near the CdS interface (corresponding to the increase in S content and decrease in Te content) is clearly seen. The amount of Cl accumulated near the CdS interface increased with higher temperatures and longer treatment times, while the Cl content remained constant within the CdTe layer. (Adapted with permission from Mahathongdy [76]).

treatment of CdTe is well known to improve device performance. SIMS analysis of vapor-CdCl<sub>2</sub> treated cells (at 320°C, 360°C and 400°C) led to a substantial and rapid accumulation of Cl at the CdS interface (for example, by 30 min at 360°C and by 30 s at 400°C). The SIMS profiles in Fig. 5b clearly show accumulation of Cl near the CdS interface of a CdTe/CdS/SnO<sub>2</sub>:F structure following vapor-CdCl<sub>2</sub> treatment at 360°C for 1 h. Similar results are reported in Ref. [77] (see below). Based on the diffusion behavior of Cl in single-crystal CdTe ( $D_{\text{Cl}} = 7.5 \times 10^{-14} \text{ cm}^2/\text{s}$  at 400°C [78], bulk diffusion of Cl through a 10  $\mu\text{m}$  CdTe film is calculated to take almost 40 d [76]). Therefore, from the observation of fast Cl accumulation at the CdS interface following a 30 s CdCl<sub>2</sub> treatment (at 400°C), the author concluded that Cl must move via GB diffusion through the CdTe layer [76]). The amount of Cl that accumulated there increased with treatment times, while the level of Cl remained constant at an apparent saturation limit in the CdTe itself. The accumulation of Cl near the CdS interface was proposed to be due to the greater GB area in the smaller-grain CdS layer compared to the CdTe. The improvement of cell performance following CdCl<sub>2</sub> treatment was correlated to this accumulation, noting that increased times and temperatures of vapor-CdCl<sub>2</sub> treatment further improved overall cell efficiency. Thus the presence of Cl appears to benefit the properties of the p–n junction [76]. We note, though, that no other factors were considered as possible parallel mechanisms for improvement in cell conversion efficiency. Other researchers have also shown, from SIMS profiles, an accumulation of Cl near the CdS interface of non-stressed CdTe/CdS solar cells [77].

An increase in the amount of Cl near the CdS interface of CdTe/CdS cells (contacted with Cu/HgTe-doped graphite) which had been stressed (illumination at short circuit at 100°C for 76 d), compared to non-stressed cells, both prepared at the National Renewable Energy Laboratories (NREL) [79] has been recently observed [80]. No increase in the amount of Cl was found in the CdTe layer following cell stressing. Finally, CdCl<sub>2</sub> treatment of CdS films prior to deposition of CdTe during device preparation has recently been shown to improve device performance [20,81,82].

These observations may suggest a possible correlation of Cl and Cu diffusion in CdTe and/or accumulation near the CdS interface. In this context, it is also of interest to note that photo-conducting CdS can be prepared by recrystallization of CdS, promoted by Cu and Cl at elevated temperatures. Cu and Cl also act as dopants which increase the dark electrical resistance and, therefore photoconductivity, of CdS by compensation [71–73]. This can be explained by formation of complexes such as  $(\text{Cu}_{\text{Cd}}^- - \text{Cl}_{\text{Te}}^+)$ ,  $(\text{V}_{\text{Cd}}^{2-} - 2\text{Cl}_{\text{Te}}^+)$ ,  $(\text{Cu}_{\text{Cd}}^- - \text{Cu}^+)$  and the like, in analogy to what has been proposed for other II–VI compounds [73]. Currently, however, to our knowledge no study of the role of Cu, Cl or other species accumulated in/near the CdS layer, on cell degradation has been reported. While the presence of Cl and/or Cu has been shown to improve CdTe/CdS cell performance, an increase in resistance of the CdS itself, due to accumulation of the diffused species, may be considered to be a significant factor in the degradation of these devices. Other possible detrimental effects may include lowering of n-doping of CdS, resulting in an increased space-charge layer width, which may also affect the cell's  $V_{\text{oc}}$ .

## 2.4. Driving force for Cu diffusion/drift

The mere fact that Cu is present somewhere in the cell structure is insufficient to explain its ability to move throughout the cell structure. This is illustrated by the striking difference in behavior of Cu ions in  $\text{Cu}_2\text{S}/\text{CdS}$  cells and  $\text{CuInSe}_2/\text{CdS}$  (and related) cells [9]. Work on the former cell was stopped because no simple ways were found to prevent Cu from spreading through the cell into the CdS, forming Cu nodules and shorting the cell. In contrast no significant Cu contamination outside the  $\text{CuInSe}_2$  grains has been observed in the latter type of cells. This difference has been explained using so-called ion-potential diagrams, where the electrochemical potential of a mobile ion is calculated and plotted as a function of depth in the device structure [83]. Use of those diagrams for the  $\text{Cu}_2\text{S}/\text{CdS}$  and  $\text{CuInSe}_2/\text{CdS}$  cells immediately showed that while in the former case Cu is expected to accumulate in the CdS near the junction, in the latter case the  $\text{CuInSe}_2$  is a Cu sink, i.e., the Cu ions have their lowest electrochemical potential in the ternary material, *away from* the junction with CdS [84,85]. From the earlier work we know that  $\eta(\text{Cu}^+)$  in CdS is some 200 mV from the reference ( $\eta(\text{Cu}^\circ)$ ) level, while for CdTe we calculate this level to be 300 mV below the reference (from  $10^{19} \text{ cm}^{-3}$  Cu at saturation and  $10^{14} \text{ cm}^{-3}$  residual Cu in CdTe). We need to consider furthermore the direction of the built-in electric field at the CdTe/CdS junction, the magnitude of which we can take for the sake of argument, to be  $\sim 1$  V. We then find a barrier for  $\text{Cu}^+$  migration of more than 1 V, so that even at open circuit no spontaneous Cu movement from bulk CdTe into bulk CdS grains is predicted.

If  $\text{Cu}_2\text{Te}$  is present at the back contact, Cu migration into CdTe is expected to be facile, assuming  $\eta(\text{Cu}^+)$  values in  $\text{Cu}_2\text{Te}$  to be similar to those in  $\text{Cu}_2\text{S}$ , because of the significantly lower  $\eta(\text{Cu}^+)$  in CdTe than in  $\text{Cu}_2\text{Te}$ , also if we take into account a small space charge field at their interface. Thus, while we can expect Cu to be in CdTe, it is not clear how Cu penetrates further in the cell. The most likely mechanism would appear to be GB and surface reaction to form Cu–S bonds, a process that would be aided by S/Te interdiffusion. The driving force for such a process could be the significantly higher strength of the Cu–S than the Cu–Te bond, as derived from their heats of formation [86].

## 2.5. Bias-dependent degradation

An electric field is expected to affect degradation processes such as electromigration (drift) or ionic diffusion. It has been shown that different types of bias (forward or reverse), combined with elevated temperatures, result in different degradation phenomena (see, for example, [87]). Some of these effects, related to Cu migration, were found to be reversible [16,48,87].

Hiltner et al. [22] stressed cells at different biasing conditions (at  $100^\circ\text{C}$  in  $100 \text{ mW/cm}^2$  light for 37 d) with a Cu-containing back contact. They noted that the least degradation occurred for cells stressed at the maximum power point, compared with cells stressed at  $V_{\text{oc}}$  (which displayed the fastest degradation) or at reverse bias. The same trends were also noted by Trefny et al. [88].

Meyers et al. [87] noted that stressing cells at reverse bias ( $-0.5$  V, at  $72$ – $112^{\circ}\text{C}$ , in the dark and  $70\text{ mW}/\text{cm}^2$  illumination) resulted in effects associated with degradation of bulk CdTe properties. This was deduced from the severity of the light-dark cross-over of the  $I$ - $V$  curves, interpreted as a manifestation of light-induced changes in the internal electric field distribution. Mo diffusion from the contact metallization layer into the CdTe was also observed under the same conditions, and therefore may be related to the degradation mechanism, as no significant Mo in-diffusion was seen under forward bias [87].

Stressing at forward bias ( $5\text{ mA}/\text{cm}^2$ , same conditions) resulted in effects that Meyers et al. [87] interpreted as being associated with the formation of a reverse diode at the back contact. Again some accumulation of Cu at the CdS–CdTe interface was also noted, which may be related to a depletion of Cu near the Mo back contact, thus affecting the current transport [87]. Grecu et al. [16] noted changes in the PL spectra of Cu-contacted cells after stressing at forward bias ( $1$  V) or at open-circuit ( $150^{\circ}\text{C}$ ,  $70$  h) (Fig. 6), which was again correlated with Cu diffusion. These changes could be partially reversed by application of reverse bias (Fig. 6) for a longer time ( $40$  h), and the effect did not appear after stressing only at reverse bias ( $-1$  V) [16]. Reversal of  $V_{\text{oc}}$  stressing effects with time (and enhancement at  $100^{\circ}\text{C}$ ) was also noted by Hegedus et al. [48].

Most of these results correlate with the assumption that Cu moves as a positively charged ion. The built-in voltage at the heterojunction slows the concentration gradient-driven diffusion towards the junction, while forward bias and/or light lowers that barrier for diffusion [16,27,88].  $\text{Cu}^+$  is then likely to form ( $V_{\text{Cd}}^2- - \text{Cu}_i^+$ )

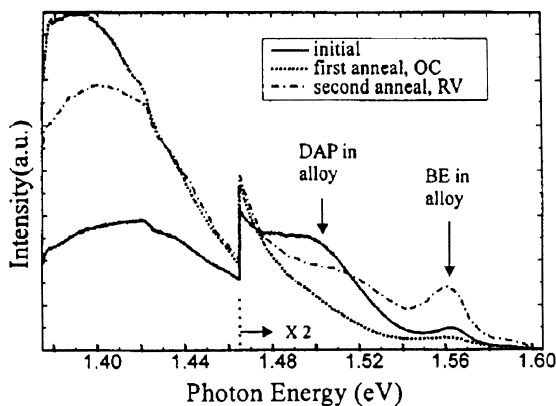


Fig. 6. Junction PL spectra of CdTe/CdS sample (prepared by vapor transport deposition) after two successive anneals: first under open-circuit (OC) conditions ( $150^{\circ}\text{C}$  for  $70$  h) followed by a second anneal under an applied reverse bias (RV) ( $-1$  V for  $40$  h). Changes in the spectra following stressing at open circuit can be correlated with Cu diffusion. The figure shows that these changes could be partially reversed following a second anneal at reverse bias. (Reprinted with permission from Grecu and Compaan [17]).

complexes and/or  $\text{Cu}_{\text{Cd}}$  acceptor states in the vicinity of the cell junction, thus affecting the junction properties and its PL spectrum. The same effect was also assumed to explain the change in the PL spectrum after heating, with temperature reducing the influence on the junction [66]. Dissociation of these acceptor defects under later applied reverse bias, or just aging in the dark, would account for the restoration of the original PL spectrum [16,66]. Therefore  $\text{Cu}^+$  drift should explain the decrease in  $V_{\text{oc}}$  and shunting resistance following forward bias stressing seen by Trefny et al. [88] (it also explains the enhanced degradation in light). We note that the acceptor defect  $\text{Cu}_{\text{Cd}}$  has a charge of 0 or  $-1$  relative to the lattice, and therefore is expected to drift in the opposite direction [27] (see also footnote 2), but at a much slower rate (since it is a substitutional defect). The combined two processes might explain the initial increase in the shunting resistance followed by its decrease at longer times, as seen by Trefny et al. [88] after stressing under reverse bias.

## 2.6. *Cu-related issues — summary*

Addition of Cu to back contacts is commonly used to improve the performance of CdTe/CdS solar cells [11,12], but also reduces the stability of these devices with respect to non-Cu containing back contacts [22]. Degradation is enhanced when devices are stressed under illumination [22,38].

Recent crystallographic investigations have shown that a  $\text{Cu}_2\text{Te}$  phase is formed following deposition of Cu contacts, and an increased level of  $\text{Cu}_2\text{Te}$  was correlated to improved cell performance [40]. A substantial decrease in the  $\text{Cu}_2\text{Te}$  phase was observed following stressing and subsequent degradation of cell performance, including the appearance of ‘roll-over’ in the  $I$ – $V$  behavior at forward bias. From these results we suggest that  $\text{Cu}_2\text{Te}$  assists formation of, or is itself, a low-resistance contact to CdTe. The observations following stress testing of these cells also indicate that  $\text{Cu}_2\text{Te}$  is a good source for Cu diffusion into the CdTe layer. Furthermore, back-contact deterioration, due to loss of  $\text{Cu}_2\text{Te}$ , may well be an additional factor for cell degradation.

Investigations of the effect of stressing cells with back contacts containing varying amounts of Cu, have shown that cell degradation is enhanced with increasing Cu content [59]. However, the appearance of ‘roll-over’ at forward bias was faster with back contacts of lower Cu content. Both these and the previous crystallographic observations, appear to confirm that ‘roll-over’ in  $I$ – $V$  behavior is the result of a decrease in the concentration of acceptors in the CdTe near the back contact and that cell degradation occurs as a result of excessive Cu diffusing further into the cell toward the PV junction.

Even though Cu is known to be a relatively fast diffuser in single crystal CdTe [51], GBs would appear to be the likely pathways for diffusion of species in polycrystalline CdTe [14]. That GB diffusion is the dominant pathway in these cells is supported by SIMS investigations of Cu diffusion in CdTe layers of increasing grain size. Following annealing of Au/Cu back contacts, a substantial uptake of Cu in small-grain (2  $\mu\text{m}$ ) polycrystalline CdTe (as used in conventional CdTe/CdS cells)

and a notably smaller uptake in larger grain (10  $\mu\text{m}$ ) films was measured [14] (see Section 2.2.3).

The results and conclusions obtained from PL studies of the role of diffused Cu in CdTe/CdS solar cells have been contradictory, suggesting for example,

- Cu diffuses through the CdTe and is active at the CdTe/CdS junction [16],
- Cu highly dopes both grains and GBs equally with no change in the sample PL spectrum [62], or
- Cu is only active in CdTe within 1  $\mu\text{m}$  of the back surface [64].

Thus, while these studies are of interest, and the observed differences may be attributed to variations in samples, anneal treatments, measurement conditions, etc, further experiments, preferably in conjunction with complementary SIMS investigations, are needed to determine the location and electronic nature of diffused Cu within CdTe/CdS solar cells.

Interdiffusion of Cu from Cu-containing back contacts backwards to Au metallization layers has been shown to improve stability of CdTe/CdS cells, due to less Cu being available for diffusion [65]. Comparative cells completed with metals that do not allow Cu interdiffusion, e.g., Ni, exhibited poorer stability [65].

Accumulation of diffusing species near the CdS may be expected to occur because of the higher GB area in the small grained CdS layer than in the CdTe one [76] and/or the formation of Cu–S bonds. The former suggestion would be compatible with the partial reversibility of stress-induced degradation [48]. The extent of Cu accumulation was shown to be affected by contact-metallization and contact thickness [69,70]. We suggest that it could also be correlated to accumulation of Cl near the CdS interface following  $\text{CdCl}_2$  treatment. Indeed there is the possibility that changes to CdS properties, which may be detrimental to cell performance, could occur when significant amounts of Cu, Cl or other species are present within the CdS film [71–73]. Ion-potential diagrams indicate that Cu will have a higher affinity for bulk CdTe than for bulk CdS. This suggests that any Cu present in the CdS film must be diffusing in the GBs. While no thorough studies regarding the effect of cell stress on the observed accumulation have been reported, preliminary results indicated an increase in the amount of accumulated Cl in stressed cells compared to non-stressed devices [80]. Note that the electric field at the junction opposes  $\text{Cu}^+$  diffusion to CdS.

The implication of Cu, Cl or other diffused species accumulating in or near the CdS layer, and doping CdS grains and/or GBs, has not been considered hitherto. This is still to be confirmed as being necessary for, or detrimental to, good cell performance or even as an artifact of the SIMS technique. We should caution that the observed accumulation could also be an artifact of diffusion within the cell superstrate. That is, it could be modeled as a case of diffusion in a thin layer between a diffusion source and a diffusion barrier [89], for example, such as between the back contact interface and the  $\text{SnO}_2$ /glass substrate of CdTe/CdS solar cells. In that case, when the diffusing species reaches the barrier layer, it is reflected and produces a symmetrical U-shaped diffusion profile within the thin layer [62,89].

### 3. The role of diffusion of other metals

As the best CdTe/CdS cells to date used Cu-containing back contacts, much less attention has been given to the possible role of diffusion of other species in cell degradation.

#### 3.1. *Te (see also Section 1.4)*

Te was shown to diffuse into CdTe from a Te contact by changes in the PL spectrum after 30 min annealing at 300°C in He atmosphere [62]. The formation of NiTe and NiTe<sub>2</sub> in Ni:P back contacts (after annealing in air at 200–350°C) [19] suggest the occurrence of Te out-diffusion. This also explains YbTe formation in evaporated Yb layers on CdTe single crystals (after several hours of aging at room temperature) [90]. Such tellurides may be the cause of barrier formation at the back contact. However, in other cases they may improve the contact if, for example, the telluride that forms has a higher work function than the contacting metal. It was found that under certain conditions, electroless deposition of 'Ni' on CdTe forms NiTe<sub>2</sub> instead of metallic Ni and that this contact is superior to one of truly metallic Ni formed by the same basic method [91].

Te interdiffusion may change the CdTe doping level by changing the acceptor defect concentration, thus changing the band bending at the back contact interface and possibly creating or increasing a barrier there. Such a change of doping concentration near the Au/CdTe interface was detected by *C–V* measurements [39], and used to explain the change in  $E_F$  at these interfaces [90]. We suggest this observation may also be partly related to Au diffusion into the CdTe. It should be noted that excess Te in CdTe single crystal was shown to enhance Ag and Cu diffusion. This was explained by diffusion along extended defects of Te precipitates [92], or by complex formation with  $V_{Cd}$ . Indeed, Uda et al. [13] observed a decrease in cell PV properties with increasing thickness of the sputtered Te layer of Cu–Te contacts. They proposed that the Te thickness could play a role in controlling the diffusion depth of Cu from the CdTe surface, but no further stability investigations were carried out. The simultaneous diffusion of Te with Cu in CdTe was also suggested to enhance the p-type character of the CdTe film and hence to be an important factor in forming ohmic contacts to CdTe [13].

#### 3.2. *Hg*

Hg is a relatively fast diffusing metal in CdTe ( $D \cong 5 \times 10^{-15} - 5 \times 10^{-13} \text{ cm}^2/\text{s}$  in the temperature range of 350–450°C [93]). Its diffusion coefficient is higher than the Cd self-diffusion coefficient in undoped CdTe ( $D \cong 10^{-14} (500^\circ\text{C}) - 5 \times 10^{-16} (400^\circ\text{C}) \text{ cm}^2/\text{s}$ ), and should be comparable to that of Cd self-diffusion in lightly doped CdTe [94]. Hg diffusion was found to be controlled by diffusion of Cd vacancies (which were introduced by Cd out-diffusion) [93]. Therefore a Te-rich surface layer is expected to enhance diffusion of Hg from a Hg-containing contact such as HgTe, which may be important in degradation processes.

### 3.3. *Mo*

Mo was found to show significant diffusion into the CdTe layer when stressed under reverse bias, but showed minimal diffusion after stressing under forward bias (in both cases stress was for 24 h at 75°C followed by 48 h at 143°C, in N<sub>2</sub> under illumination). Mo in-diffusion was associated with the evolution of high trap density and/ or mobile charges in the CdTe bulk, thus changing the internal electric field distribution and causing degradation [87]. Mo was introduced in this case from a metallization layer on a Cu-containing contact. Therefore, its diffusion may also be related to bias-dependent Cu diffusion (see Section 2.5).

### 3.4. *Other elements*

Changes in the PL spectra of CdTe/CdS cells with Ni, Cr or Pd evaporated on their back surfaces, after 30 min annealing at 300°C in He, were explained in terms of a model, assuming fast GB diffusion of the metals [62]. Such PL changes may indicate changes in the PV behavior of the cells. The model assumed that the metallic impurities are active as dopants, making the GBs channels of high conductivity. These are connected to the back surface, which acts as a ‘grounding layer’, and reach the front surface, and was suggested to produce band bending there [62], though, as mentioned in Section 2.2.2, the reasons for this are not clear. Reversal of this effect was possible by removing the metal layer and some of the CdTe layer adjacent to it. This no longer connects the GB’s and they ‘float’ at the potential of the surrounding bulk material, eliminating the band bending at the front surface. The samples with Cr and Pd required further ion-beam milling, indicating deeper penetration of these metal species compared to that of Ni, an observation that was also supported by SIMS measurements [62]. The authors conclude that fast diffusion of metals from the contact along GBs may create shunting paths through the junction, and change the distribution of the internal field by connecting the front and the back CdTe surfaces.

As a possible solution to avoid diffusion of contact constituents into the CdTe, a thin Yb layer was used successfully, possibly due to formation of a YbTe layer at the surface, as an interlayer between Au and CdTe to suppress interdiffusion [90].

## 4. **Oxide formation at the back contact**

Some researchers have suggested that oxygen migration through the back contact might play a role in back contact degradation. This could result in the formation of an insulating oxide layer on the CdTe surface (especially when stressed in forward bias) [44,87]. However, the formation of a back contact barrier was also observed after stressing in oxygen-free ambient (in a glove box with flowing N<sub>2</sub> (relative humidity lower than 2%), for example [95]), and oxygen can be avoided by proper encapsulation. The native oxide layer on the CdTe surface is often assumed to be thin enough (1–2 nm) to allow tunneling and thus not to present a serious barrier to carriers [44].



Post-contacting etching was shown to improve the cell performance, probably due to removal of surface oxides from beneath the contact (see Section 1.4).

## 5. Aspects of degradation related to cell interfaces

### 5.1. *CdTe/CdS interface*

CdTe/CdS intermixing is thought to be enhanced by the  $\text{CdCl}_2$  heat treatment [4]. This is not surprising, since the  $\text{CdCl}_2$  acts as a flux, facilitating solid solution formation between different Cd (and Zn) chalcogenides [96,97]. The intermixing was correlated with relatively high cell efficiency [2]. Reasons suggested to explain this include reduction of the lattice mismatch, thus lowering the interface defect density, and/or a decrease of the leakage current caused by tunneling and interface recombination [2].

The formation of an interface of a  $\text{CdTe}_{1-x}\text{S}_x$  layer after post-deposition heat treatment has been shown by a number of methods, including SIMS [2,4], angle-dependent X-ray fluorescence [98] and micro-EDS [4]. It was also suggested by optoelectronic measurements that showed the presence of a layer with a slightly smaller band-gap than that of CdTe, corresponding to a  $\text{CdTe}_{1-x}\text{S}_x$  alloy with  $x \leq 0.25$  [4,45,99].

The width of the intermixed layer, as well as its structure and composition, were found to depend strongly on the post-deposition treatment parameters ( $\text{CdCl}_2$  concentration, temperature, duration, etc.) and the layers' deposition process and properties [20,45,98,100,101]. However, no data were published to date about possible variations in that layer after stressing. Therefore, its influence on the stability of CdTe/CdS cells is still unknown. Further CdTe/CdS intermixing may cause a reduction in the window transmission, reducing the maximum possible photocurrent. Changes in the doping level due to intermixing could lead to a change in the junction mechanism and in the space-charge-layer width, possibly resulting in decreased  $V_{oc}$ . Changes in the interface layer composition, and therefore in its band gap, might change the junction location and affect the built-in voltage. In addition, it was suggested rapid GB diffusion, as shown for S in CdTe [4], may cause increased shunting, due to a reduced band-gap or formation of a metallic-like alloy in the intermixed region, thus resulting in degraded cell performance.

### 5.2. *SnO<sub>2</sub>/CdS interface*

The transparent conducting oxide (TCO)/CdS interface is usually considered to be a stable and low-resistance contact [40]. Soft XPS measurements did not reveal interdiffusion of Sn, Cd and S across the interface after a 400°C annealing [102]. SIMS, however, revealed some  $\text{SnO}^+$  and  $\text{Sn}^+$  present in the CdS layer after standard cell processing, including a 400°C  $\text{CdCl}_2$  anneal [2]. These results maybe artifacts of the measurement and, thus, while it is possible that this interface is a locus for cell instability, it is not likely.

## 6. Conclusions and further suggestions

Addition of impurity species, and in particular Cu, to back contacts on CdTe improves the PV performance of CdTe/CdS solar cells [11,12]. The presence of excess Cu also leads to poor stability of cells under working conditions [22]. Increasing the amount of Cu present in the back contact increases the rate of cell degradation following stress testing.

Deposition of Cu on Te-rich CdTe surfaces forms a  $\text{Cu}_2\text{Te}$  phase there [60]. Increasing amounts of  $\text{Cu}_2\text{Te}$  were correlated with improved cell performance. Following cell degradation the amount of  $\text{Cu}_2\text{Te}$  phase was substantially diminished [59]. This suggests that  $\text{Cu}_2\text{Te}$  helps the formation of successful low resistance contacts to p-CdTe, but also acts as a source for further Cu diffusion into the cell, suggesting back-contact deterioration as an additional cause for cell degradation.

Cu uptake is larger in conventional small-grain CdTe films, than in larger-grained films and single crystal CdTe, under the same diffusion conditions [14]. Hence GBs appear to be the most likely pathways for diffusion of Cu and other species in polycrystalline CdTe films, and faster diffusion is expected there than in the bulk.

Similarly, Cl movement through CdTe polycrystalline films during  $\text{CdCl}_2$  treatment is also likely to occur via GB diffusion [76]. 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.

We have highlighted some interesting recent SIMS observations, which indicate an accumulation of diffused Cu, Cl and other species in, or at least near, the CdS layer of CdTe/CdS solar cells [69,70,76,77]. This accumulation may be due to the increased GB area of the smaller-grain CdS (and perhaps also the bottom layer of the CdTe grains) [76]. Ion potential considerations indicate that Cu is unlikely to diffuse into the bulk CdS grains, leaving GB diffusion as a likely path, with the assistance of a surface reaction with sulfur as a driving force. It has also been suggested that diffusion and accumulation of Cl and Cu may be correlated, e.g. formation of  $(\text{Cu}_{\text{Cd}}^- - \text{Cl}_{\text{Te}}^+)$  complexes, and some considerations of possible effects of enhanced concentrations of these species in the CdS layer have been described in the text. It would appear worthwhile to investigate these ideas further, to make sure that they are not due to artifacts, and assess any role of these accumulation phenomena on PV performance and the stability of CdTe/CdS solar devices. In this respect it may also be of interest to examine the PV performance of CdTe solar cells made with intentionally Cu-doped CdS layers.

SIMS and PL data have highlighted that Cu and Cl already accumulate near the CdS interface of CdTe/CdS solar cells already after standard back-contact anneal treatments. We suggest that at this stage the Cu is only *on* the grain surfaces. The degradation of cell performance following stress could be the result of penetration of impurity species *into* the bulk of the CdS grains. This would be expected to decrease n-doping of CdS and make the layer more insulating, an effect that will be enhanced in the presence of both Cu and Cl [71–73].

Fig. 7 shows a schematic representation of some of the processes proposed to be involved in Cu-induced instability of CdTe/CdS solar cells which have been

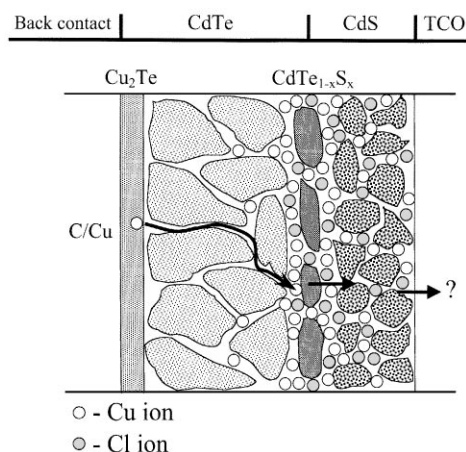


Fig. 7. Schematic illustration of the behavior of Cu and Cl within CdTe/CdS solar cells. Processes shown are: formation of Cu<sub>2</sub>Te at back contact/CdTe interface, GB diffusion of Cu from the Cu<sub>2</sub>Te to the intermixed and CdS layers, accumulation of Cu and Cl ions in the GBs in this region and further GB diffusion to, and possibly penetrating, the TCO interface.

highlighted in this review. These include formation of Cu<sub>2</sub>Te following deposition of Cu-containing back contacts, fast GB diffusion of Cu from the surface telluride (resulting in depletion of the Cu<sub>2</sub>Te with cell degradation) and accumulation of Cu and Cl in GBs in or near the alloy and/or CdS regions. Further 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.

CdTe/CdS intermixing creates a CdTe<sub>1-x</sub>S<sub>x</sub> layer ( $x < 0.25$ ) close to the heterojunction. Mixing is more extensive at the GBs, probably due to fast GB diffusion of elemental sulfur [4]. Possible degradation mechanisms connected with this intermixing are:

- reduction in optical transmission of the window, and therefore in the photocurrent
- changes in the internal field distribution, resulting in decreased  $V_{oc}$  and changes in the space-charge-layer width.

We are not aware of published data about changes in this layer due to stressing. We suggest that such data are needed to determine whether, and to what extent, the intermixing process proceeds under working conditions. The effect of compositional changes of the GBs on the PV behavior of the cell is also of interest.

To overcome Cu-induced CdTe/CdS cell instability, new approaches to cell construction must be developed. Ideally the use of Cu-free back contacts is needed, but, in general, cells currently completed with such contacts exhibit poorer initial PV performance. However, recent promising results from cells back contacted with Sb<sub>2</sub>Te<sub>3</sub>, appear to indicate that reasonable cell performance and stability can be achieved without the use of Cu [20].

Further focussed investigations, using controlled experiments to understand the nature of Cu (e.g. oxidation state, coordination number, etc.) within degraded CdTe/CdS solar cells, can help in first determining and then preventing Cu-related cell degradation mechanisms.  $\text{CdS}_x\text{Te}_{1-x}$ /CdS cells, where CdTe is replaced with the Cd(S, Te) alloy [103], may be expected to exhibit improved stability over conventional CdTe/CdS cells. This is due to the fact that Cu diffusing from the back contact would form  $\text{Cu}_2\text{S}$  within the alloy and thus be prevented from reaching, and reacting within, the CdS layer. Also the use of a different fluxing agent for CdTe (and CdS) post-deposition treatment, such as  $\text{CdI}_2$ , may limit the possible detrimental symbiotic behavior related to the presence of Cl and Cu within the cell, and hence, may be beneficial to both cell performance and stability. Finally, we stress the need for systematic research to understand apparent differences between the stability behavior of average modules, on the one hand, and that of high efficiency cells, on the other.

## Acknowledgements

This research was supported through the United States DOE, via the National Renewable Energy Laboratories' Thin-Film Photovoltaics Partnership Program. The authors thank K. Zweibel and D. Albin of NREL, A. Compaan and D. Grecu of the University of Toledo, J. Sites of Colorado State University and B. McCandless, S. Hegedus and R. Birkmire of University of Delaware, for their assistance and advice, and K. Gartsman (Weizmann Institute) for discussions.

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