Photo-assisted Scanning Probe Microscopies on Solar Cells

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Abstract

We performed photo-assisted Kelvin probe force microscopy and photothermal atomic force microscopy on Cu(In,Ga)Se₂ [CIGS] solar cells to investigate their local photovoltaic properties and photo-carrier dynamics. By means of those techniques, the spatial distribution and temporal decay of photovoltage as well as the non-radiative recombination properties in the CIGS solar cells were examined. As a result, the spatial separation effect of photo-carriers and the contribution of fast process in the whole recombination processes of photo-carriers in the CIGS solar cells have been discussed, and the possibility that sub-gap states with discrete energy levels exist in the CIGS material has been pointed out.

1. Introduction

Thin film solar cells made from Cu(In,Ga)Se₂ [CIGS] materials have attracted growing interest in recent years because of their potential for high performance. Most of the CIGS materials used in solar cells have a microcrystalline structure which includes many small grains and their boundaries. In order to investigate local behavior of the grain boundaries (GBs) in the CIGS solar cells, scanning probe microscopies (SPMs) are very useful because their spatial resolution is high enough to identify the GBs.

In this article, photo-assisted SPMs, such as photo-assisted Kelvin probe force microscopy (P-KFM) and photothermal atomic force microscopy (PT-AFM), on CIGS solar cells will be described. In P-KFM, photovoltaic properties in CIGS were investigated through surface potential measurements under light illumination, and a spatial separation effect of photo-carriers has been discussed. In addition, recombination process of photo-carriers in the CIGS solar cells has been analyzed by P-KFM under intermittent light illumination at various modulation frequencies. In PT-AFM, on the other hand, non-radiative recombination properties in the CIGS solar cells were examined through the precise measurements of thermal expansion induced by the light illumination onto the sample surface, and we have found the possibility that sub-gap states with discrete energy levels exist in the CIGS material.

2. Experimental Methods

2.1 Photo-assisted Kelvin Probe Force Microscopy (P-KFM)

In the conventional KFM, the contact potential difference between a sample surface and an AFM tip, which is called surface potential, is determined by adjusting a d.c. bias to nullify the electrostatic force generated by an a.c. voltage applied between them. In P-KFM, on the other hand, we operate KFM under light illumination, and consequently it enables us to obtain the surface photovoltage at a very high spatial resolution. Figure 1 shows a setup of our P-KFM system, consisting of a commercial AFM system (SPI4000/SPA300HV, Hitachi High-Tech Science Corp., Japan) combined with some external optical modulator for tunable TiAl₂O₅ laser, and the intensity of the incident light is modulated by an acousto-optic modulator (AOM) for photovoltage decay measurements.

Fig. 1 Experimental setup for P-KFM. As a light source, a tunable TiAl₂O₅ laser is used, and the intensity of the incident light is modulated by an acousto-optic modulator (AOM) for photovoltage decay measurements.
electronics and light sources for accurate measurements of the surface potential as well as the surface photovoltage\(^2,3,6\). We operated this system at a high vacuum pressure (typically, \(10^{-5}\) Pa) at room temperature and in an intermittent contact mode in AFM. In order to avoid the influence of stray light on the photovoltage measurement by P-KFM, a piezoresistive cantilever having a Pt-coated tip (PRC400, Hitachi High-Tech Science Corp., Japan) was used. Its spring constant and resonant frequency were about 3 N/m and 60 kHz, respectively. As a light source, the monochromatic light in the wavelength range between 700 and 1000 nm from a tunable Ti:Al\(_2\)O\(_3\) laser system (Model 890, Coherent, USA) was used. This laser light was guided by an optical fiber and focused on the sample surface just beneath the KFM tip, and the typical light intensity on the sample surface was 100 - 200 mW/cm\(^2\). To measure the surface photovoltage by P-KFM, the surface potentials were evaluated sequentially in darkness and under light illumination, and the potential change was regarded as the surface photovoltage. For the photovoltage decay measurements to discuss the photocarrier recombination process, an acousto-optic modulator (AOM) was used as shown in Fig. 1 to modulate the incident light at various frequencies with a duty ratio of 50%.

2.2 Photothermal Atomic Force Microscopy (PT-AFM)

Figure 2(a) shows our experimental setup for PT-AFM, which was based on the same AFM system as that for P-KFM and was operated at room temperature in nitrogen gas at 1 atm\(^9\). In the photothermal (PT) measurements in PT-AFM, the sample surface was illuminated by an intermittent light and the output of the deflection sensor for the AFM cantilever was sampled by a home-made dual sampling (DS) circuit\(^9\). Then, the periodical change in output signal from the DS circuit at the modulation frequency of the incident light, which corresponded to periodical thermal expansion caused by the intermittent light illumination, was extracted by the lock-in amplifier and treated as the PT signal\(^9\). Similarly to the P-KFM method, a Si piezoresistive cantilever (PRC-DF40P, Hitachi High-Tech Science Corp., Japan) was used to avoid the influence of stray light. Its spring constant and resonant frequency were about 40 N/m and 450 kHz, respectively. Figure 2(b) shows the light sources used for photo-excitation above and below the bandgap of CIGS. For the former, we used the Ti:Al\(_2\)O\(_3\) laser in continuous wave mode, whose photon energy was set at 1.38 eV in this study, and its typical light intensity was about 100 mW/cm\(^2\) at the sample surface. For the latter source, near-infrared laser diodes (LD-1600-0010-AR-1 and LD-1400-0020-AR-1, TOPTICA, Germany) whose central photon energies were 0.78 and 0.89 eV, respectively, were used, and their output power was set at 10 mW. The incident light from the Ti:Al\(_2\)O\(_3\) laser and laser diodes were periodically modulated by an optical chopper and a drive current in a square waveform, respectively, with a duty ratio of 50% at a frequency of 180 Hz.

2.3 Sample Structures

The basic structure of the CIGS solar cells investigated in this study was ITO (tin-doped indium oxide)/ZnO/CdS/CIGS/
Mo/SLG (soda lime glass), as shown in Fig. 3. We fabricated four samples by a three-stage co-evaporation process with Ga contents \([=\text{Ga/(In+Ga)}]\) in a range between 23% and 50% in the CIGS absorption layer, referred to as Samples A, B, C and D. Their solar cell characteristics, such as open circuit voltage \((V_{oc})\), short circuit current density \((J_{sc})\), fill factor \((F. F.)\) and conversion efficiency \((Eff.)\), are summarized in Table I.

### 3. Results and Discussion

#### 3.1 Photovoltage Distribution and Band Diagram around GBs Investigated by P-KFM

Figures 4(a)-(c) shows images and line profiles of the topography, surface potential in darkness, and photovoltage, respectively, obtained by P-KFM on Sample A\(^7\). The line profiles were analyzed along the line L-R, indicated by the white lines in the images. In Fig. 4, we can identify abrupt potential drops around the GBs. Here “potential” means electron potential, and therefore it is expected that regions of low potential will easily attract the electrons which are the minority carriers in the CIGS layer because the CIGS material is a p-type semiconductor. This expectation is very consistent with a fact that the photovoltage observed by P-KFM was clearly enhanced around GBs, as shown in Fig. 4(c). If we now assume that the electron affinity is nearly uniform over the whole surface, the potential distribution shown in Fig. 4(b) can be regarded as a profile of the conduction band edge of the CIGS material, except for their raw numerical values. We also performed scanning tunneling spectroscopy (STS) on the same sample to investigate the bandgap distribution, and the results indicate that the bandgap was broadened near GB\(^7\). By considering the P-KFM and STS results together, we can estimate the band profiles around GBs as shown in Fig. 5\(^7\). According to the estimated band profile, we can expect that photo-generated electrons and holes near the GB will be easily separated by the built-in electric field and that the recombination rate of these carriers will be lower at the GB, regardless of the activity level of the GB. This is considered to be one of the primary advantages of CIGS as a solar cell material.

Fig. 4 Images and line profiles of (a) the topography, (b) the potential in darkness, and (c) the photovoltage under light illumination, obtained by P-KFM on Sample A.

### 3.2 Photovoltage Decay Measurements by P-KFM

Under a modulated incident light at a frequency higher than the bandwidth of the potential feedback in KFM, P-KFM gives a temporally-averaged photovoltage over the modulation period\(^4,6\). The temporally-averaged photovoltage \(V_{ave}\) as a function of the modulation frequency \(f\) of incident light measured on individual grain interiors in Samples A and D having the lowest and highest Ga contents among our whole samples was shown in Fig. 6\(^6\). At a low modulation frequency, the photovoltage seems to follow the modulated light intensity.
and consequently $V_{\text{ave}}$ should be a half of the photovoltage under the continuous light illumination $V_{\text{Cont}}$. If, on the other hand, the modulation frequency is high enough to make the photovoltage decay by the slow recombination process negligible, a plateau region should appear where a value of $V_{\text{ave}}/V_{\text{Cont}}$ is almost independent of the modulation frequency. In the intermediate frequency region, where the modulation period $T = 1/f$ is comparable with a time constant $\tau$ for the photovoltage decay by the slow recombination process, a value of $V_{\text{ave}}/V_{\text{Cont}}$ is given by

$$V_{\text{ave}}/V_{\text{Cont}} = \frac{1}{2} + \frac{r}{T}(1-r)\left[1 - \exp\left(-\frac{T}{2\tau}\right)\right],$$

where $r$ is the contribution ratio of fast carrier recombination process in the entire recombination processes evaluated from the plateau region at the high modulation frequency. By solving this equation after substituting the empirical values of $V_{\text{ave}}$, $V_{\text{Cont}}$, $T$ and $r$ into it, the time constant $\tau$ for the photovoltage decay by the slow recombination process can be calculated. The values of $\tau$ and $r$ obtained on Samples A and D are also indicated in Fig. 6, and we clearly found the elongation of $\tau$ and the increase of $r$ in Sample D compared with Sample A\textsuperscript{12).} Since we consider that $\tau$ represents a time constant required for the carrier transport across the potential barriers at the hetero-interfaces in the cell structure, this elongation of $\tau$ in CIGS with high Ga content is attributable to a deduction that the electron transport is slightly disturbed due to the broadening of the CIGS bandgap, especially to the upward shift of the energy level of the conduction band edge, as an increase of Ga content.

From the values of $r$, on the other hand, we can evaluate the contributions of the photo-carriers which should be extinguished by the fast or slow recombination processes to the total photovoltage, and those contributions acquired on the whole samples are summarized in Fig. 7\textsuperscript{12). As shown in this figure,}

Figure 8(a) shows a topographic image taken on the surface of Sample A, and Fig. 8(b) shows the PT signal image on the same area taken under above-gap excitation condition\textsuperscript{10). These images indicate that the PT signal was enhanced near the GB. In the above-gap excitation condition where Fig. 8(b) was taken, both free electrons and free holes would be excited, but the recombination probability in CIGS should be dominated by the number of electrons as the minority carrier, rather than the number of holes, because the CIGS material is a p-type semiconductor. Based on the band profile we estimated, indicated in Fig. 5, it is expected that photo-generated free electrons accumulate near the GB, and therefore this electron accumulation around the GB enhances the PT signal, as shown in Fig. 8(b).

On the other hand, Figs. 8(c) and 8(d) are the PT images taken under below-gap excitation conditions\textsuperscript{13).} As shown in Fig. 8(c), apparent PT signals were observed even in the
below-gap excitation condition at the incident photon energy of 0.89 eV, and their distribution became more uniform than that observed in the above-gap condition shown in Fig. 8(b). In addition, we found that the PT signals became very weak under light at a photon energy of 0.78 eV, as shown in Fig. 8(d), indicating that no sub-gap excitation occurred in this energy range. From these results, we concluded that some discrete subgap states that caused a carrier transition around an energy of 0.9 eV existed over the individual grains throughout the CIGS material, but were not localized near the GB. The existence of such sub-gap states in a similar energy region was also suggested from photoluminescence studies\textsuperscript{15}, from transient photocapacitance spectroscopy\textsuperscript{16}, and from two-wavelength excited photoluminescence spectroscopy\textsuperscript{17}, reported by other groups.

Next, we observed the PT signal images on Sample D, as shown in Fig. 9 in (b). In the above-gap excitation condition shown in Fig. 9(b), the area exhibiting the strong PT signal appears broadened compared with Sample A. In the CIGS material with high Ga content, the reduction of a built-in electric field around GB has been reported\textsuperscript{13,14}. This weakens the electron accumulation effect around GBs. Consequently, the PT signal distribution broadened, as shown in Fig. 9(b). In the below-gap excitation condition under light at 0.89 eV, on the other hand, a distinct PT signal also appeared on Sample D, and an apparent enhancement of the PT signal intensity was observed, especially around the GB, in contrast to the case of Sample A. Under light at 0.78 eV, on the other hand, we only observed very weak PT signals, as shown in Fig. 9(d), similarly to Sample A.

Based on these results, we discuss what kind of transition is the most plausible in the below-gap excitation condition at 0.89 eV. Figure 10(a) shows three candidates for such transitions: generation of (i) bound electrons and free holes, (ii) bound electrons and bound holes, and (iii) free electrons and bound holes. In the model (iii), the generated free electrons in Sample A in particular should accumulate near the GB, similarly to the case of the above-gap excitation. The PT signal would then be enhanced there. However, this is not consistent with the results observed on Sample A, where the distribution of the PT signals was not localized around the GB, but was nearly uniform over the sample surface, as shown in Fig. 8(c). Based on model (ii), both bound states for electrons and holes should be relatively shallow. In general, the shallow level in the semiconductor obeys the effective mass approximation, and therefore the energy separation between the shallow level and the conduction or valence band edge should be almost constant even when the bandgap value changes. In this case, the energy difference between the bound states for electrons and holes in
Sample D should be about 0.15 eV larger than that in Sample A, as illustrated in Fig. 10(b), because the bandgap of Sample D is 0.15 eV wider than that of Sample A. However, this is also inconsistent with our experimental results, where PT signal enhancement was observed within a similar energy region around 0.9 eV on both Samples A and D. Consequently model (ii) does not seem to apply either. Hence, we conclude that model (i), in which a deep electron trap exists in the bandgap, is the most plausible.

The deep energy level should be insensitive, to a certain extent, to the upward shift of the conduction band edge and the consequent broadening of the bandgap as the Ga content increases. The origin of such a deep level around 0.9 eV above the valence band edge may be antisite defects like In\textsubscript{Ga} and/or Ga\textsubscript{In} as theoretically predicted by Zhang et al.\textsuperscript{193-197}. The difference in the spatial distribution of PT signal observed in Figs. 8(c) and 9(c) suggests a possibility that the distribution of such deep levels can be visualized by our PT-AFM method.

4. Conclusion

We performed photo-assisted Kelvin probe force microscopy (P-KFM) and photothermal atomic force microscopy (PT-AFM) on CIGS solar cells to investigate their photovoltaic properties and recombination processes of photo-carriers. By P-KFM, the spatial distribution and temporal decay of photovoltage were investigated, and the spatial separation effect of photo-carriers and contribution of fast process in the entire recombination processes of photo-carriers in the CIGS solar cells have been discussed. In PT-AFM, on the other hand, non-radiative recombination properties in the CIGS solar cells were examined, and the possibility that sub-gap states with discrete energy levels exist in the CIGS material has been pointed out.

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