



Influence of Surface Preparation on Scanning Kelvin Probe Microscopy and Electron Backscatter Diffraction Analysis of Cross Sections of CdTe/CdS Solar Cells

Preprint

Helio R. Moutinho, Ramesh G. Dhere,
Chun-Sheng Jiang, and Mowafak M. Al-Jassim

*Presented at the 2011 Materials Research Society Spring Meeting
San Francisco, California
April 25–29, 2011*

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Conference Paper
NREL/CP-5200-51629
June 2011

Contract No. DE-AC36-08GO28308

NOTICE

The submitted manuscript has been offered by an employee of the Alliance for Sustainable Energy, LLC (Alliance), a contractor of the US Government under Contract No. DE-AC36-08GO28308. Accordingly, the US Government and Alliance retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information

P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: <mailto:reports@adonis.osti.gov>

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/help/ordermethods.aspx>

Cover Photos: (left to right) PIX 16416, PIX 17423, PIX 16560, PIX 17613, PIX 17436, PIX 17721



Printed on paper containing at least 50% wastepaper, including 10% post consumer waste.

Influence of Surface Preparation on Scanning Kelvin Probe Microscopy and Electron Backscatter Diffraction Analysis of Cross Sections of CdTe/CdS Solar Cells

H.R. Moutinho, R.G. Dhere, C.-S. Jiang, and M.M. Al-Jassim
National Renewable Energy Laboratory, Golden, CO 80401, USA

ABSTRACT

Electron backscatter diffraction (EBSD) provides information on the crystallographic structure of a sample, while scanning Kelvin probe microscopy (SKPM) provides information on its electrical properties. The advantage of these techniques is their high spatial resolution, which cannot be attained with any other techniques. However, because these techniques analyze the top layers of the sample, surface or cross section features directly influence the results of the measurements, and sample preparation is a main step in the analysis.

In this work we investigated different methods to prepare cross sections of CdTe/CdS solar cells for EBSD and SKPM analyses. We observed that procedures used to prepare surfaces for EBSD are not suitable to prepare cross sections, and we were able to develop a process using polishing and ion-beam milling. This process resulted in very good results and allowed us to reveal important aspects of the cross section of the CdTe films. For SKPM, polishing and a light ion-beam milling resulted in cross sections that provided good data. We were able to observe the depletion region on the CdTe film and the p-n junction as well as the interdiffusion layer between CdTe and CdS. However, preparing good-quality cross sections for SKPM is not a reproducible process, and artifacts are often observed.

INTRODUCTION

EBSD [1] is performed inside a scanning electron microscope (SEM), where the electrons from the beam are diffracted by the top layers of the material and collected by a detector positioned close to the sample surface. To increase the yield of diffracted electrons, the sample is tilted by 70° , which requires a flat surface to avoid surface features from preventing the electrons from reaching the EBSD detector (the shading effect). Furthermore, because the diffracted electrons come from the region close to the surface (about 20 nm deep), the quality of the surface is a key parameter for obtaining good EBSD data. In addition to conventional information, such as pole figures and inverse pole figures, EBSD provides unique information on orientation maps and boundaries' misorientation profiles, and it is the most reliable technique to provide surface grain size information.

SKPM [2] provides measurements of the electrical potential and electric field distribution on the sample surface. The technique provides maps of the surface potential simultaneously with atomic force microscopy (AFM) topographic images, which allows for the correlation between topography and electrical properties. As with EBSD, the advantage of SKPM over other techniques is the high spatial resolution. When applied to cross sections of biased CdTe/CdS solar cells, it reveals the location of the p-n junction and the distribution of the depletion region on the CdTe film and also allows for studying the interdiffusion layer between CdTe and CdS.

Because these techniques analyze the surface of the sample, sample preparation is a key step toward obtaining meaningful data. For instance, close-spaced sublimation (CSS) CdTe films are too rough to provide good EBSD data because of shading effects. Polishing the films

produces a flat surface, but with poor quality, resulting in no Kikuchi patterns on the EBSD detector and, consequently, no EBSD data. In previous work [3], we found that good samples are produced by ion-beam milling, a combination of polishing and ion-beam milling, or polishing and etching in bromine methanol solution.

Although there are no shading effects in AFM, the maximum vertical range of the tip is about 7 μm , requiring that sample features be no taller than about 4 μm . However, because of convolution between topography and surface potential data, steps should be as flat as possible (no more than a few dozens of nanometers). Because of this, only samples that cleave provide good cross sections with minimal preparation. CdTe/CdS films, which are deposited on glass, require a polishing stage before any meaningful SKPM data can be obtained. After this, a light ion-beam milling stage can also be applied.

In this work we investigate procedures to prepare CdTe/CdS solar cell cross sections for EBSD and SKPM analysis, and report the information that can be obtained from the samples.

EXPERIMENTAL PROCEDURE

The samples used in this work had the following structure: Ag paste/Cu-doped graphite paste/CdTe/CdS/i-SnO₂/SnO₂/glass. The samples received a standard vapor CdCl₂ treatment at 400°C for 5 min.

The samples were polished in a MultiPrep system from Allied High Tech Products, Inc., using diamond lapping films with 30, 9, 3, 1, 0.5, 0.25 and 0.1- μm grits. Different polishing solutions and procedures were tried, but the results were similar. A last step using 0.05- μm alumina suspension was sometimes used, but again, the results of the analyses were similar. After polishing, some samples were etched in bromine/methanol solution for 2 s, while other samples were ion-beam milled on a Fischione system, model 1010 LAIMP. To avoid rounding the film during the polishing process, the samples were sandwiched using epoxy and glass slide. For the EBSD analysis, we used a conductive epoxy to diminish charging effects caused by the electron beam. For the SKPM analysis, because we wanted to analyze the sample under different bias conditions, we attached a wire to the back contact and used non-conductive epoxy to avoid short-circuiting the solar cell. It is important to mention that the procedures reported in this work may need to be modified for other materials and CdTe films deposited by other methods.

The EBSD analysis was performed in a SEM FEI Nova 630 NanoSEM using a EDAX Pegasus/Hikari A40 system. The SKPM measurements were performed in a ThermoMicroscope AutoProbe CP Research scanning probe microscope using Pt-Ir-coated Si tips.

RESULTS AND DISCUSSION

EBSD

We initially attempted to cleave (break) the samples, but no useful results were obtained due to shading between the several layers that were formed. Next, we tried to polish the sample and then etch using a bromine/methanol solution. This was the natural choice, because this process had been used successfully before to prepare the surface of CdTe films for EBSD [3], and a system for ion-milling cross sections was not available. The results are shown in Fig. 1. On

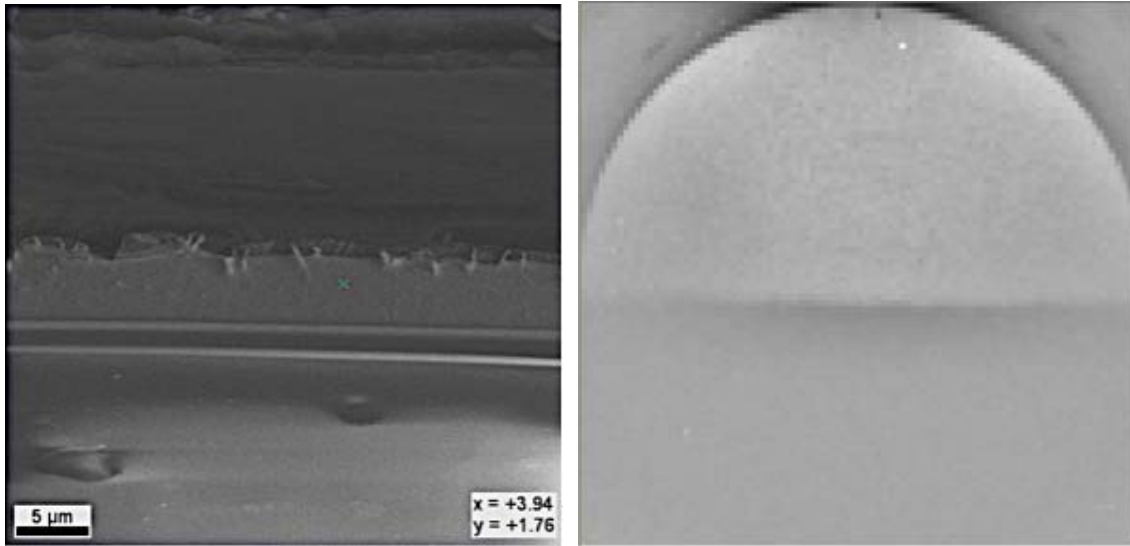


Fig. 1. Left: SEM image of the cross section of a CdTe/CdS cell after polishing and etching with bromine methanol solution. From the top: graphite paste/CdTe/CdS-SnO₂/glass. Right: Image on the EBSD detector at the location marked by a green x on the SEM image.

the SEM image we notice that the films are not as flat as we would expect. Also, there is a step between the graphite paste and the CdTe, and there is some residue on the surface of the CdTe film. The image on the detector shows a strong shading effect (the bottom half of the detector is dark, showing no detection of electrons) due to the step observed on the SEM image. On the top part of the detector, although there is no shading, there are no Kikuchi lines, indicating that the CdTe surface does not have good crystallinity. This is probably caused by the features on the CdTe film observed on the SEM image. We tried to solve this problem by changing the polishing process, but we were not successful. For every sample treated with bromine/methanol, there was some deposit on the CdTe film and a step between the back contact and the CdTe observed by SEM, and shading effects and no Kikuchi patterns observed on the EBSD detector. These experiments allowed us to conclude that bromine/methanol attacks the back contact and the epoxy, creating the step and leaving a residue layer on the CdTe, preventing EBSD data from being acquired.

To solve this problem, we were able to adapt an ion-beam milling used to prepare samples for TEM to mill our cross sections. The new cross sections were flat, without steps between the back contact and the CdTe, and excellent Kikuchi patterns were observed on the detector. However, we observed that, for strong ion milling, there was a small step between the CdTe and CdS-SnO₂ films, which would cause some shading close to this interface. To avoid this problem, we optimized the ion-beam milling process. Fig. 2 shows two inverse pole figure orientation maps of CdTe cross sections. For light ion milling (left) it is difficult to clearly see the film crystalline structure because only part of the damaged layer was removed. For intermediate milling conditions (not shown), although the crystalline structure could be easily observed, there was a lot of variation in the crystallographic orientation inside the grains. For the optimized milling conditions, the data was excellent (right). Using polishing followed by ion-beam milling, we are able to create good cross sections for EBSD on a routine basis.

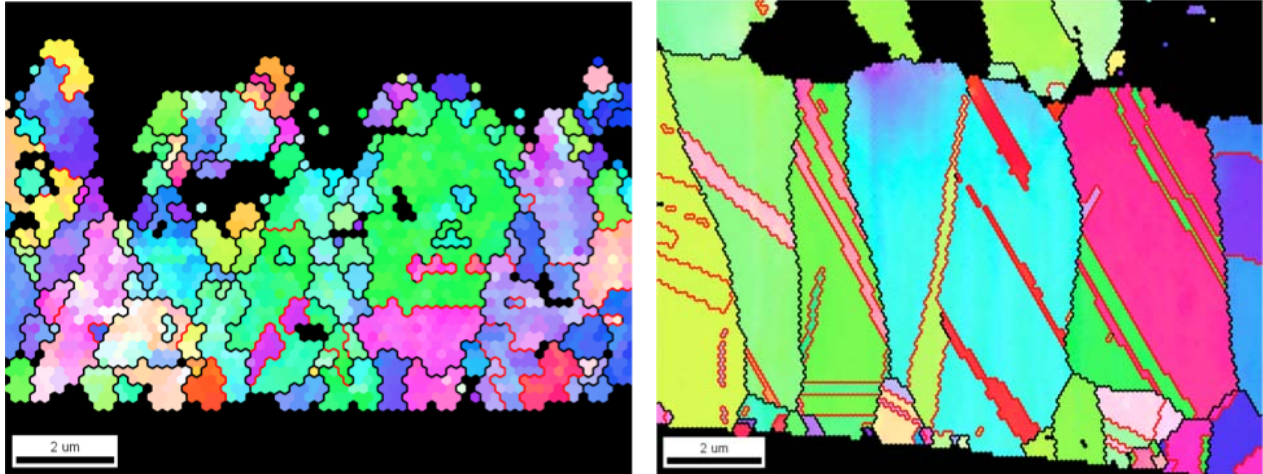


Fig. 2. EBSD of the cross section of a CdTe/CdS solar cell. Left: Light ion-beam milling (4 kV, 4 mA, 5°, 10 min). Right: Optimal ion-beam milling conditions (5 kV, 5 mA, 6°, 30 min). Dark lines denote grain boundaries, and red lines denote CSL $\Sigma 3$ boundaries.

The analysis of the samples show that the CdTe film grows in a columnar way and has small grains that nucleate in the first stages of film growth at the interface with CdS. Analysis of pole figures shows that the film is randomly oriented. Almost every grain has few low-energy coincidence site lattice (CSL) $\Sigma 3$ boundaries [4]. These boundaries are twins, generated by a rotation of 60° around a [111] crystallographic direction and have been observed before [5].

SKPM

For the SKPM measurements, to avoid the problems observed in the EBSD analysis, we did not use bromine/methanol etching. The best results were obtained by polishing or polishing followed by a light ion-beam milling, which provided very similar data. Some of the results are displayed in Fig. 3, which shows representative linescans of the potential (left) and electric field (right) on the cross section of CdTe/CdS cells. The figure on the left shows that there is a sharp decrease in the potential at the interface between CdTe and CdS. As the reverse bias is increased, there is an increase and spread in the potential inside the CdTe film, corresponding to the expansion of the depletion region with reverse bias. As expected, the potential drop inside the SnO₂ film is small. The figure on the right shows the electric field inside the device obtained by taking the first derivative of the potential linescans. There is a strong electric field at the junction, which is caused by the higher doping interdiffusion layer created during the formation of the device. The existence of this layer was confirmed by transmission electron microscopy (TEM) [6]. The position of the p-n junction coincides with the maximum of the electric field. The expansion of the depletion region on the CdTe with the increase in reverse bias is also observed in the figure. We applied Poisson's equation on the straight part of the electric field on the CdTe film on polished samples, and we were able to calculate the doping for several samples [6]. The calculated values varied from 1.1×10^{14} to 3.3×10^{14} cm⁻³, which agrees well with values reported on the literature for CdTe.

Analyzing Fig. 3, we notice that the electric field at forward bias is negative, when it should be positive. This indicates the existence of an inversion layer on the CdTe/CdS surface,

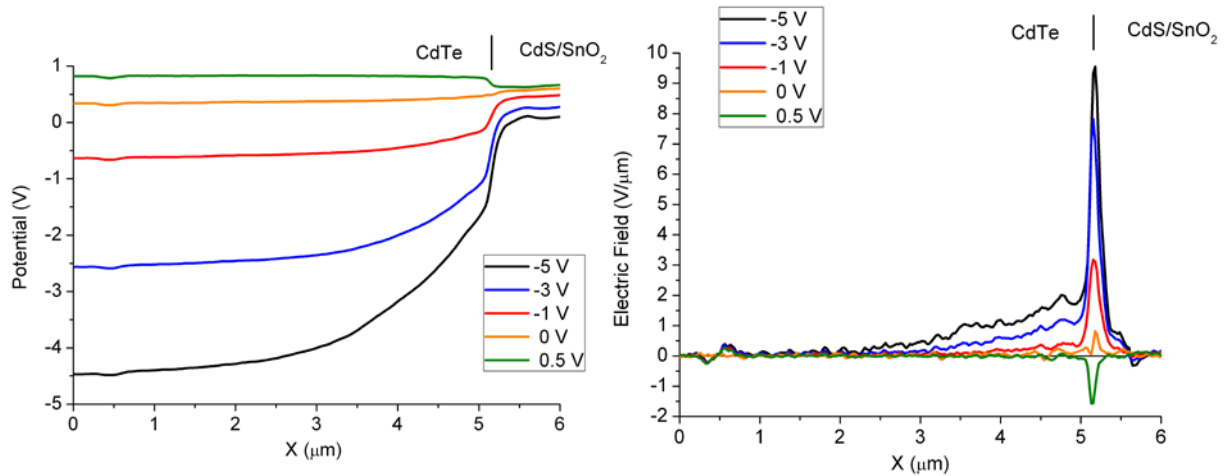


Fig. 3. Left: Linescans of the surface potential on the cross section of a CdTe/CdS solar cell after polishing and high ion-beam milling under different bias conditions (inset). Right: Corresponding linescans of the electric field.

which is caused by pinning of the Fermi level due to surface states. These surface states are affected by the sample preparation method, and only-polished samples present even stronger effects, such as a negative electric field at 0 bias. These results serve as a reminder that SKPM analyzes the surface of the sample, and care is needed when comparing the results with the bulk of the sample. Unfortunately, this is not the main problem. Fig. 4 shows linescans of the surface potential and electric field for another CdTe/CdS solar cell after polishing. The most striking feature on the surface potential linescans (left) is the crossing of the curves on the right (SnO₂ region). During the analysis, the SnO₂ film is grounded, and the reverse and forward biases are applied on the back contact. Because there is a drop in potential from where the SnO₂ is grounded to where the tip starts scanning, the linescans on the SnO₂ side are supposed to be slightly separated, as in Fig. 3. However, the theory cannot explain the behavior or the linescans on the SnO₂ side observed in Fig. 4. Furthermore, on the electric field linescans (right), we don't see a clear increase in the depletion region on the CdTe film as the reverse bias is increased, and we cannot explain the large electric field on the SnO₂ film, which is related to the strange shape of the potential signal on that region. We measured the efficiency parameters of the cell in Fig. 4, and V_{oc} before sample preparation and after analysis was around 800 mV, and efficiency was around 9.5%, which shows that the device was working during the measurements. We analyzed many samples and could not predict when a sample would behave like in Fig. 3 or Fig. 4. The conclusion is that we cannot reproduce the polishing/ion-beam milling process to the level required by SKPM. This problem makes it difficult to analyze unknown samples because it is difficult to separate results due to the sample properties from artifacts caused by the preparation process. Currently we are investigating new methods to prepare cross sections for SKPM.

CONCLUSIONS

Although etching with bromine/methanol solution produces good surfaces for EBSD analysis of CdTe, when applied to cross sections it attacks the film structure, resulting in large steps and contamination, and no useful EBSD data.

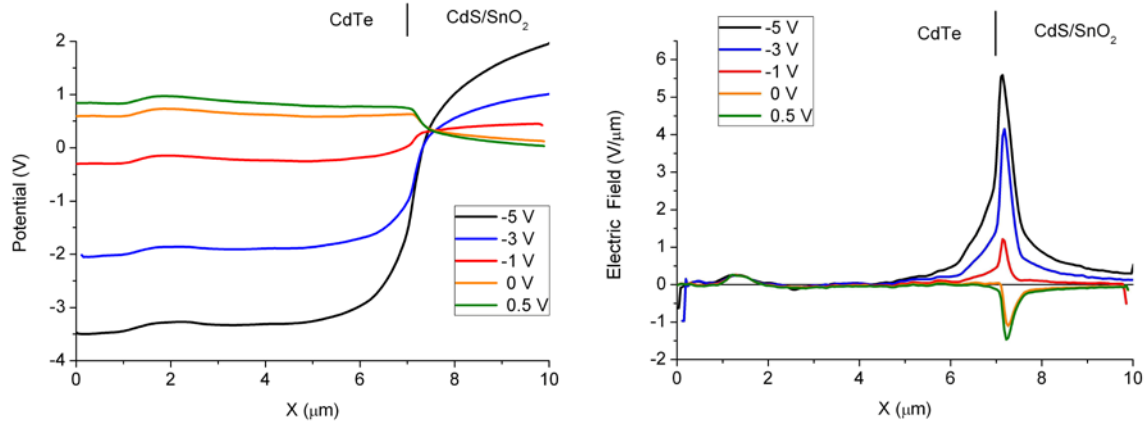


Fig. 4. Left: Linescans of the surface potential on the cross section of a CdTe/CdS solar cell after polishing under different bias conditions (inset). Right: Corresponding inescans of the electric field.

We developed a reliable procedure to prepare cross sections of CdTe/CdS solar cells for EBSD, which consists of polishing followed by ion-beam milling. An optimization of the milling parameters is important for the fabrication of good quality samples with just a small step between the SnO₂/CdS and CdTe films. Very good EBSD data can be routinely obtained, revealing the columnar character of the CdTe growth and details on the crystallographic structure of the film, such as grain size and boundary characteristics.

The best procedure to prepare cross sections of CdTe/CdS solar cells for SKPM was by polishing and polishing with a light ion-beam milling. Good SKPM data was obtained showing important aspects of the junction, such as the intermixed layer between CdTe and CdS, and the location of the p-n junction. However, the sample preparation process is not reliable, and the results are not always reproducible. Improvements in sample preparation will be needed before this technique can be used in a routine basis to study CdTe/CdS junctions.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08-GO28308 with the National Renewable Energy Laboratory.

REFERENCES

1. D. J. Dingley and D. P. Field, *Mater. Sci. Technol.* **13**, 69 (1997).
2. P. A. Rosenthal and E. T. Yu, *J. Appl. Phys.* **87**, 1937 (2000).
3. H. R. Moutinho, R. G. Dhere, M. J. Romero, C.-S. Jiang, B. To, and M. M. Al-Jassim, *J. Vac. Sci. Technol. A* **26**, 1068 (2008).
4. Y. Yan and M. M. Al-Jassim, *J. Appl. Phys.* **90**, 3952 (2001).
5. J. Quadros, A. L. Pinto, H. R. Moutinho, R. G. Dhere, and L. R. Cruz, *J. Mater. Sci.* **43**, 573 (2008).
6. H. R. Moutinho, R. G. Dhere, C.-S. Jiang, Y. Yan, D. S. Albin, and M. M. Al-Jassim, *J. Appl. Phys.* **108**, 074503 (2010).