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Local Built-in Potential on Grain Boundary of Cu(In,Ga)Se2 Thin Films

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C.-S. Jiang, R. Noufi, K. Ramanathan,
J.A. AbuShama, H.R. Moutinho, and
M.M. Al-Jassim

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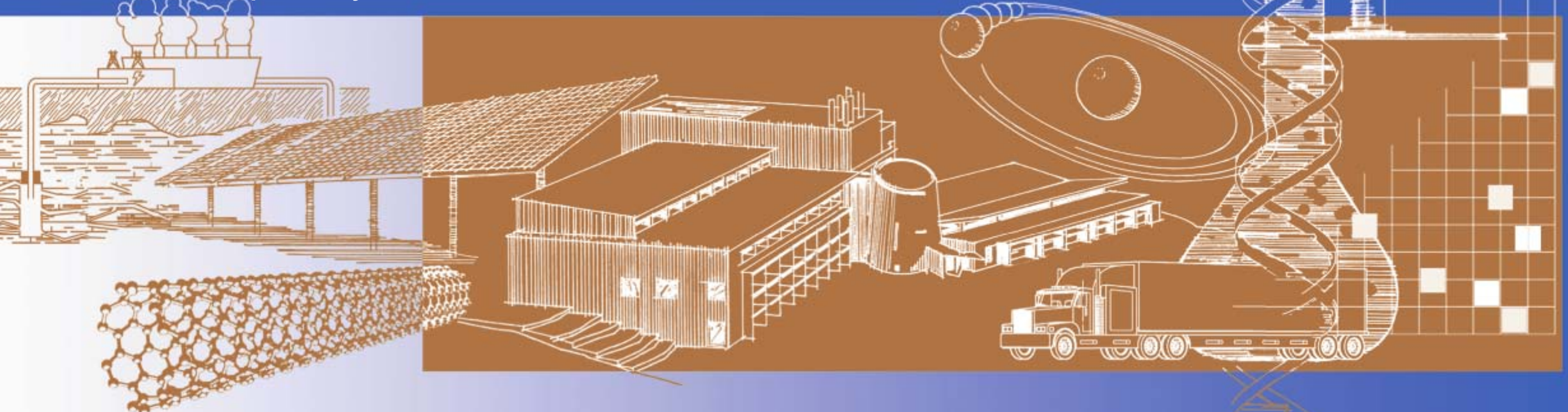

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Local Built-in Potential on Grain Boundary of $Cu(In,Ga)Se_2$ Thin Films

C.-S. Jiang, R. Noufi, K. Ramanathan, J. A. AbuShama, H. R. Moutinho, M. M. Al-Jassim
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd., Golden, CO 80401, Email: chun_sheng_jiang@nrel.gov

ABSTRACT

We report on a direct measurement of two-dimensional potential distribution on the surface of $Cu(In,Ga)Se_2$ (CIGS) thin films using a nanoscale electrical characterization of scanning Kelvin probe microscopy (SKPM). The potential measurement reveals a higher surface potential or a smaller work function on grain boundaries (GBs) of the film than on the grain surfaces. This demonstrates the existence of a local built-in potential on GBs and that the GB is positively charged. The role of the built-in potential in device performance was further examined by tuning Ga content or band gap of the film. With increasing Ga content, the GB potential drops sharply in a Ga range of 28%~38%. Comparing the change in the built-in potential to the theoretical and experimental photoconversion efficiencies, we conclude that the potential plays a significant role in the device conversion efficiency of NREL's three-stage CIGS device.

1. Objectives

The superior photovoltaic performance of the CIGS thin film compared to its single-crystal counterpart has been a puzzle in the PV community for many years, and the behavior of GBs in the films remains unclear. A classical model [1] of interface states suggests a local built-in potential around a GB as a result of trapped charges at the interface states on the GB. However, this general model does not specify whether or not a given polycrystalline material such as CIGS has the potential around the GB, because it relies on the electronic structure and the energy location of the interface states. In this work, we aim to probe the local potential on the GB and investigate the role of GB potential in the CIGS device performance.

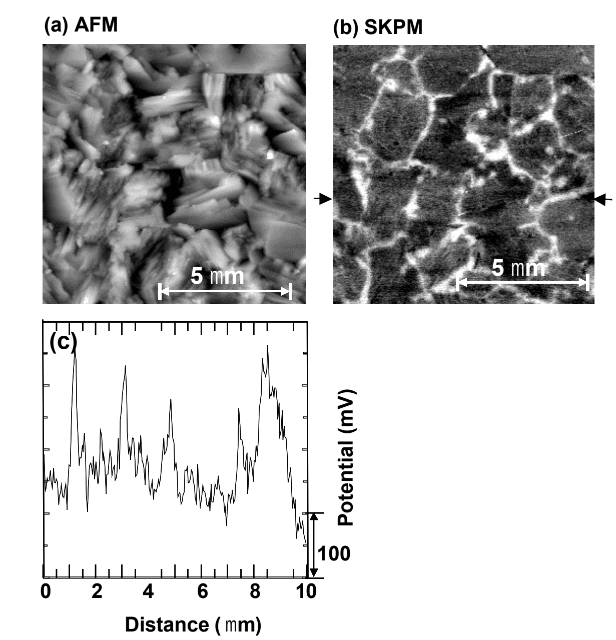

Fig. 1(a) AFM and (b) the corresponding SKPM images of the CIGS film after water-rinsing; (c) a line cut in (b).

2. Technical Approach

We used SKPM to measure two-dimensional potential distribution on surfaces of NREL's three-stage CIGS films. The SKPM technique is based on atomic force microscopy (AFM) [2]. In addition to the atomic force between the AFM tip and the sample surface, which gives a two-dimensional AFM topographic image of the surface, there is a Coulomb force between the tip and the sample, based on a difference in work functions between the tip and the sample and a charge transfer between them. The Coulomb force gives a useful signal to measure the work function of the sample. Like the classical Kelvin probe, SKPM applies a dc voltage, which is the Kelvin probe signal, to compensate the work function difference between the tip and the sample, and to thus nullify the Coulomb force. Unlike the classical Kelvin probe, SKPM monitors the Coulomb force instead of an ac current in the classical Kelvin probe. The extremely sensitive AFM cantilever to the force (~nN/m) and the miniature size of the AFM tip (~10 nm) give rise to a high spatial resolution of a few tens of nanometers for the SKPM technique.

3. Results and Accomplishments

The SKPM measurement reveals a higher electrical potential or a smaller work function (~150 meV) on the GB than on the grain surface (Fig. 1). The measurement was made on a CIGS film after high-purity water rinsing, and the film was fabricated by a process that produced the recent record device efficiency of 19.2%. Water-rinsing was used to remove the Na residing on the film surface, which diffused from the soda lime glass substrate onto the surface. The surface Na makes the measured potential peak on the GB broad due to the Na-induced surface dipoles [3]. The potential on the GB demonstrates a positively charged GB, and the charge dipoles give rise to the local built-in potential in the space charge region around the GB. However, the mechanisms of the charged donor state cannot be deduced from the potential measurement. Our measured potential height (~150 mV) seems to be small compared to the band gap (~1.15 eV) of CIGS. Most likely, the depletion on the grain surface reduces the contrast of potential between the GB and the grain surface and makes the measured potential peak on the GB smaller than the potential barrier on the GB in the bulk (Fig. 2). Such surface depletion exists widely on semiconductor surfaces. Therefore, our potential measurement indicates that the GB potential in the bulk should be lager than the measured value of ~150 mV.

The effect of GB potential on device conversion efficiency was further examined by varying the Ga content in the CIGS films [4]. The band gap of CIGS can be tuned from 1.01 to 1.68 eV by adjusting the Ga content of Ga/(In+Ga) from 0 to 100%. With varying Ga content, we found that the GB potential drops from ~150 mV to zero sharply in a range of 28%~38% Ga [Fig. 3(a)]. By comparing the plot of the GB potential to the theoretical [5] and experimental plots of the conversion efficiency [Fig. 3(b)], we found that the GB potential correlates well with the measured device efficiency. The increase of efficiency in the 0~28% Ga range is due mainly to the increase of the band gap, and the GB potential in this Ga range stays strong. However, at the higher Ga content, the absence of the GB potential seems to be significant compared to the effect of the band gap widening. Thus, the drop in the measured efficiency is slower compared to the precipitous drop in the GB potential. The current record efficiency device has the maximum Ga content or band gap under the condition of a strong GB potential. Even though the measured efficiency of a thin-film device is affected by other factors in addition to band gap and built-in potential at the GB, such as the nature of the junction partner and its related band alignment with that of the absorber (e.g., the CIGS in this study), the condition stated above is strong enough to demonstrate a significant benefit of the built-in potential on GBs in thin-film CIGS-based devices.

Although the physics underlying why the GB potential benefits the photovoltaic performance cannot be directly deduced from the potential measurement, a possible mechanism is the GB potential-assisted minority–carrier collection, because the GB potential attracts electrons and repulses holes. A study of CIGS devices by tuning Ga content pointed out that the low conversion efficiency at high Ga content results from voltage-dependent minority carrier collection and low value of fill factor [6], which is consistent with the GB potential-assisted minority-carrier collection mechanism.

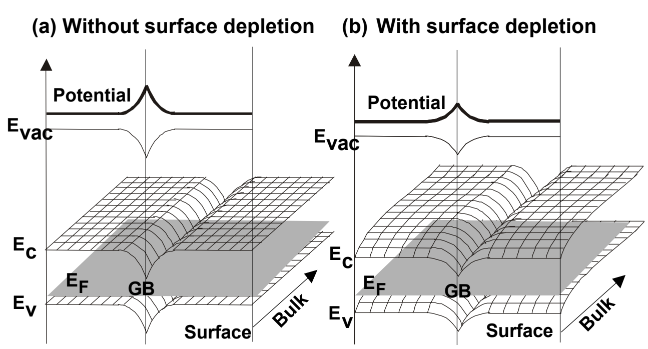

Fig. 2 Schematics of two-dimensional band diagram around the GB.

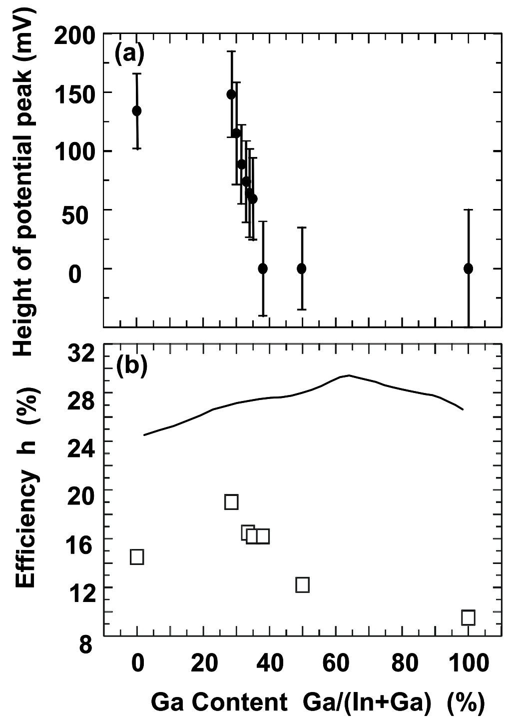

Fig. 3(a) Changes in the GB potential with Ga content; (b) experimental and theoretical efficiencies.

4. Conclusions

We demonstrated the existence of local built-in potential at the GB that arises from the positively charged GB, and that the GB potential plays a positive role in device conversion efficiency. This points out an approach for cell design in which the band gap or Ga content is increased while the built-in potential on the GB has to be kept strong. In addition, our finding that the GB potential drops sharply in the Ga range of 28%~38% may open both theoretical and experimental research to investigating what happens to the atomic and electronic structures of the GB in this Ga content.

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