

# Cross-Sectional Conductive Atomic Force Microscopy of CdTe/CdS Solar Cells: Effects of Etching and Back-Contact Processes

## Preprint

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# CROSS-SECTIONAL CONDUCTIVE ATOMIC FORCE MICROSCOPY OF CdTe/CdS SOLAR CELLS: EFFECTS OF ETCHING AND BACK-CONTACT PROCESSES<sup>1</sup>

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## ABSTRACT

We investigated the effects of the etching processes using bromine and nitric-phosphoric acid solutions, as well as of Cu, in the bulk electrical conductivity of CdTe/CdS solar cells using conductive atomic force microscopy (C-AFM). Although the etching process can create a conductive layer on the surface of the CdTe, the layer is very shallow. In contrast, the addition of a thin layer of Cu to the surface creates a conductive layer inside the CdTe that is not uniform in depth, is concentrated at grain boundaries, and may short circuit the device if the CdTe is too thin. The etching process facilitates the Cu diffusion and results in thicker conductive layers. The existence of this inhomogeneous conductive layer directly affects the current transport and is probably the reason for needing thick CdTe in these devices.

## INTRODUCTION

Over the years there has been numerous studies on the formation of ohmic back-contacts to solar cells using CdTe [1,2]. However, many issues still require a better understanding, such as the exact role of the etching processes and Cu incorporation. It is generally accepted that the etching of the CdTe surface is an important step in fabricating good back contacts. The most common etches use bromine/methanol (BM) or nitric/phosphoric acids (NP) solutions, and are supposed to leave a rich conductive Te layer on the surface of the CdTe [3] that facilitates the formation of an ohmic contact. In addition, in one way or another, all back contacts used in CdTe cells use Cu. Some back-contact configurations use Au/Cu, graphite paste, or ZnTe:Cu. Copper is believed to dope the CdTe close to the surface [4], increasing the carrier concentration and allowing for tunneling, and/or favoring the creation of  $\text{Cu}_{2-x}\text{Te}$  at the surface, which lowers the potential barrier at this location [5]. It is also known that Cu diffuses into the CdTe, even reaching the CdS film [6].

In this work, we study the conductivity of the bulk of

CdTe/CdS solar cells using conductive atomic force microscopy (C-AFM), which is a new analytical technique that uses the sharp tip of an AFM to produce images of the electrical current going through the sample [7]. In this technique, a conductive tip is scanned over the surface of a sample in contact mode, while an electrical potential is maintained between the tip and the sample. The position of the cantilever, as well as the current, are both measured at the same time, and topographic and current images are generated from the same area. Also, the voltage can be ramped, giving rise to current versus voltage curves. The advantage of this technique over standard electrical measurements is the high spatial resolution that can detect variations in the electrical properties of the sample in very small regions. For instance, in this work, we can detect differences in electric current going through the material when the tip is placed inside grains or at grain boundaries.

In previous work [8], we have applied C-AFM to study CdTe/CdS solar cells after NP and BM etching processes. At that time, we applied a potential between the tip and the  $\text{SnO}_2$  film, while the tip was scanned over the film surface. Among other findings, we observed that the BM etch created a more conductive layer at the grain-boundary regions, whereas the NP etch created a conductive layer on the whole surface of the film. In the present work, we investigated the effect of these two etching processes in the bulk of CdTe by performing C-AFM on cross sections of the CdTe/CdS solar cells. We also studied the cells with and without a back-contact layer containing Cu, which was shown to be the most important factor for creating a conductive layer inside the CdTe film.

## EXPERIMENTAL PROCEDURE

In this work, we used the following solar cell structure: CdTe/CdS/*i*- $\text{SnO}_2$ / $\text{SnO}_2$ /substrate. The CdTe was deposited by close-spaced sublimation, with a thickness of about 8  $\mu\text{m}$ . The CdS was grown by chemical-bath deposition and was about 100 nm thick. The  $\text{SnO}_2$  bi-layer (conductive and insulating) was

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deposited by chemical-vapor deposition. We used two types of substrates: glass and GaAs. Although the real devices are prepared on glass, it is difficult to prepare flat cross-sections on samples deposited on this substrate. Often, the glass and the CdTe film do not break at the sample level, resulting in a step between them, which makes imaging with the AFM difficult. GaAs is very easy to cleave, and, in general, there was no step between the GaAs and the CdTe film. In the beginning of this work, we compared samples using both substrates, and the results of the C-AFM analyses were very similar. For this reason, we used GaAs in the subsequent depositions. After deposition, the films were treated in CdCl<sub>2</sub> vapor at 400°C for 5 minutes. Some films were then etched with nitric/phosphoric or bromine/methanol solution. We varied the etching time to verify its effect on the formation of the conductive layer inside the CdTe film. We used times from 15 to 120 s for the NP etch and from 1 to 5 s for the BM etch. Some samples received the deposition of an Au/Cu layer to investigate the effects of Cu diffusion into the film. The thickness of the Au film was about 150 nm, and the thickness of the Cu film was 5 and 10 nm; both films were deposited at room temperature by electron-beam deposition. Several samples were heat treated at 150°C for 90 minutes to study the effect of temperature on the observed conductive layer. For comparison, we also analyzed films with ZnTe:Cu, instead of the Au/Cu layer. Finally, we analyzed standard solar cell devices, which use graphite paste or ZnTe:Cu to form the back contact. Because the objective of the measurement was to investigate the resistivity of the bulk CdTe, we placed one contact on the sample surface while the other contact was provided by the tip. We also contacted the SnO<sub>2</sub> to allow current through this layer, making it visible in the current images.

The C-AFM analysis was performed in a Veeco Dimension 3100 scanning probe microscope with Nanoscope IV electronics. The analysis was performed in contact mode, and we used doped-diamond-coated tips, which have low resistivity and are resistant to wear [9].

## RESULTS AND DISCUSSION

The C-AFM analysis showed a highly conductive layer inside the CdTe films with Au/Cu contact and after the etching process, as shown in Fig. 1. Figure 1a shows the topography of the solar cell. On the left is the GaAs substrate, then the SnO<sub>2</sub>/CdS layers (the individual CdS film is not visible), then the CdTe film. Figure 1b shows a current image from the same area, with negative bias applied to the SnO<sub>2</sub> and Au films, and Fig. 1c shows the same image with positive bias. The conductive SnO<sub>2</sub> layer and part of the CdTe film close to the sample surface are clearly seen in both current images. The CdTe deeper in the film is much more resistive and practically no current is observed for the applied dc bias. By applying opposite polarities (Figs. 1b and 1c) and performing I-V measurements, we found an ohmic behavior between the conductive region and the doped-diamond tip. Comparing the topographic and current images, we observe that the

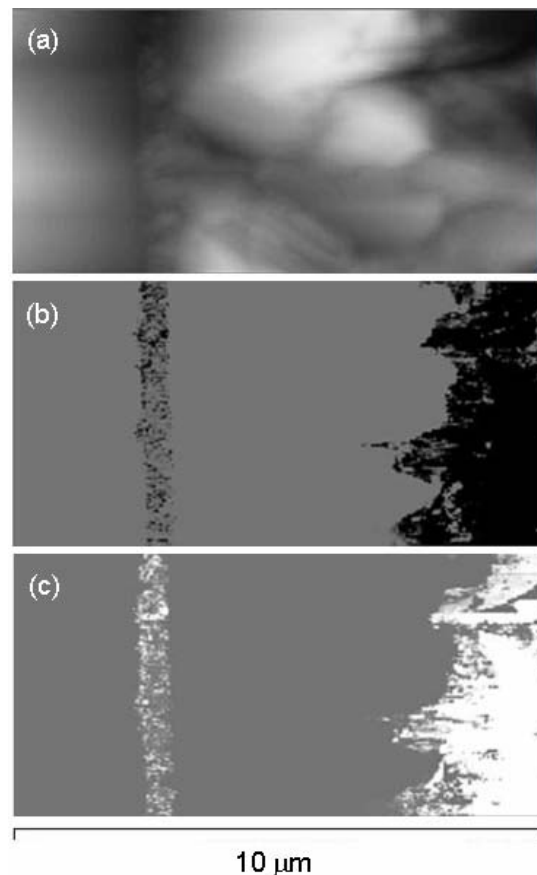


Fig. 1- Topographic (a) and current images (b,c) of a CdTe/CdS solar cell with Au/Cu back contact after NP etch for 120 s. Figures b and c were taken with dc bias equal to -100 mV and 100 mV, respectively.

higher conductivity region is concentrated on the grains close to the surface, whereas there is no significant current on the grains located deeper into the CdTe. We notice the formation of a high-current region inside most CdTe films that had a Cu film on the surface and that were subjected to NP or BM etches. However, in general, the conductive layer is not as uniform as in Fig. 1. The penetration can be deeper in a given area, while it is shallower in another. An example of this behavior is shown in Fig. 2. In this figure, we traced the conductive area on the CdTe (Fig. 2b) and placed the trace over the topographic image (Fig. 1a). It is clear that the conductive area extends up to a grain close to the CdS film and that it is highly non uniform. The depth and distribution of the high-current area depend on many factors, such as treatment and back contact, but also on the type of cross-section fracture. A difficulty in interpreting our results lies in the fact that we are studying the conductivity of the bulk of the sample, a three-dimensional property, while we are analyzing cross sections of the sample, which are two-dimensional slices of the film. The analysis of the topographic images indicates that the CdTe fracture occurs in a complex way, with a mixture of intragrain



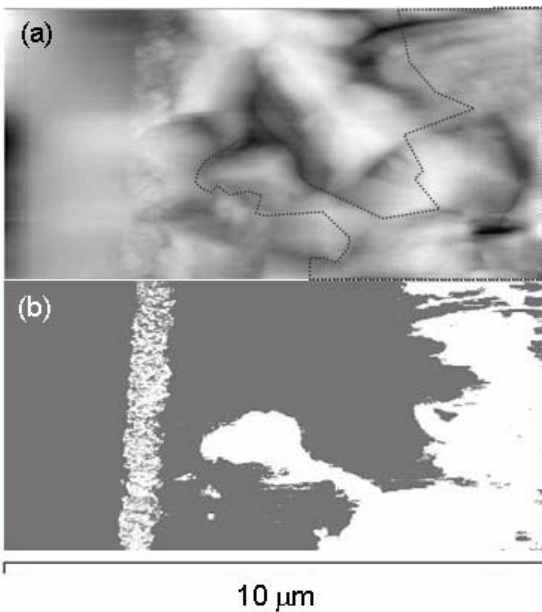


Fig. 2 – Topographic (a) and current (b) images of a CdTe/CdS cell with Au/Cu back contact after NP etch for 60 s. The dc bias applied in b was 100 mV.

(through the grain) and intergrain (through grain boundaries) fractures. Figure 3 shows a sample with a grain having a mixture of intragrain and intergrain fractures. The large grain on the bottom shows several terraces that are extremely flat and clearly indicate intragrain fracture. Notice that the area with high conductivity stops at this grain, where the interior is exposed. This feature was observed in several images, and, in general, grains with intragrain fracture did not showed significant conductivity. On the contrary, grains with high conductivity, in general, have a rougher topography, which is characteristic of intergrain fracture. These results indicate that most of the observed high conductivity was observed at grain-boundary regions, whereas the interior of the grains have still high resistivity. This agrees with the work of Chou et al., who observed that Cu diffuses faster in polycrystalline CdTe than in single-crystal CdTe [10], and associated this fact with faster Cu diffusion at grain boundaries.

We did not notice any major differences in the current images in samples etched with BM or NP solutions. We also changed the etching times for both processes, but could not establish a clear correlation between this parameter and the depth of the conducting layer in the CdTe. A clear example is shown in Figs. 1 and 2, where the high-conductivity area is thicker in the sample etched for a lower time. To investigate relevance of the etching process and to determine the most important factor in creating the high-conductivity layer inside the CdTe film, we analyzed etched samples without Cu film on the surface, and samples with Cu film but with no etching. The results showed that there is no high-conductivity area inside the CdTe film if there is no Cu

deposited on the film surface, independent of the etching process. To confirm that the high conductivity is caused by Cu, we deposited only Cu, without the Au film, and the results were equivalent (Fig. 3). The correlation of Cu contents and the high-current areas was confirmed by secondary-ion mass spectrometry. Due to lack of space here, these results will be reported in a future publication. Similarly, we found that if there is Cu on the CdTe surface, but the film is not subjected to etching, in general, the high-conductivity layer is shallow or non-existent. This indicates that, besides helping the formation of an ohmic contact, the etching process facilitates the diffusion of Cu into the material. The mechanics of this process may include the generation of defects that facilitate the diffusion of Cu through the grain boundaries. However, further studies will be needed before an explanation for the process can be provided.

To verify if the creation of the high-current area is present in regular devices, we analyzed standard solar cells with two different types of back contacts: HgTe/CuTe-doped graphite paste and ZnTe:Cu. In the case of the cells using ZnTe:Cu, there is no wet-etching process, but an ion-beam milling before the ZnTe:Cu deposition. The objective of this treatment is to clean and create a nearly stoichiometric surface [11]. The current image for a cell with graphite paste back-contact is shown

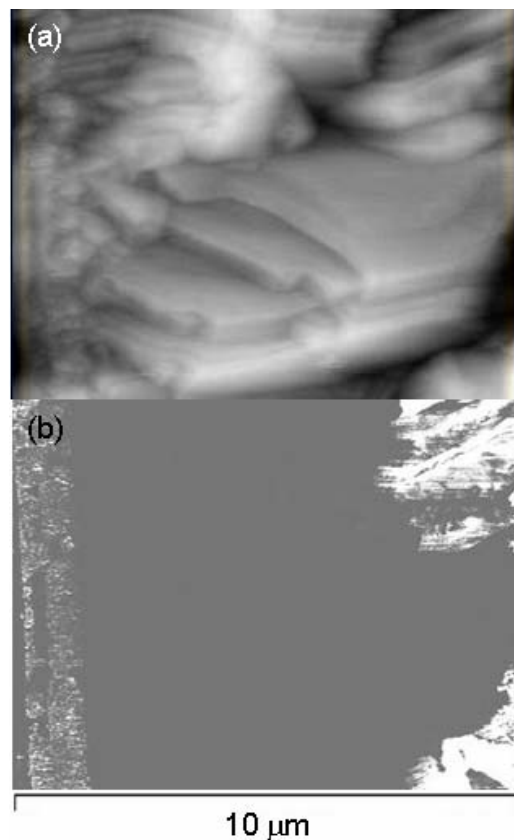


Fig. 3 – Topographic (a) and current (b) images of a Cu/CdTe/CdS cell after NP etch for 60 s.

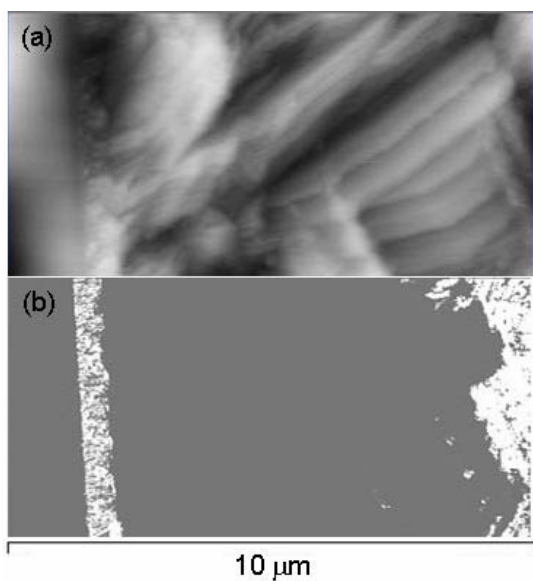


Fig. 4 – Topographic (a) and current (b) images of a standard CSS CdTe/CBD CdS solar cell using graphite paste in the back contact.

in Fig. 4. In this device, the observed high-current region is shallow in all the analyzed areas. This cell had an efficiency ( $\eta$ ) equal to 10.6 %, open-circuit voltage ( $V_{oc}$ ) equal to 0.813 V, short-circuit current ( $J_{sc}$ ) equal to 21.2 mA/cm<sup>2</sup>, and fill factor (FF) equal to 61.3%. In contrast, we analyzed another cell that showed a deep high-conductivity layer in all analyzed areas, with the high-current areas approaching the junction in some spots. This cell had  $\eta$  equal to 4.6 %,  $V_{oc}$  equal to 0.588 V,  $J_{sc}$  equal to 17.7 mA/cm<sup>2</sup>, and FF equal to 43.8. It is possible that the poor performance of the latter cell is due to local shunts caused by the deep penetration of the conductive areas. Solar cells with the ZnTe:Cu back contact also presented high-conductivity areas inside the CdTe layer.

The above results indicate that the effect of the etching process is to enhance the diffusion of Cu into the material, mainly at grain boundaries. Cu is a faster diffuser into CdTe, and the observed penetration happened without any intentional heating of the substrates during film deposition. Due to the relatively high currents observed here, we believe that Cu forms a high-conductivity region inside the CdTe that may cause micro shunts if it reaches the junction. For our samples, in over more than a hundred measurements, we observed very deep penetration in only a few cases, as seen in Fig. 2, including shunting of the device twice. This potential short-circuit explains why these cells need a thick layer of CdTe, although only about 1  $\mu$ m is needed to absorb the solar radiation. For our base line devices, using a wet-etch process, the optimal thickness of the CdTe is about 8  $\mu$ m.

## CONCLUSIONS

We have used C-AFM to study cross-sections of CdTe/CdS solar cells with high spatial resolution. We observed that Cu, present in the back contact, diffuses into the material, creating high-conductivity regions inside the CdTe film. This diffusion process is enhanced by both etching processes, using nitric-phosphoric acids or bromine/methanol. The conductive layer inside the material is concentrated at grain boundaries and may reach the junction in a few areas of the sample, causing short circuits. These results may explain the need for thick CdTe layers used in our devices.

## ACKNOWLEDGEMENTS

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