

# Copper Migration in CdTe Heterojunction Solar Cells

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CdTe solar cells were fabricated by depositing a Au/Cu contact with Cu thickness in the range of 50 to 150Å on polycrystalline CdTe/CdS/SnO<sub>2</sub>/glass structures. The increase in Cu thickness improves ohmic contact and reduces series resistance ( $R_s$ ), but the excess Cu tends to diffuse into CdTe and lower shunt resistance ( $R_{sh}$ ) and cell performance. Light I-V and secondary ion mass spectroscopy (SIMS) measurements were performed to understand the correlations between the Cu contact thickness, the extent of Cu incorporation in the CdTe cells, and its impact on the cell performance. The CdTe/CdS/SnO<sub>2</sub>/glass, CdTe/CdS/GaAs, and CdTe/GaAs structures were prepared in an attempt to achieve CdTe films with different degrees of crystallinity and grain size. A large grain polycrystalline CdTe thin film solar cell was obtained for the first time by selective etching the GaAs substrate coupled with the film transfer onto a glass substrate. SIMS measurement showed that poor crystallinity and smaller grain size of the CdTe film promotes Cu diffusion and decreases the cell performance. Therefore, grain boundaries are the main conduits for Cu migration and larger CdTe grain size or alternate method of contact formation can mitigate the adverse effect of Cu and improve the cell performance.

**Key words:** CdTe, Cu migration, heterojunction, solar cells

## INTRODUCTION

Polycrystalline CdTe solar cells are one of the leading candidates for cost-effective photovoltaics due to near-optimum bandgap (1.44 eV), high absorption coefficient, and manufacturability.<sup>1-3</sup> High-efficiency (>10%) polycrystalline CdTe/CdS solar cells have been made by various techniques.<sup>4</sup> However, cells made by different groups show a significant variation in cell parameters, and there is a considerable lack of understanding of the efficiency-limiting mechanism in the CdTe/CdS cells. One of the principal barriers to obtaining higher efficiency CdTe solar cells is the resistive and/or unstable contact to p-type CdTe.<sup>5</sup> The difficulties come from the compensation mechanism in II-VI semiconductors and the large work function of p-type CdTe.<sup>6</sup> Several investigators have obtained reasonable cell efficiencies by utilizing Au/Cu metal films<sup>7</sup> or graphite paste doped with Cu or Hg<sup>8</sup> to form ohmic contacts on CdTe. We have shown<sup>9</sup> that copper

plays a dual role in the CdTe/CdS solar cells with a Au/Cu contact. On one hand, it helps in the formation of better ohmic contact to CdTe and increases the acceptor doping concentration; but on the other hand, excess Cu diffuses all the way to the CdTe/CdS interface, forms recombination centers and shunt paths, and degrades the cell performance. However, the source and magnitude of Cu migration need to be understood in order to control the Cu incorporation into the CdTe films and to enhance the solar cell performance intelligently. In this paper, an attempt was made to understand the correlation between Cu thickness, Cu distribution in the CdTe films, and the cell performance. CdTe thin films with different degrees of crystallinity and grain size were grown by varying substrates and growth conditions. CdTe solar cells were then fabricated on these CdTe films by lift-off/etch back and film transfer techniques in an attempt to understand the effect of crystallinity and grain boundaries on Cu incorporation in the CdTe films and its impact on the CdTe cell performance. Detailed material and cell characterization was per-

**Table I. CdTe Solar Cell Parameters with Different Au/Cu Contact**

	400Å Au/50Å Cu	400Å Au/150Å Cu
$V_{oc}$ (V)	0.73	0.71
$J_{sc}$ (mA/cm <sup>2</sup> )	22.28	22.4
$R_s$ ( $\Omega$ -cm <sup>2</sup> )	4.7	3.62
$R_{sh}$ ( $\Omega$ -cm <sup>2</sup> )	1104	272
Fill factor	0.61	0.58
Efficiency (%)	9.9	9.2

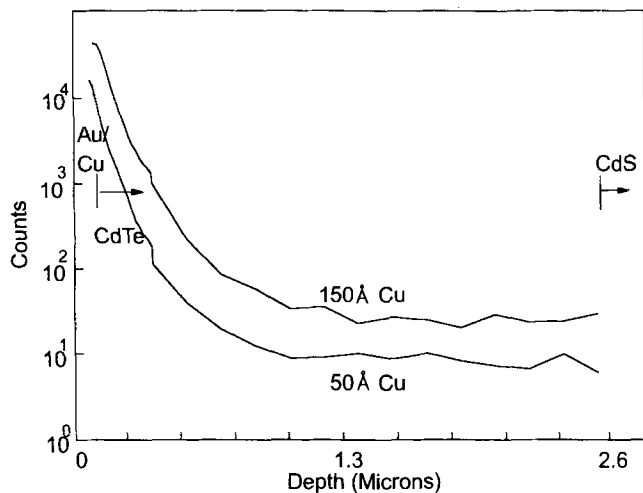


Fig. 1. Cu depth profiles from SIMS measurement on the cells with 50 and 150Å Cu contacts for a Au/Cu/CdTe/CdS/SnO<sub>2</sub> cell structure. The signal was plotted as a function of eroded depth based on the measured CdTe layer thickness. The uncertainty of interface position is estimated to be about 200 nm due to collisional atom mixing and surface roughness.

formed by light I-V measurement, scanning electron microscopy (SEM), x-ray diffraction, and secondary ion mass spectroscopy (SIMS).

### EXPERIMENTAL TECHNIQUES

CdS films were first deposited on textured SnO<sub>2</sub>/glass substrates by a solution growth technique using cadmium chloride, thiourea, ammonium chloride and ammonia.<sup>10</sup> The CdS/SnO<sub>2</sub>/glass substrates were then treated with a CdCl<sub>2</sub>:CH<sub>3</sub>OH solution and annealed in a furnace at 450°C for 50 min in N<sub>2</sub> ambient. Polycrystalline CdTe films with a thickness of ~2.6 μm were grown by MOCVD on the annealed CdS/SnO<sub>2</sub>/glass substrates at a temperature of 400°C. After the CdTe deposition, these CdTe/CdS structures were again treated in a CdCl<sub>2</sub>:CH<sub>3</sub>OH solution followed by an air anneal at 400°C for 30 min. This treatment was performed to enhance the grain growth and to improve the cell performance.<sup>11</sup> Ohmic back contacts were formed on the CdTe surface by sequentially evaporating Cu and Au. The thickness of the Cu layer was varied from 50 to 150Å. After the metallization, the cells were annealed at 150°C in Ar for 90 min. Cell fabrication was completed by etching the CdTe surface in 0.1% Br<sub>2</sub>:CH<sub>3</sub>OH, followed by a DI water rinse and N<sub>2</sub> blow-dry.

Several characterization techniques were utilized

to determine the CdTe film quality, atomic distribution of Cu, Te, and Cd, and the electrical properties of the finished devices. Cell efficiencies were measured under 100 mW/cm<sup>2</sup> air-mass (AM) 1.5 illumination. The microstructure and grain size of the CdTe layer was determined by SEM with a beam voltage of 15 kV. X-ray diffraction (XRD) measurements were performed to study the orientation and crystallinity of CdTe layer by using a Phillips PW 1800 automatic diffractometer with 1.5418Å Cu-K<sub>α</sub> radiation with the diffraction angle 2θ in the range of 20 to 70°.

The depth distribution of Cu, Cd, and Te through the CdTe cell was determined by using an ATOMIKA-ADIDA 3500 SIMS system. Profiling was done with a 40 nA, 12 keV O<sub>2</sub><sup>+</sup> beam. The beam was generally rastered over a 600 micron square area when profiling through the region of the Cu/CdTe interface and then the raster area was reduced to a 200 micron square for a faster profile through the much thicker CdTe/CdS layers. Signals of the monoatomic positive ions were recorded. Detection only from the central 30% of the rastered area was examined in order to avoid crater edge effects. Profiles were terminated when the eroded crater penetrated through the CdTe/CdS layers to the SnO<sub>2</sub>/glass interface.

There are a number of well known complexities in the interpretation of SIMS depth profiles. The technique provides a reliable relative indication of impurity concentration when the impurity is dilute and the matrix is homogeneous. In the present case, analysis is performed through a series of layers, Au/Cu/CdTe/CdS, in each the detection sensitivity of a species is unknown. Moreover, the detection sensitivity for each species will vary from one layer to the next and where concentration is high, a signal may not linearly relate to atomic concentration.

In drawing conclusions from the SIMS analysis, we used only the relative variation of a particular signal with depth through a single layer of the structure to represent relative variation of concentration. In addition, we used ratios of signals from different samples to represent ratios of atomic concentrations. These analyses do not involve any assumptions concerning detection sensitivity nor how such sensitivity might vary as an interface is crossed. Further complications arise in the establishment of the positions of interfaces in the SIMS profile. The first concern is that, with the TENCOR profilometer, the surface of the solar cells was found to be "rough," with topographical irregularities of the order of 200 nm. This is perhaps not surprising since the samples are polycrystalline and grown on glass. But it does mean that the record of buried interfaces will be "smeared" by this amount. Moreover, it is well known that collisional mixing will further distort the indication of an interface. A rough indication of distortion in the metallic layers can be extrapolated from the measurements of King and Webb<sup>12</sup> on an interface between silver isotopes, which results in an interface width of 10 nm for the conditions of the present experiment. The inherent roughness of the samples will thus limit any attempt to

establish an interface position. Another complexity is a possible interference from doubly ionized Te with the  $\text{Cu}^+$  ions at mass 63 and 65. To correct for this, the signal of mass 128  $\text{Te}^{2+}$  (mass to charge ratio of 64) was monitored and the  $\text{Te}^{2+}$  signals at masses 126 and 130 were calculated using the well known isotope ratios; these were then subtracted from the signals at mass to charge ratios 63 and 65 to give the true signals from  $\text{Cu}^+$ . The resulting copper signals were consistent with generally accepted isotope ratios.

## RESULTS AND DISCUSSION

### The Effects of Cu Thickness on Cell Performance

In order to achieve better and reliable CdTe solar cells with Au/Cu contact, it is important to understand the correlation between the Cu contact thickness, the amount of Cu incorporated into the CdTe layer and near the CdTe/CdS interface, and the resulting cell performance. CdTe solar cells with 50 and 150 Å thick Cu contacts were fabricated with the same Cu deposition rate of 0.3 Å/s, while the Au thickness was maintained at 400 Å. Light I-V measurements were performed to quantify the change in  $R_s$ ,  $R_{sh}$ , and cell performance. Cell parameters in Table I show that both  $R_s$  and  $R_{sh}$  decreased when the Cu thickness increased from 50 to 150 Å. This is due to the increase in Cu thickness, which results in a better ohmic contact, thus reducing  $R_s$ , but the excess Cu causes shunt paths or recombination centers, which tends to lower  $R_{sh}$  and cell performance. These results support the dual role of Cu on CdTe cell performance. In order to investigate how the amount of Cu in the contact affects the Cu distribution in the CdTe films, SIMS measurements were performed on the cells with 50 and 150 Å Cu contacts. Figure 1 shows the SIMS profiles of Cu found in the CdTe films for the above two cells. The profiles were normalized to constant beam current density. At all depths, the density of Cu in the CdTe for the 150 Å Cu was significantly higher than that for the 50 Å Cu layer. Thus, increase in Cu thickness in the Au/Cu contact increased the diffused Cu concentration in the CdTe film and at the CdTe/CdS interface of the cell. This reduced  $R_{sh}$  and led to degradation in cell performance. Therefore, reduction of Cu concentration in CdTe films is essential in order to increase  $R_{sh}$  and cell efficiency.

The Cu distributions obtained by SIMS measurements in Fig. 1 clearly show that Cu penetrates into the CdTe, exhibiting a diffusion-like profile, and retains a significant concentration even at a depth of 2.6  $\mu\text{m}$ , where the CdTe/CdS interface is located. We reported in a previous study<sup>9</sup> that Cu found in the CdTe layer arrives via diffusion during the metallization process. In polycrystalline CdTe solar cells, the penetration depth of the Cu into the CdTe might be enhanced by fast diffusion of small  $\text{Cu}^+$  ion along grain boundaries. In addition, the ionic radius of  $\text{Cu}^+$  is close to that of  $\text{Cd}^{2+}$ , enabling easy substitution for  $\text{Cd}^{2+}$ .<sup>13</sup>

### Investigation of the Source of Cu into CdTe Solar Cells

#### Growth of CdTe Films with Different Degrees of Crystallinity

In order to understand the role of grain boundary on Cu incorporation, CdTe films with different degrees of crystallinity and grain sizes were grown by selecting different substrates and growth conditions. The CdTe layer grown on a CdS/GaAs substrate is expected to have higher crystallinity (due to the single crystal GaAs substrate) than the CdTe film grown on a CdS/SnO<sub>2</sub>/glass or SnO<sub>2</sub>/glass amorphous substrate. However, due to the inferior crystallinity of the CdS layer, which is formed by a low-temperature solution growth process, the crystallinity of the CdTe on CdS/GaAs was not as good as the CdTe grown directly on the GaAs substrate. CdTe/CdS/SnO<sub>2</sub>/glass,

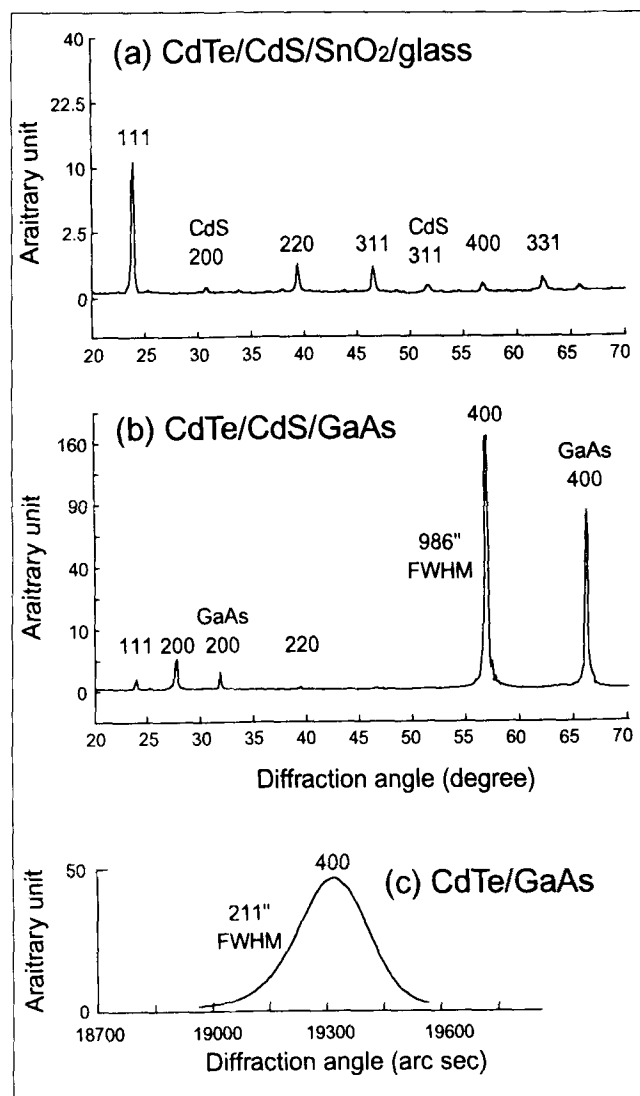


Fig. 2. XRD patterns for the CdTe in the CdTe/CdS/SnO<sub>2</sub>/glass structure (a), and in the CdTe/CdS/GaAs structure (b). Double crystal rocking curve (DCRC) x-ray diffraction pattern for the CdTe in the CdTe/GaAs structure (c).

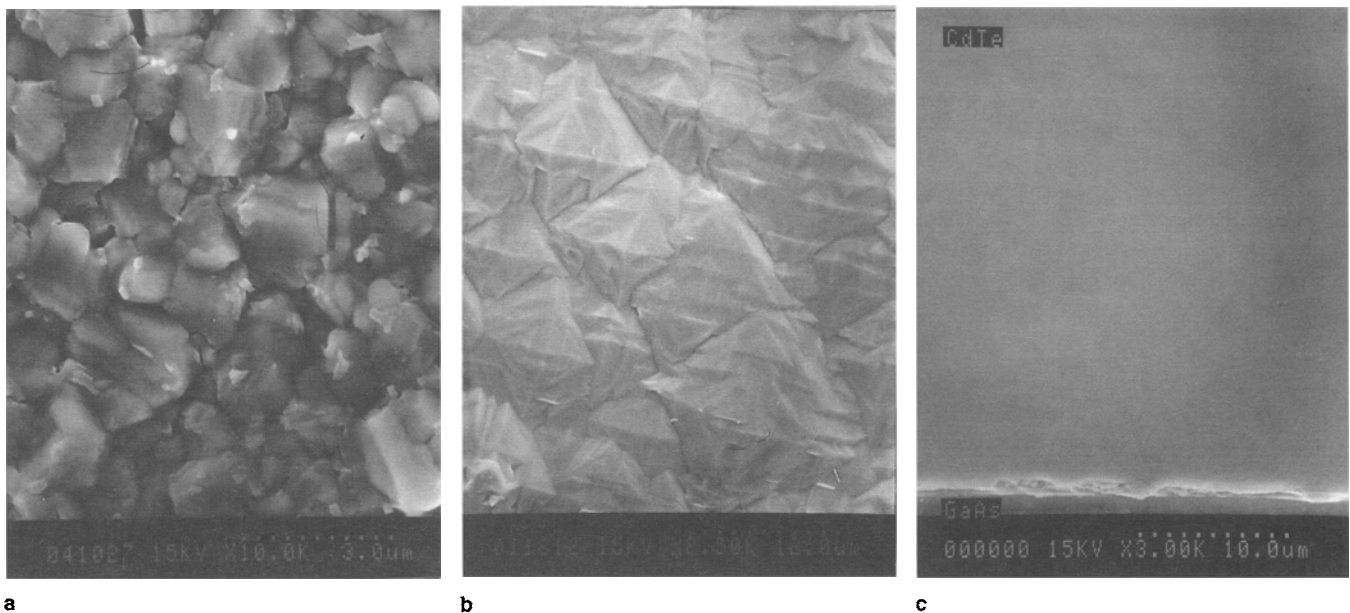


Fig. 3. SEM measurements on the CdTe layers for (a) CdTe/CdS/SnO<sub>2</sub>/glass, (b) CdTe/CdS/GaAs, and (c) CdTe/GaAs structures.

CdTe/CdS/GaAs, and CdTe/GaAs structures were grown to achieve different degrees of crystallinity in the CdTe films. A 600Å thick CdS layer was first grown on a (100) GaAs substrate by solution growth, followed by growth of a 2.6 μm thick CdTe layer by MOCVD to complete the CdTe/CdS/GaAs structure. For the CdTe/GaAs structure, CdTe layer was directly grown by MOCVD on a (100) with 10° off to (110) GaAs substrate.

SEM and XRD measurements were performed to verify the different degrees of crystallinity of the CdTe films grown on different substrates and under different growth conditions. X-ray diffraction measurements were first performed to study the orientation and crystallinity of the CdTe films (Fig. 2). For the CdTe/CdS/SnO<sub>2</sub>/glass structure, used to fabricate CdTe cells, the XRD data revealed a polycrystalline structure with various grain orientations (Fig. 2a). In contrast to the CdTe/CdS/SnO<sub>2</sub>/glass structure, the XRD patterns for the CdTe/CdS/GaAs structure showed a very intense (400) peak located at  $2\theta = 56.75^\circ$  with full-width at half-maximum (FWHM) of 986 arc sec, together with some smaller peaks of other orientations (Fig. 2b). This indicates a polycrystalline CdTe layer in the CdTe/CdS/GaAs structure with preferential (100) orientation. XRD patterns could not be obtained for the CdTe/GaAs structure by using the Phillips PW 1800 diffractometer due to the orientation of the GaAs substrate, which is (100) with 10° off to (110). In order to investigate the quality of the CdTe layer, double crystal rocking curve (DCRC) x-ray diffraction measurements were performed on the CdTe/GaAs structure. A Bede Scientific QC2a diffractometer with a (400) Si monochromator and CuK<sub>α</sub> radiation was used to measure the (400) CdTe rocking curve. The FWHM value for the CdTe grown on GaAs substrate was 211 arc sec (Fig. 2c), compared to a 986 arc sec value for CdTe grown on CdS/GaAs

substrate. This indicates a highly oriented, high quality CdTe layer in the CdTe/GaAs structure.

SEM measurements were performed in order to investigate the microstructure of various CdTe layers grown in this study. The CdTe layer grown on CdS/SnO<sub>2</sub>/glass substrate showed a loose, random grain structure with much smaller grain size (about 1–2 μm), implying a larger grain boundary surface area per unit volume,  $S_v$  (Fig. 3a). The  $S_v$  value can be obtained by<sup>14</sup>

$$S_v = 2 P_L, \quad (1)$$

where  $P_L$  is the average number of intersections of a randomly oriented test line of unit length with the observed grain boundaries. The  $S_v$  value for the CdTe layer grown on CdS/SnO<sub>2</sub>/glass substrate was about 1.66 μm<sup>-1</sup>. In contrast, the average grain size of the CdTe layer on CdS/GaAs was approximately 10 μm, along with some smaller grains (Fig. 3b). By using Eq. (1), the  $S_v$  value was estimated to be about 0.24 μm<sup>-1</sup> for the CdTe on CdS/GaAs substrate. SEM measurements on the CdTe grown on a GaAs substrate showed a smooth, mirror like surface morphology with no grain boundaries (Fig. 3c), indicating a single crystal CdTe structure. Thus, SEM measurements are consistent with the XRD measurements, supporting the growth of CdTe films with different degrees of crystallinity.

#### *Development of Large Grain CdTe/CdS and Single Crystal CdTe Thin Film Structures by Selective Etching*

In order to examine Cu incorporation in the CdTe films of different crystallinity, thin film solar cell structures were fabricated by utilizing a selective etch to separate the epitaxial films from the growth substrate. The separation of epitaxial CdTe has been demonstrated for CdTe grown onto Si substrate.<sup>15</sup> In

this work, we separated CdTe and CdTe/CdS layers grown on GaAs.

As shown in Fig. 4, a 400Å Au/100Å Cu metal contact was first deposited on the CdTe/CdS/GaAs and CdTe/GaAs structures and then the structure was inverted and bonded to a glass substrate with Ag-epoxy or In/Au solder. The thin films were then separated from the GaAs substrate by selectively etching the GaAs with NaOH-H<sub>2</sub>O<sub>2</sub> solution. After the GaAs substrate removal, an ITO film was deposited to complete the fabrication of ITO/CdS/CdTe/Cu/Au/glass (p-n heterojunction), and ITO/CdTe/Cu/Au/glass (Schottky junction) cell structures, in which the incident sun light enters through the ITO layer. This is the first time a single crystal and a large grain polycrystalline thin-film CdTe solar cell structure has been fabricated by selective etch and substrate transfer.

*Cu Migration in the CdTe Solar Cells with Varying Degree of CdTe Crystallinity*

The above cell structures with different CdTe crystallinity were subjected to SIMS analysis. SIMS measurements were performed on the thin film single crystal CdTe cells (ITO/CdTe/Cu/Au/glass), CdTe/CdS cells (ITO/CdS/CdTe/Cu/Au/glass) with large CdTe grains, and the conventional small grain polycrystalline Au/Cu/CdTe/CdS/SnO<sub>2</sub>/glass cells. Cu depth profiles in Fig. 5 clearly show that the Cu concentration in the CdTe/CdS cell structure with 10 μm grain size is more than an order of magnitude less than the Cu in the conventional small grain polycrystalline CdTe/CdS solar cell structure with 1–2 μm grain size. The Cu concentration in the single crystal CdTe structure is much lower and was in fact below the detection limit of our SIMS system. This suggests that the grain boundaries in the CdTe films are the main conduits for Cu diffusion and are responsible for Cu-induced cell degradation. Therefore, large CdTe

grains or less grain boundary surface area per unit volume can mitigate the adverse effect of Cu on the cell performance.

Even though we are able to reduce the Cu incorporation in the cells with large grain structure, the cell efficiency was only 3.4% for the large grain CdTe/CdS cell and 5.1% for the ITO/CdTe single crystal cell structure. One possible explanation is that fast diffusers, such as Ga from the GaAs substrate, may diffuse into the CdTe film and degrade the cell performance. This hypothesis was supported by SIMS measurement on the finished large grain CdTe/CdS devices (Fig. 6), which showed a significant amount of Ga in the CdS and CdTe layers. Ga outdiffusion during the CdTe growth or the subsequent heat treatment may be responsible for the large amount of Ga observed in the CdTe and CdS layers. Contact bonding, which was not perfected, may also contribute to lower efficiency. Therefore, even though the Cu incorporation in the CdTe was reduced in the large grain CdTe film, a higher defect density due to Ga near the CdTe/CdS interface causes shunt paths and degrades the cell performance.

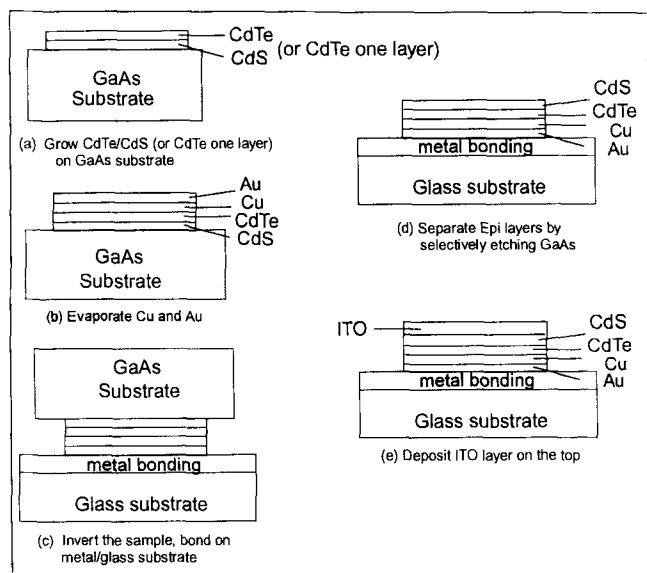


Fig. 4. Separation of thin film CdTe/CdS structures from the GaAs growth substrate.

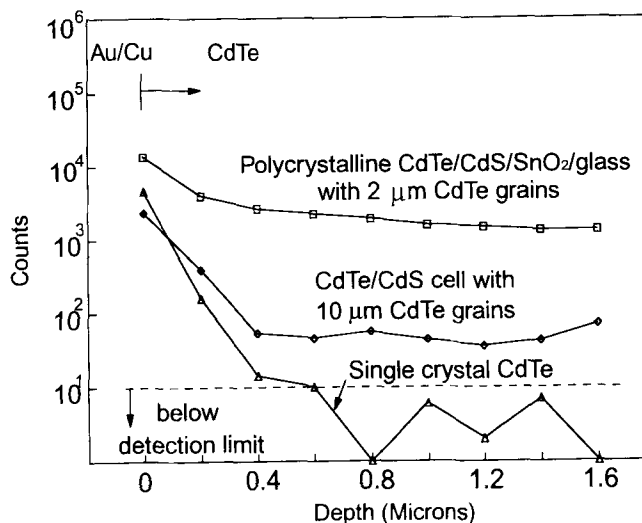


Fig. 5. Comparison of Cu SIMS profiles in the CdTe layers with different degrees of crystallinity.

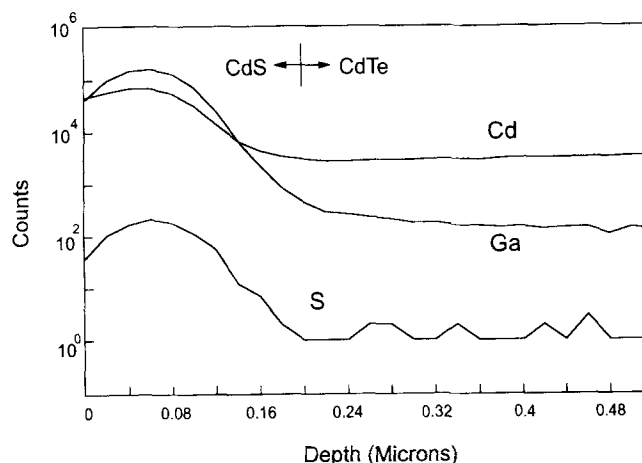


Fig. 6. SIMS record of Ga, S, and Cd ions near the CdTe/CdS region.

## CONCLUSION

Cu plays a dual role in CdTe/CdS solar cells. The increase in Cu thickness in the Au/Cu ohmic contact results in a better ohmic contact, which reduces  $R_s$ , but the excess Cu tends to lower  $R_{sh}$  and cell performance. Light I-V and SIMS measurements showed that an increased Cu thickness also increases the Cu concentration in the CdTe film and at the CdTe/CdS interface, reduces  $R_{sh}$ , and leads to degradation in the cell performance. CdTe films with varying degree of crystallinity were grown in the CdTe/CdS/SnO<sub>2</sub>/glass, CdTe/CdS/GaAs, and CdTe/GaAs structures. CdTe/CdS/SnO<sub>2</sub>/glass had a CdTe grain size of 1–2  $\mu\text{m}$ , CdTe/CdS/GaAs thin film structure had a CdTe grain size of 10  $\mu\text{m}$ , while the CdTe/GaAs had a single crystal CdTe. Large grain and single crystal thin film solar cell structures have been achieved for the first time by a combination of etch back and film transfer techniques. SIMS measurement showed that the Cu concentration in the CdTe/CdS cell structure with large grain size is about two orders of magnitude less than the conventional small grain polycrystalline CdTe/CdS/SnO<sub>2</sub>/glass solar cell structure. The Cu concentration in the single crystal CdTe structure was even lower, below the detection limit of SIMS. Even though larger CdTe grains in the CdTe/CdS/GaAs structure reduced the adverse effects of Cu, however, a higher defect density due to Ga diffusion into the CdTe resulted in lower cell performance.

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