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Conductive Atomic Force Microscopy Applied to CdTe/CdS Solar Cells

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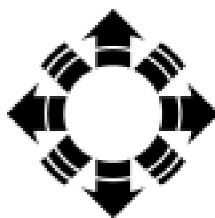

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CONDUCTIVE ATOMIC FORCE MICROSCOPY APPLIED TO CdTe/CdS SOLAR CELLS

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ABSTRACT: In this work we describe for the first time the use of conductive atomic force microscopy (C-AFM) in the study of CdTe/CdS solar cells, before and after the etching processes used in device fabrication. C-AFM is a new technique that provides information on the electrical properties of the sample in conjunction with topographic images with high lateral resolution. At the same time, this technique allows for the generation of I-V curves at very well-defined locations. A potential is applied between the sample and a very sharp tip, which scans the sample in contact mode. The current images showed that different CdTe grains produce different contrast. Etching the CdTe with a bromine/methanol solution enhanced the current along grains boundaries when compared to the intragrain material. Etching with a solution of nitric and phosphoric acids did not show this effect. Instead, it increased the current through the whole sample surface.
Keywords: Conductive-AFM, CdTe, etching.

1 INTRODUCTION

Conductive atomic-force microscopy (C-AFM) is a recently developed technique that uses an AFM to apply a voltage between a conductive tip and the sample surface, and to measure the current [1,2]. Together with the topographic image, a current image is obtained. In addition, the tip can be placed on any point of the surface, and current x voltage (I-V) curves can be obtained. The advantage of C-AFM over other techniques is the high spatial resolution, which, for instance, allows for the isolated study of grain boundaries, as well as intragrain regions in polycrystalline materials.

In the past few years, C-AFM has been used to study the properties of many material systems [3-5], but, to the best of our knowledge, this is the first time that it has been applied for the investigation of CdTe/CdS solar cells. We have studied the samples before and after $CdCl_2$ treatment, and after bromine/methanol (BM) and nitric phosphoric (NP) etches. The $CdCl_2$ treatment is an essential process during the production of high-efficiency devices, promoting recrystallization and grain growth, and improving the electrical-optical properties of the devices [6-7]. The BM and NP etches create a Te-rich highly conductive layer on the top of the CdTe film [8-9], important for the fabrication of an ohmic back contact.

2 EXPERIMENTAL PROCEDURE

The samples used in this study had the following structure: glass\\SnO_2\CdS\CdTe. The CdS was grown by chemical-bath deposition and the CdTe by close-spaced sublimation. After the deposition of the CdTe films, the whole structure was treated in $CdCl_2$ vapor at 400°C for 5 minutes. Some cells were then subjected to an etching treatment with a 0.5% bromine in methanol solution (BM etch), for 2 seconds, followed by a thorough rinse with methanol. Finally, these samples were dried with a nitrogen gas jet. Other cells were subjected to another etching process, in a phosphoric acid:nitric acid:deionized water (88:1:35) solution (NP etch), for 30 to 45 seconds, until the entire surface was covered with tiny bubbles as a result of the reaction. These samples were then thoroughly washed in running DI water, and dried with a nitrogen gas jet.

Four groups of samples were analyzed by C-AFM: as deposited, after $CdCl_2$ treatment, after BM etch, and after NP etch. The analysis was done in a Digital Instruments Dimension 3100 scanning probe microscope, using diamond-coated Si tips, which have high conductivity and are resistant to wear [10,11]. The cantilever spring constant was about 42 N/m. To allow the current to pass through the sample, this kind of analysis is done in contact mode. The electric contact to the sample holder was made on the conductive SnO_2 film, using silver paint, while the tip was grounded. A positive or negative potential was applied to the tip, as well as a ramp voltage for the I-V measurements.

3 RESULTS AND DISCUSSION

A setup of the experiment is shown in Fig. 1. The path of the current is represented by a cone-shaped surface starting at the tip and going down the CdTe, through the CdS, and ending at the SnO_2 film, where the current is collected. Notice that the current is higher (darker color) in the region below the tip and decreases as we move laterally on the film. Also, the current passes through a very small cross-sectional area just below the tip. This results in a high spatial resolution at the CdTe surface, and, consequently, in the detection of variations in the electrical properties in very small areas. As the current goes into the CdTe, the cross-sectional area increases, and the current at these locations reflects the average of the properties of the bulk CdTe. So, we expect that most of the variation in the C-AFM images will be produced by variation in the properties of the CdTe close to the surface. Figure 2 shows a typical I-V curve obtained from the device. Because the voltage is applied to the SnO_2 layer, a positive voltage means that the cell is polarized in reverse bias, and a negative voltage means that it is polarized in forward bias. The behavior in Fig. 2 is opposite to what we would expect for the CdTe/CdS junction. This indicates that the I-V curve is being

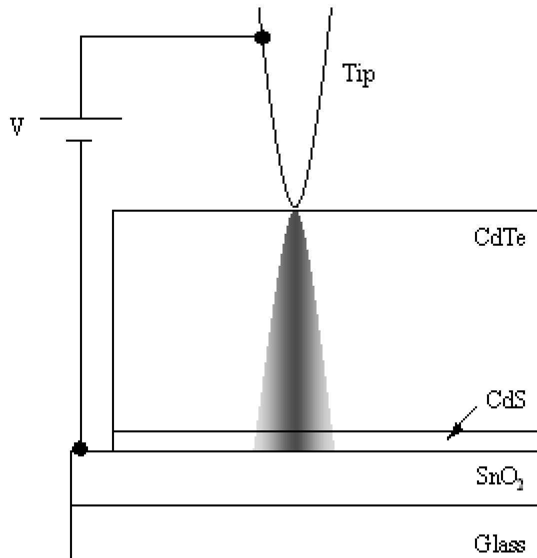


Figure 1: Set-up for the C-AFM measurements. The shaded area under the tip corresponds to the electric current.

controlled by another junction, which has to be the one between the tip and the sample surface, and which has the opposite polarity as the CdTe/CdS junction. Indeed, the boron-doped p-type diamond tip and the p-type CdTe can form a rectifying junction depending on the position of the Fermi levels of the two materials. Unfortunately, the work function and electron affinity of the diamond layer are not available, but our results can only be explained by a rectifying junction at this interface. So, the current when a negative bias is applied to the SnO_2 behaves like a reverse current, and when a positive bias is applied to the SnO_2 behaves like a forward current, as observed in Fig. 2. It is important to mention that this behavior is observed for the as-deposited, $CdCl_2$-treated, and BM-etched samples.

The force used in the analysis varied from about 10^{-7} to 10^{-6} N. Although both forces would produce the same results, images taken with the lowest force were, in general, more stable. Also, the tips lasted longer and there was no degradation of the surface. The degradation effect is shown on Fig. 3a, for a force of $5x10^{-7}$ N. The image

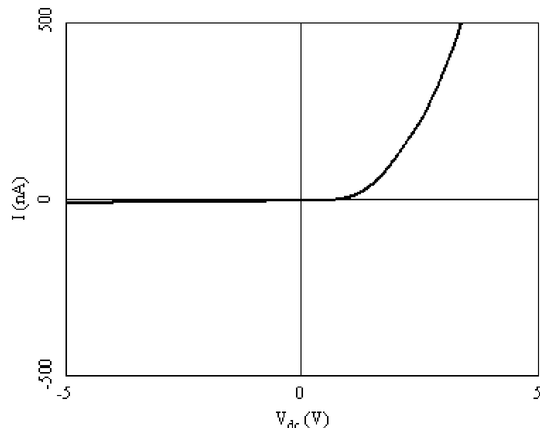
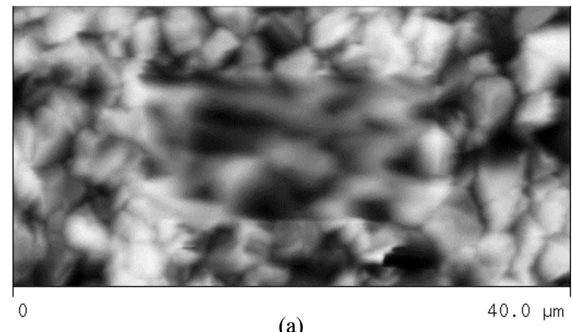
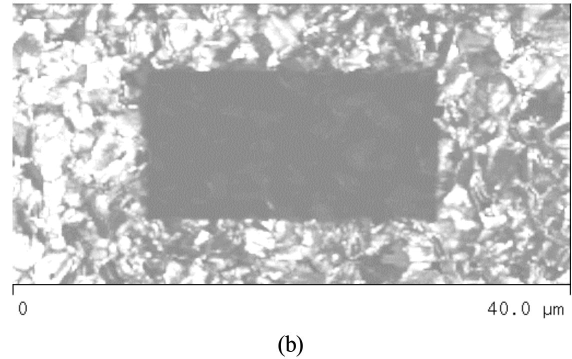


Figure 2: I-V curve for a CdTe/CdS sample after $CdCl_2$ treatment.



(a)



(b)

Figure 3: (a) Topographic image of an as-deposited CdTe film after being analyzed at a scan area of 20 µm. (b) Corresponding C-AFM image.

was initially taken at 20 µm, and then at 40 µm. The disappearance of sharp features at the center, where the original image was taken, is clear. Besides destroying the surface, this effect may produce artifacts on the C-AFM image, because material is moved around the surface, and probably some material is deposited at the grain boundaries, which may change the electrical signal. Another effect of the analysis is shown in Fig. 3b, where the decrease in the current on the previously analyzed area is also clear. Indeed, in several analyses, we observed a decrease in the current with time, and the reason for this has not been determined yet. Nevertheless, for the majority of the analyses, there was no significant change of the signal with time, and image imprinting, as shown in Fig. 3, was not observed.

Our equipment is able to detect currents down to a few pA. Although the qualitative results did not change with a change in voltage (and consequently, current), we noticed that the images tend to be more stable at higher voltages and currents. For this reason, we obtained most of the data with voltages from 2 to 10 V, and the current in the range of a few to hundreds of nA. Furthermore, unless stated otherwise, the C-AFM data shown in this work were taken with the CdTe/CdS junction polarized in reverse bias.

Figure 4 shows an AFM image (top) of an as-deposited sample, and the corresponding C-AFM image (bottom). There is a very good correspondence between both images, and the grain structure is clearly observed in both images. The difference in brightness from grain to grain in the C-AFM image indicates that the conductivity is not uniform. This is probably due to different grains having different doping levels and/or different carrier mobilities, which are caused by differences in the defect

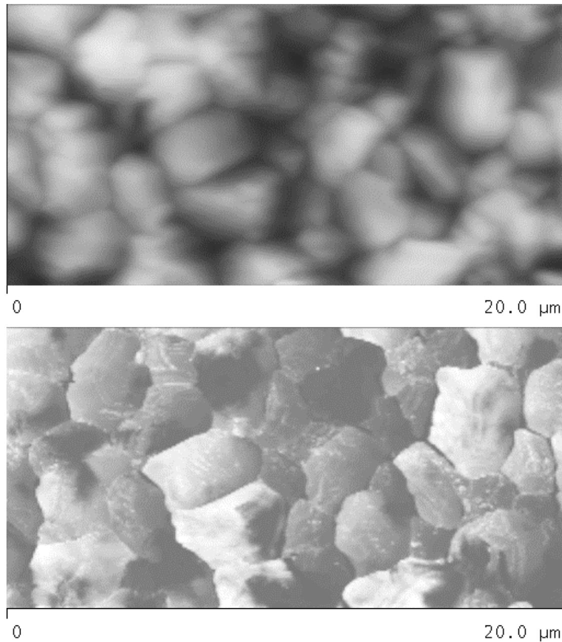


Figure 4: Topographic image of an as-deposited CdTe film (top) and corresponding C-AFM image (bottom).

structure. Notice also that the current can change even inside a grain. No special contrast was observed at grain boundaries, which suggests that, for as-deposited samples, there is no significant change in conductivity at this region. It is important to mention that there is no sign of interference of the topography on the current image, which is commonly observed in electrical measurements done with AFM, such as in scanning capacitance microscopy.

After the $CdCl_2$ treatment, we observed that there is a general increase in current levels. Nevertheless, it is difficult to correlate this increase in current with changes in the properties of the CdTe film, because there may be an oxide layer between the film and the tip, and the properties of this layer may be changed by the $CdCl_2$ treatment, consequently changing the magnitude of the current. The C-AFM image of a CdTe film after the $CdCl_2$ treatment is shown in Fig. 5. The current contrast from grain to grain, and even inside a given grain, is still observed. Nevertheless, most of the grain boundaries now are darker than the intragrain material. This indicates a decrease in conductivity after the treatment, and agrees with the work from Visoly-Fisher et al., who observed a

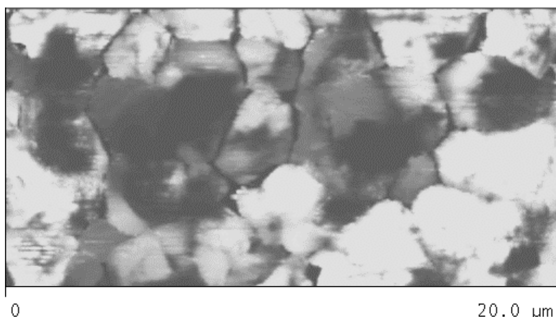


Figure 5: C-AFM image of a CdTe film after $CdCl_2$ treatment.

lower carrier concentration at grain boundaries for CdTe samples after the $CdCl_2$ treatment [12].

Figure 6a shows an AFM image of the CdTe surface after BM etch. There are no major changes on the topographic features, but there is a significant change in the relative current going through grains and grain boundaries, as seen in Fig. 6b. The enhanced conductivity at grain boundaries is probably due to preferential etching at these locations. Danaher et al. [13] observed that Br_2 penetrated the CdTe film, presumably through the grain boundaries, reaching the indium tin oxide layer. Figure 6c shows a linescan from Fig. 6b, where the enhanced conductivity along grain boundaries, and the difference in conductivity for different grains, can be observed more clearly. It is also obvious from the figure that, as pointed out before, there is no noticeable effect of topographic features on the current image. Still, most of the I-V curves showed a rectifying character of the surface junction. Nevertheless, the grain boundaries showed higher conductivity, providing an equivalent image when the dc bias was reversed. This effect indicates that the BM treatment was somewhat effective in improving the conductivity of grain boundaries, probably by creating a Te-rich layer at these regions, but it may not be as effective for the other regions of the surface.

Finally, we discuss the results obtained after the NP etch, which are shown in Fig. 7. There is a substantial

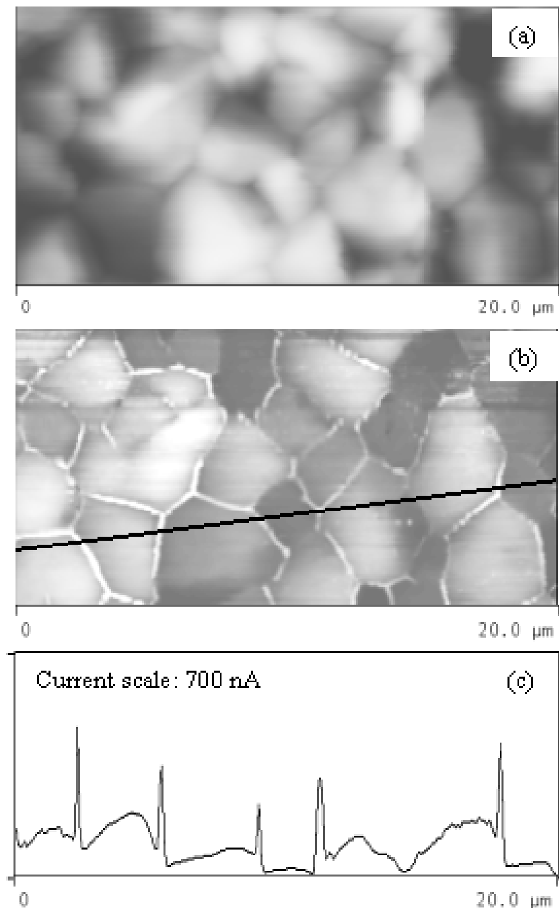


Figure 6: (a) AFM image of a CdTe surface after BM etch. (b) Corresponding C-AFM image. The line indicates the position of the linescan shown in (c).

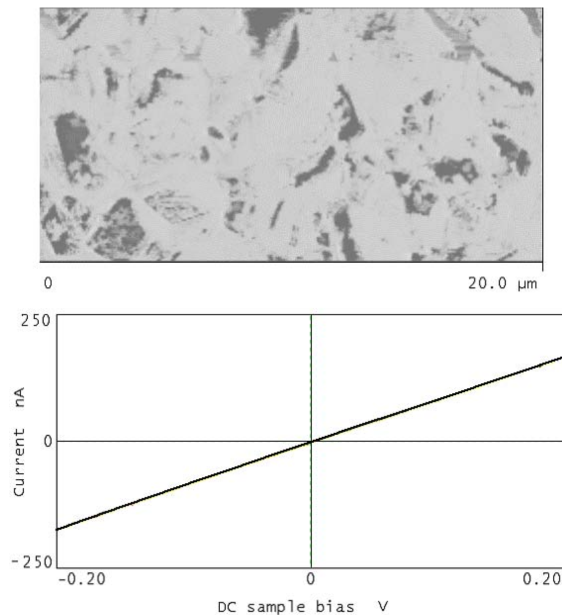


Figure 7: C-AFM image of a CdTe film after NP etch (top), and I-V curve taken at a point on the surface (bright area).

increase in the current for these films. Most images had to be taken at voltages below 1 V, so that the current did not overload the detector. Also, for these conditions, the current images lose lateral resolution and no longer match the topographic images. This is caused by the conductive Te-rich layer, which allows current flowing through a larger area on the surface during image acquisition. An I-V curve taken on a bright area of the current image is shown on the bottom of Fig. 7. Contrary to what has been observed for the other samples, the I-V curve is characteristic of an ohmic contact. These results agree with other studies that show the formation of a highly conductive Te-rich layer on the CdTe surface after the NP etch [9]. The NP process may also etch grain boundaries preferentially. Nevertheless, the C-AFM from the surface does not show this effect, possibly because of the highly conductive Te layer covering the whole surface. To investigate this effect, we will follow this work by studying the cross section of CdTe/CdS devices. The above results support the observations of our device group, which has found that the NP etch is essential for the production of high-efficiency CdTe/CdS solar cells, and that it is more effective than the BM etch for this purpose.

We have noticed a strong effect of illumination on the current images of samples after the NP etch, which was not observed in other samples. Even with ambient light, there was a photocurrent that increased when the sample was submitted to direct illumination. This effect will be discussed in detail in a future publication.

4 CONCLUSIONS

We applied C-AFM for the first time to CdTe/CdS solar cells, and demonstrated that this technique can be of great value in investigating the electrical properties of this device. High spatial resolution was obtained, which allowed the study of the properties of the CdTe films close to the surface.

The C-AFM measurements showed that the as-deposited samples have grains with different conductivities, which indicate differences in carrier concentration and/or mobility, caused by a different defect structure. After the $CdCl_2$ treatment, there was a relative decrease in the current at grain boundaries, indicating a decrease in carrier concentration at these locations. Treatment with BM etch showed a relative increase in current at grain boundaries, whereas the NP etch resulted in an increase in the current over the entire CdTe surface, as well as a change in the contact between the tip and the sample surface from rectifying to ohmic. Based on our results, we conclude that, when performed with the parameters used in this work, the NP etch is more suitable than the BM etch for fabricating ohmic back contacts in CdTe/CdS solar cells.

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14. ABSTRACT *(Maximum 200 Words)*

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