A study on the optoelectronic properties of $CuIn_{1-x}Ga_xSe_2$ grain boundaries by electrostatic force microscopy

Yoonmook Kang[a], Jae Ho Yun[b], Kyung Hoon Yoon[b], K. S. Jeon[c], Yung-Doug Suh[c] and Donghwan Kim[a]

[a].Department of Materials Science and Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 137 - 713, Korea
[b] New Energy Department, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Korea
[c] Micro-Chemical Technology Laboratory, Korea Research Institute of Chemical Technology, 100 Jang-dong, Yuseong-gu, Daejeon, 305-343, Korea

Abstract

We investigated the electric charge distribution in $CuIn_{1-x}Ga_xSe_2$ films, with particular emphasis on grain boundaries. Hall measurements, electron beam-induced current and optical beam-induced current measurements are commonly used for the characterization of solar cells, but they do not provide the resolution necessary for the investigation of individual grain boundaries. Therefore, we used an electrostatic force microscopy (EFM) capable of probing the electric charge distribution and the potential gradient of sample surface. EFM experiments were performed at 300K with a Dimension ™ 3100 scanning probe microscope (Digital Instruments). We suggest that grain boundaries should be electron-accumulated area and the inner grain area be the hole-accumulated area. The potential variations between the grain boundaries and inner grain area were estimated to be 60~180meV.

Introduction

The chalcopyrite materials have desirable properties for photovoltaic applications. $CuIn_{1-x}Ga_xSe_2$ (CIGS) with a band gap of 1.02 eV is considered a promising material for photovoltaic application. The material properties can be changed by partially replacing the indium by gallium and/or the selenium by sulfur. High conversion efficiency of near 19.5 % has been achieved using CIGS [1]. In general, recombination at grain boundaries in polycrystalline materials is limiting the cell efficiency. However, polycrystalline CIGS is believed to have a potential for higher efficiency. The pathways for the improvement do not seem to be well understood at present. Charge separation and transport in CIGS solar cells are likely to be very different from those in single-crystal devices. Significant effort has been focused on studying the physical and electronic properties of this material system at nanoscale. Hall measurements and other measurements such as electron beam-induced current and optical beam-induced current are commonly used for the investigation of solar cells, but they do not provide the resolution necessary for the investigation of individual grain boundaries. In this study, we investigated the charge distribution in CIGS films, with particular emphasis on grain boundaries.

Experimental Procedures

We prepared the CIGS absorber layer by a three-stage coevaporation process of In, Ga, Cu and Se [2][3]. The three-stage coevaporation of CIGS from elemental sources in the presence of excess Se vapor is the most successful absorber deposition method for high efficiency solar cell [4].
Electrostatic force microscopy (EFM) is used to map the vertical gradient of the electric field between the tip and the CIGS surface [5]. EFM is a special type of atomic force microscopy (AFM).
The electric charge distribution in the film surface can be investigated by a direct measurement of the magnitude and the sign of the local potential on a grounded surface. EFM experiments were performed

at 300K with a Dimension ™ 3100 scanning probe microscope (Digital Instruments). We adopted Co/Cr-coated Si cantilevers with a frequency of 60kHz and a spring constant of 2.8~5 N/m. Measurements were made with the excitation wavelength of 514 nm.

Results and Discussions

Figure 1 shows the transmission electron microscopy (TEM) image and copper element mapping of CIGS film. TEM images in Fig. 1 plus the copper element mapping reveal that some copper components existed on top of CIGS layer. Copper rich grains with diameters between 150 and 200 nm formed on the surface. The crystal structure of the CIGS was investigated by x-ray diffractometry (XRD) (Fig. 2). The XRD pattern contains three peaks that are clearly distinguishable. The 2θ values of diffraction peaks are 26.8, 44.62, and 53.04 that correspond to the reflections from (112), (220)/(204), and (312)/(116) planes of CIGS. No binary Cu composite peaks were detected.

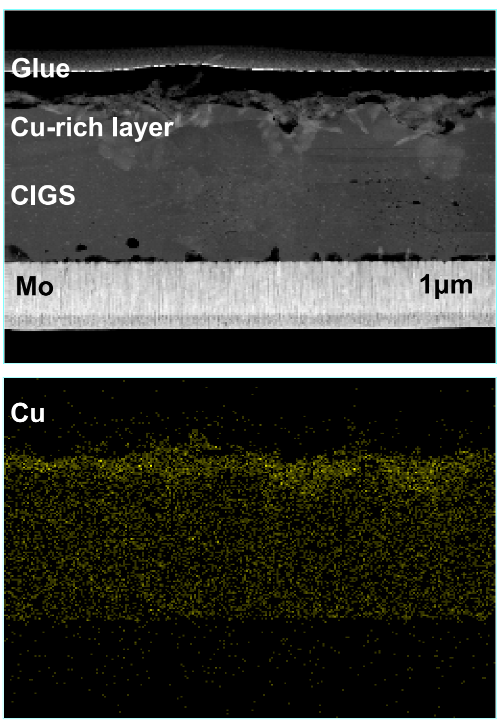


Fig. 1 Cross-sectional TEM image and Cu element mapping of a CIGS film.

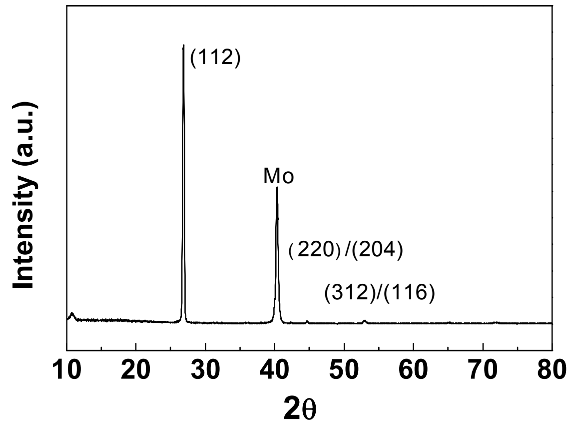
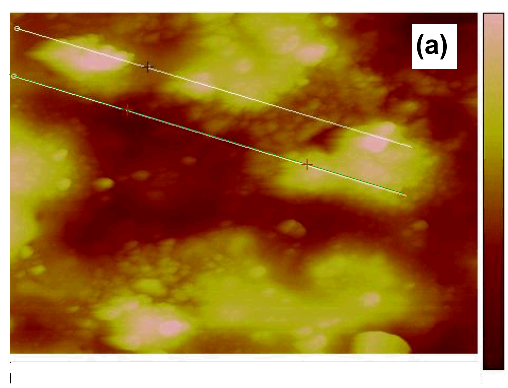


Fig. 2. X-ray diffraction pattern of a CIGS film

An AFM and a corresponding EFM image of CIGS surface are given in Fig. 3. EFM image was captured at a 3 V potential difference between the tip and the sample. The dark areas in the EFM image are parts of the grain boundaries (GB). The brighter areas indicate the interior of grains (GI). From the EFM image, it is seen that GB is electron-accumulated area and GI is hole-accumulated area, respectively. The potential variations between the GBs and GIs are observed. For the grain, the amplitude of potential variation reached 60~180 meV, as can be estimated from the profile in Fig. 3c. We attribute the potential variation to the band bending or band offset of the conduction band.



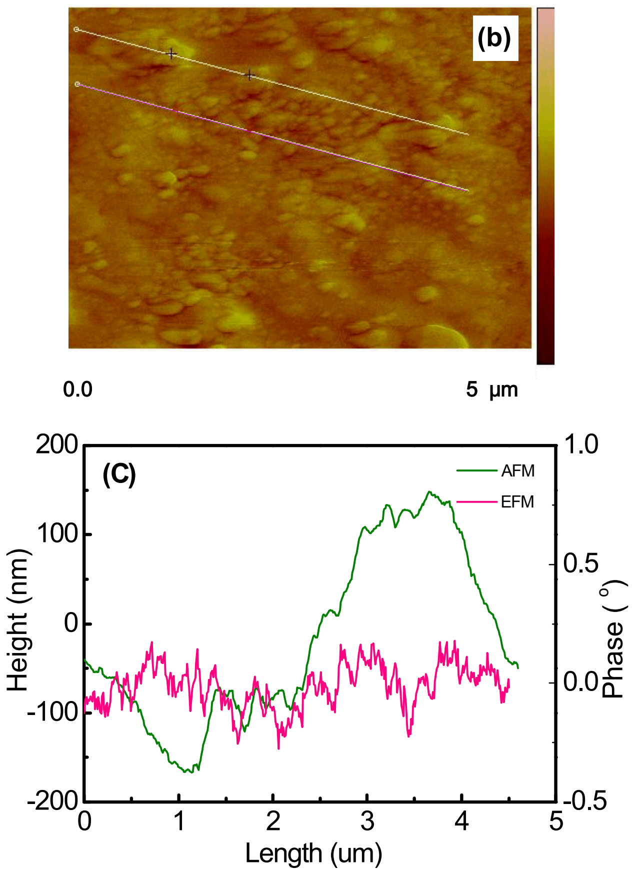


Fig. 3. (a) Non-contact mode AFM topography image of CIGS surface with a scan area of 5×5 μm^2. (b) EFM phase image under illumination for the same area, (C) line scan indicated by a solid line in (a) and (b)

When the film is illuminated with laser (514.5 nm), electron-hole pairs are formed in GB and GI (Fig. 4). As CIGS is a p-type semiconductor, it is possible to assume that the valence and conduction band at grain boundaries are bent down due to the trapping of the majority carriers. As a consequence of this band bending the Fermi level at GB is closer to conduction band. Upon illumination, the photogenerated carriers can separate under the influence of the potential difference. As the electrons accumulate on the GB, the bend bending is reduced.

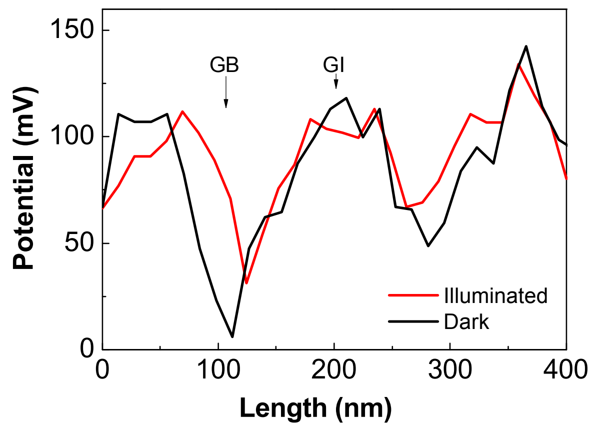


Fig. 4. Line scan along the line in Fig. 3(b). A reduction in the potential at the GB is observed.

Conclusions

We studied the electric charge and the surface potential distribution in CIGS using EFM. The amplitude of surface potential variation reached 60~180meV. We attribute the potential variation to the band bending or band offset of the conduction band.

References

[1] Miguel A. Contreras, K. Ramanathan, J. AbuShama, F. Hasoon, D. L. Young, B. Egaas and R. Noufi, Prog. Photovolt: Res. Appl.**13**, 209 (2005).

[2] M. A. Contreras, J. Tuttle, A. Gabor, A. Tennant, K. Ramanathan,S. Asher, A. Franz, J. Keane, L. Wang, J. Scofield, and R. Noufi, Proc. 1st World Conf. Photovolt. Energy Conv., IEEE, Piscataway, NJ., 68 (1994).

[3] W. E. Devaney, W. S. Chen, J. M. Stewart, and R. A. Mickelsen, IEEE Trans. Electron Dev. **37**, 428 (1990).

[4] A. M. Gabor, J. R. Tuttle, D. S. Albin, M. A. Contreras, and R. Noufi, Appl. Phys. Lett. **65**, 198 (1994).

[5] C. C. Williams and H. K. Wickramasinghe, Proc. SPIE **897**, 129 (1987)