# Potential Profiles around Grain Boundary Studied by Photoassisted Kelvin Probe Force Microscopy on Cu(InGa)Se<sub>2</sub> Solar Cells

Masaki Takihara<sup>1</sup>, Takashi Minemoto<sup>2</sup>, Youich Wakisaka<sup>2</sup> and Takuji Takahashi<sup>1</sup>

<sup>1</sup>Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan Phone: +81-3-5452-6270, E-mail: takihara@iis.u-tokyo.ac.jp

<sup>2</sup>Department of Photonics, Ritsumeikan University, 1-1-1 Noji Higashi, Kusatsu, Siga 525-8577, Japan

## 1. Introduction

Thin film solar cells based on Cu(InGa)Se<sub>2</sub> (CIGS) materials exhibit high conversion efficiency comparable with that of multicrystalline silicon solar cells<sup>[1]</sup>, even though the CIGS materials present multicrystalline structures and the behaviour of their grain boundaries (GBs) toward the solar cell performance has not been fully understood yet. In this study, potential profiles around GBs in CIGS solar cells were investigated by photoassisted Kelvin probe force microscopy (P-KFM) to reveal characteristics of GBs. The P-KFM method, we originally proposed, realizes very local measurements of the surface photovoltage (SPV) as well<sup>[2-4]</sup>. From the results of the P-KFM measurements, we will discuss how the potential depth at GB and the photovoltage depend on Ga concentration of CIGS materials.

# 2. Experimental

The CIGS layers were formed by three-stage coevaporation process<sup>[5]</sup> on Mo-coated soda lime glass substrates. Then the solar cell structures were fabricated on these CIGS layers by chemical bath deposition (CBD) of CdS buffer layer and by rf sputtering of ZnO and ITO layers. The material compositions, the bandgaps and the basic characteristics as the solar cell of the samples are summarized in Table I. Here the solar cell performances were measured by the conventional and macroscopic method under 100 mW/cm<sup>2</sup> AM 1.5 illumination at 25 °C.

A key technique in this study is the P-KFM, that is, Kelvin probe force microscopy<sup>[6]</sup> (KFM) operating under light illumination. Since KFM is one application of atomic force microscopy (AFM) and enables us to obtain the surface potential, P-KFM gives very local photovoltaic information of the samples. For SPV measurements in P-KFM, the surface potentials were evaluated sequentially in the dark condition and under light illumination, and the potential change was calculated as the photovoltage. Our P-KFM system consists of both a commercial AFM system (SPI4000/SPA300HV, SII NanoTechnology Inc., Japan) and some external electronics to obtain an accurate surface potential value<sup>[3]</sup>. This system operates in a high vacuum (typically, 10<sup>-5</sup> Pa) at room temperature and in an intermittent contact mode with piezoresistive cantilever (PRC400, SII NanoTechnology Inc., Japan) having a Ptcoated tip. As a light source, monochromatic light at a wavelength of 800 nm from a tunable Ti:Al<sub>2</sub>O<sub>3</sub> laser system was used. This laser light was guided by optical fiber and focused on the sample surface just beneath the KFM tip,

Table I  $\;$  The ratio of Ga to (In+Ga), the band gap of CIGS and solar cell performances  $\;$ 

Sample	Ga ratio [Ga/(In+Ga)]	$\stackrel{E_g}{(\mathrm{eV})}$	V <sub>oc</sub> (V)	$J_{ m SC}$ (mA/cm <sup>2</sup> )	FF (%)	Eff. (%)
(A)	0.20	1.15	0.517	36.1	55.2	10.3
(B-1)	0.234	1.13	0.606	35.0	69.3	14.7
(B-2)	0.318	1.16	0.613	30.0	62.5	11.5
(B-3)	0.378	1.22	0.652	26.7	68.4	11.9
(B-4)	0.500	1.28	0.680	22.7	58.8	9.09



Fig. 1 Images and line profiles of (a) topography, potential in dark condition and (c) photovoltage under the light illumination at wavelength of 800 nm on the surface ITO layer of the CIGS solar cell [Sample (A)].

and the typical light intensity was 10 mW/cm<sup>2</sup> just before illuminating the sample surface. The examined samples having different Ga contents are summarized in Table I.

# 3. Results and Discussion

Figure 1 shows images of (a) topography, (b) the corresponding potential and (c) photovoltage distributions on the surface ITO layer of Sample (A) as well as their line profiles along Line A-B. As shown in Fig. 1(a), the surface morphology of the ITO layer reflects the grain structure in the CIGS layer because the total thickness of the additionally formed CdS, ZnO and ITO layers was comparable to the original corrugation height of the CIGS grains. From Fig. 1(b), we can recognize abrupt drop of the potential at the GB. The similar potential distribution has been observed on the as-grown CIGS film. One possible

cause of these potential distributions is a change in the material composition near the GBs due to the segregation within the single CIGS grains. Note here that the potential in our measurements is for electrons, which means high or low potential region repulses or attracts the electrons, respectively. The observed potential distribution implies that the photogenerated electrons in the CIGS layer tend to accumulate near the GBs rather than to stay on the grains, and consequently the photovoltage will be enhanced there. Actually, such a tendency clearly appeared in the photovoltage distributions in the corresponding areas as shown in Fig. 1(c). These findings indicate that the GBs in the CIGS materials do not act as the site degrading the solar cell performance, which is quite different from the case of the polycrystalline silicon material.

To characterize the GBs in more detail, we investigated the dependence of the potential depth at GBs on a ratio of Ga to (In+Ga) in the CIGS layer. In this measurement, four samples having different Ga concentrations [Samples (B-1)-(B-4)] were used, as summarized in Table I. Figure 2 shows (a) topography and (b) the corresponding potential images of Sample (B-4), which has the highest Ga ratio of all the samples. Figure 2 indicates that the surface morphology as well as the outline of the potential distribution of Sample (B-4) were similar to those of Sample (A), while the contrast in the potential was slightly weakened in Sample (B-4). We evaluated the potential depth at GB from the difference between the potential at the center of the grain [Point P indicated in Fig. 2(a)] and the average potential over five points [Points a-e indicated in Fig. 2(a)], and it was 47 mV. Similarly, the potential depths in Samples (B-1)-(B-3) were estimated to be 114, 101 and 74 mV, respectively. The potential depth at the GB was plotted as a function of the ratio of Ga to (In+Ga) in Fig. 3. From this figure, we found that potential depth monotonically decreases as an increase of Ga content, which is consistent with the precedent results reported by Jiang *et al*<sup>[7]</sup>. This shallowing of the potential</sup> depth implies that the material composition becomes uniform inside the single grain of CIGS layer. We also found that the photovoltage generated in Sample (B-4) is higher than that in Sample (B-1) even though the potential depth at the GB was shallowed and consequently the photovoltage enhancement owing to the potential drop at GB may get smaller in Sample (B-4). Therefore this increase in photovoltage is simply attributable to the difference in the bandgap of the CIGS material.

#### 4. Conclusions

We have performed the potential and photovoltage measurements by P-KFM on CIGS solar cells to investigate the behavior of the grain-boundary. As a result, the abrupt drop of the potential and the photovoltage enhancement were observed at GBs. Moreover, we found that the potential depth at GB decreases with increasing the ratio of Ga to (In+Ga) in CIGS layer. In addition, the dependence of photovoltage on the Ga content corresponds well to the band gap of CIGS material.



Fig. 2 (a) Topographic and (b) potential images on Sample (B-4).



Fig. 3 Dependence of the potential depth at GB on the ratio of Ga to (In+Ga) in CIGS layer.

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