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Progress Toward 1000mV Open-Circuit Voltage on Chalcopyrite Solar Cell

Homare Hiroi, Yasuaki Iwata, Hiroki Sugimoto and Akira Yamada

Abstract—Previously, open circuit voltage of 960mV was reported on Se-free Cu(In,Ga)S₂ solar cell with CdS buffer layer. In this paper, we report our latest progress toward 1000mV on Se-free Cu(In,Ga)S₂ solar cell with Cd-free buffer layer. Highest open circuit voltage of 973mV was demonstrated by rapid thermal annealing and Zn_{1-x}Mg_xO buffer layer application.

Index Terms—Cu(In,Ga)S₂, High open circuit voltage, Rapid thermal annealing, Zn_{1-x}Mg_xO buffer layer.

I. INTRODUCTION

Previously, we reported a new world-record efficiency (Eff) of 15.5% on Se-free Cu(In,Ga)S₂ (CIGS) solar cell via KCN-free process[1]. Regarding open circuit voltage (V_{oc}), 960mV has been achieved[2]. It was the highest V_{oc} in the field of chalcopyrite solar cells, however, it was still lower as compared with CdTe and perovskite solar cells[3,4]. Thus, we have been exploring the potential of over 1000mV on Se-free CIGS solar cells for further improvement of Eff. As a result, the highest V_{oc} of 973mV has been demonstrated by rapid thermal annealing (RTA) for sulfurization and Zn_{1-x}Mg_xO application for buffer layer, as shown in Fig. 1. In this paper, we report our latest progress toward 1000mV on Se-free CIGS solar cell.

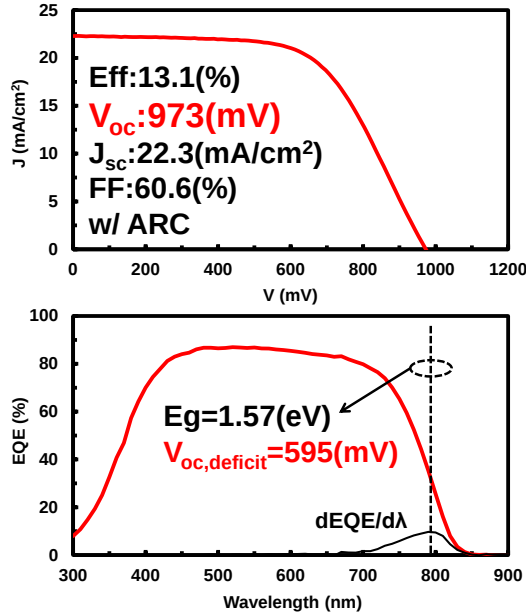


Fig. 1. J-V and EQE characteristics of 973mV Se-free CIGS solar cell fabricated by KCN-free process with Cd-free Zn_{1-x}Mg_xO buffer layer.

II. EXPERIMENTAL CONDITION

In this experiment, we prepared Se-free CIGS solar cells with an area of approximately 0.45 cm². Figure 2 shows a schematic image of our standard cell structure. First of all, Mo back-electrode layer, Cu, Ga and In metal-stack precursor layers were deposited by DC-sputtering onto glass substrate. The precursor layers were sulfurized only with H₂S gas via RTA in a furnace to form a p-type Se-free CIGS absorber layer. CdS or Zn_{1-x}Mg_xO buffer layers were deposited onto the absorber layers by chemical bath deposition (CBD) or atomic layer deposition (ALD). Then, intrinsic ZnO (i-ZnO) and In₂O₃:Sn layers were deposited by ALD and ion evaporation respectively. Finally, Ni/Al front-electrode and MgF₂ layers were deposited by electron-beam evaporation.

The current density-voltage (J-V) characteristics of our solar cells were measured at 25°C under standard air mass (AM) 1.5 spectrum condition with a constant-light solar simulator. The spectral content of the light is determined by the use of a xenon lamp (KXL-5000HFW) and five halogen lamps (JCD-100V-1000WC/Z) with an intensity of 100mW/cm² with optical lenses inside the solar simulator. The radiation power is calibrated regularly by means of a silicon reference solar cell. External quantum efficiency (EQE) characteristics of the pure-sulfide CIGS cells were investigated. The elemental composition and the depth profile of the absorber layers were measured by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and glow discharge optical emission spectrometry (GD-OES), respectively. In order to investigate the band-alignment between the buffer and the absorber layer, ultraviolet photoelectron spectroscopy (UPS) with He I light source (21.22 eV) was performed after the buffer layer deposition. For the depth-resolved UPS measurements, Ar⁺ (3kV) ion beam sputtering equipped in the UPS system was used. The reference level is the Fermi level, and the calibration was performed with Au as a standard sample.

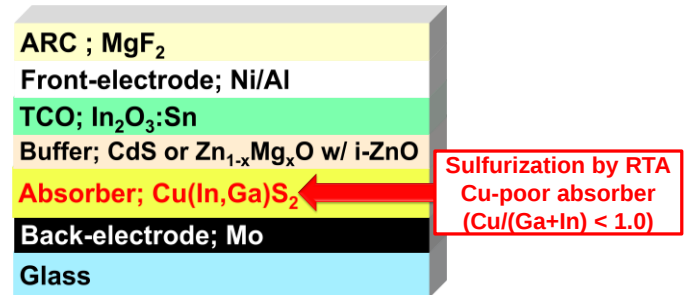


Fig. 2. Schematic image of our device structure.

III. RESULT AND DISCUSSIONS

A. Sulfurization via RTA

In this section, the benefits of sulfurization on Se-free CIGS by RTA are discussed. We used RTA for sulfurization to shorten the fabrication process. Figure 3 shows the dependence of ramp-up speed on the electrical parameters of Se-free CIGS solar cells with CdS buffer layers. It is clear that higher ramp-up speed contributed to the improvement of cell performance. It is assumed that the higher ramp-up speed has benefits of low Ga content on the surface of the absorber and superior Ga grading at the back. Figure 4 shows Ga depth profile of various ramp-up speeds (20, 40 and 140C/min) obtained from GD-OES analysis. Absorbers with various ramp-up speeds clearly show a different Ga depth profiles. The absorber fabricated with ramp-up speed of 20C/min shows a high Ga/(Ga+In) ratio of 15% at the surface compared with the others. In addition, its depth profile shows a more gradual gradient. The absorber fabricated by 40C/min shows a low Ga/(Ga+In) ratio at the surface. However, the Ga grading is less steeper than the absorber fabricated with 140C/min. In the absorber fabricated by 40C/min, both the Ga/(Ga+In) ratio at the surface and its inclination were improved. Eff of sample fabricated by 20C/min was low because of very poor electrical parameters. The poor electrical parameters are possibly caused by the high Ga/(Ga+In) ratio at the surface and the gradual Ga grading of absorber. For the sample processed with 40C/min, the cell performance improves to Eff of 14% from 7~9% due to the low Ga composition at the surface. Sample of 140C/min boosted the Eff due to the improvement of V_{oc} and J_{sc} , attributed by the increased Ga content toward the back surface (CIGS/Mo). Thus, the benefits of low Ga composition at the surface and high Ga grading at the back surface have been brought to light. Based on the depth-profile results of Ga in Se-free CIGS cells, as one of several possibilities, we believe that low Ga/(Ga+In) ratio on the surface contributes to reduced Ga_{Cu} defects and steep Ga grading can accelerate the electrons toward the space charge region. Hence, it may indicate that Ga grading can enhance J_{sc} and V_{oc} . Furthermore, the results also suggest that Ga contents on the surface and Ga grading of the absorbers are controllable by tuning the ramp-up speed. Regarding FF, it was also significantly improved by higher ramp-up speed, which suggests another benefits resulted from the ramp-up speed condition. We will try our best to find the mechanism of FF improvement in the near future.

Finally, the minority carrier lifetime was measured by time-resolved photoluminescence (PL) as a gauge to evaluate the absorber quality. The PL measurement was performed at room temperature, using a pulsed laser with a wavelength of 532nm and an excitation power of 4.67mW (excitation intensity of about 595mW/cm²). Figure 5 shows the PL lifetime of Se-free absorber fabricated by high ramp-up speed. Although with a high efficiency, its lifetime was merely 0.97ns. This short lifetime indicates that there is further room to improve the Se-free CIGS absorbers.

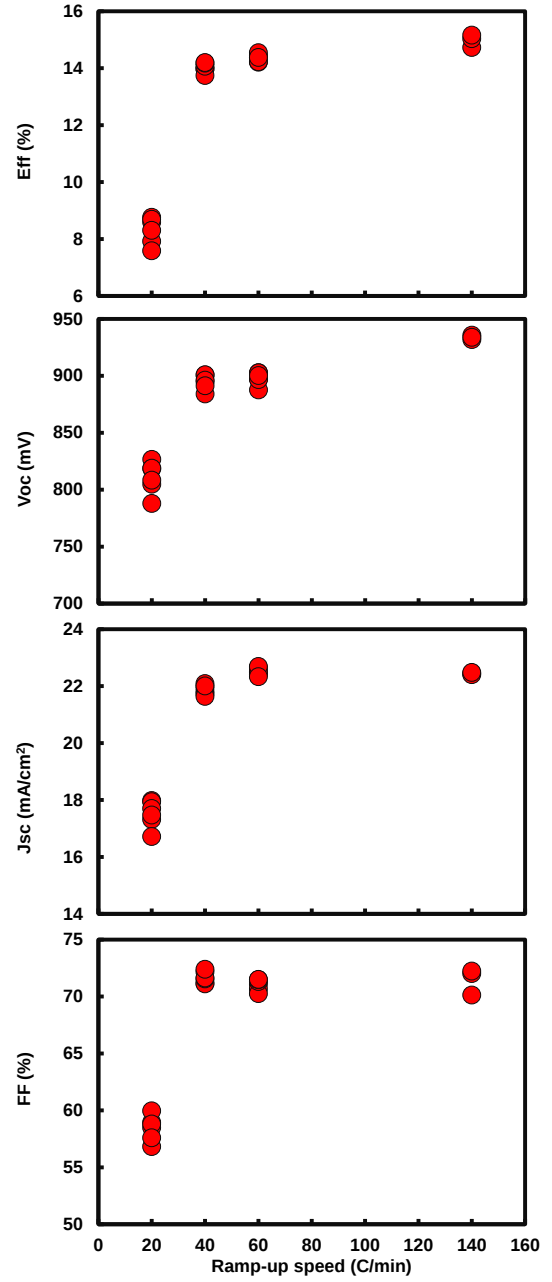


Fig. 3. Dependence of ramp-up speed on electrical parameters of Se-free CIGS solar cells with CdS buffer layers.

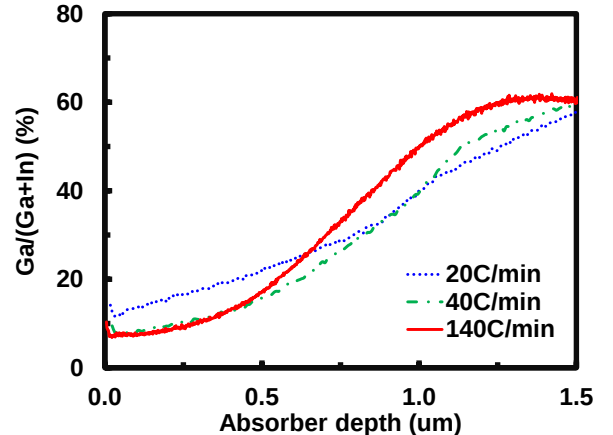


Fig. 4. GD-OES Ga/(Ga+In) ratio as a function of film depth of various ramp-up speed.

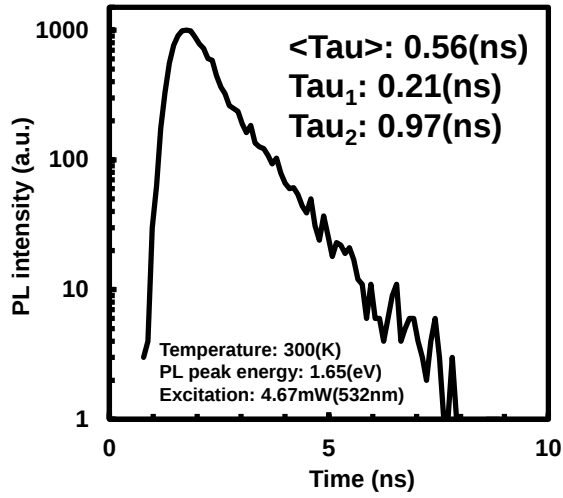


Fig. 5. PL lifetime of our Se-free CIGS absorber.

B. $Zn_{1-x}Mg_xO$ buffer layer

Figure 6 shows the dependence of Mg contents in $Zn_{1-x}Mg_xO$ buffer layer on the electrical parameters of Se-free CIGS solar cells using absorbers fabricated via the ramp-up speed of 140C/min. Higher Mg contents contribute to the improvement of cell performance. It is assumed that the conduction band-offset (CBO) between absorber and buffer layers was modulated because the E_g of $Zn_{1-x}Mg_xO$ buffer layer is known to be controllable by Zn to Mg ratio[4]. In this work, the CBO was calculated from the valence band-maximum (VBM) and the conduction band-minimum (CBM). The VBM of the $Zn_{1-x}Mg_xO$ buffer and Se-free CIGS absorber layers was measured by the UPS measurement. The CBM of the $Zn_{1-x}Mg_xO$ ($x=0.26$), $Zn_{1-x}Mg_xO$ ($x=0.15$) and Se-free CIGS was estimated by using E_g value of 3.7eV, 3.9eV and 1.55eV, respectively[5]. $Zn_{1-x}Mg_xO$ ($x=0.26$) cell shows that the CBM of buffer layer in the vicinity of the interface can be increased when compared with the $Zn_{1-x}Mg_xO$ ($x=0.15$) cell. This upward shift of CBM is potentially relevant to the V_{oc} improvement as shown in Fig. 7.

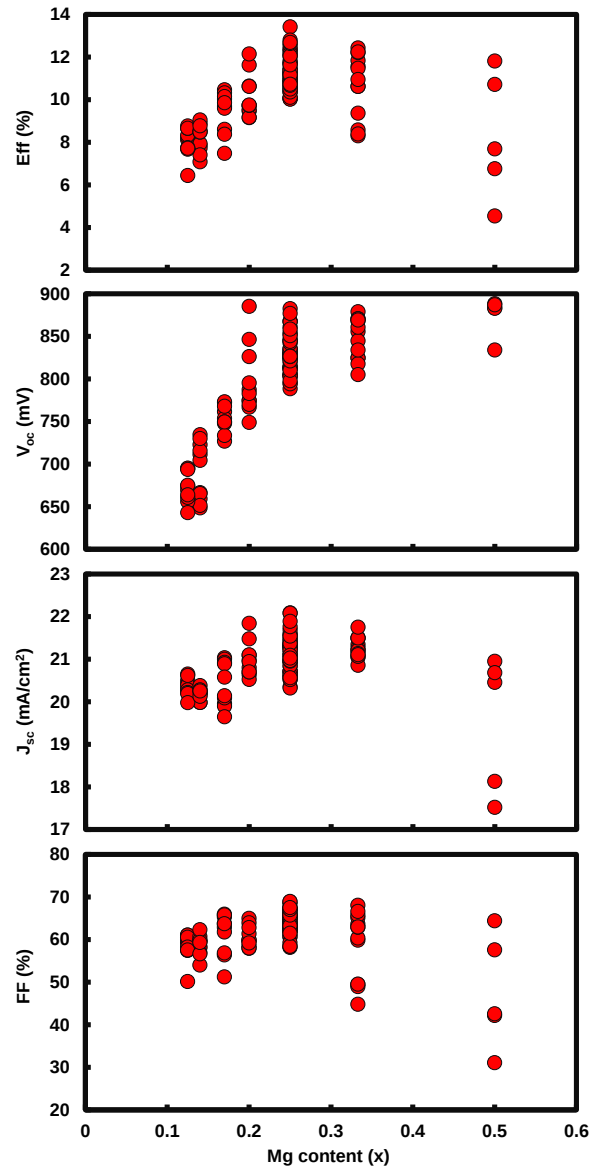


Fig. 6. Dependence of Mg contents in $Zn_{1-x}Mg_xO$ buffer layer on electrical parameters of Se-free CIGS solar cells. Higher Mg contents contributed improvement of cell performance.

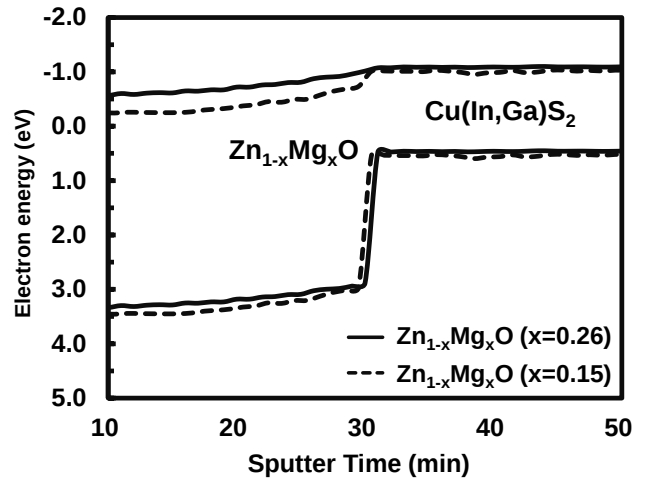


Fig. 7. Comparison of band-offset at buffer/absorber interface for Se-free CIGS cells with $Zn_{1-x}Mg_xO$ ($x=0.26$) and ($x=0.15$) buffer layers.

C. V_{oc} deficit

Figure 8 summarizes a comparison between V_{oc} and E_g of our Se-free CIGS cells fabricated via various ramp-up speed with CdS and $Zn_{1-x}Mg_xO$ buffer layers. Each triangle marker with black, blue, green, orange and red circle shows 20, 40, 60, 140C/min of ramp-up speed with CdS buffer layer and 140C/min of ramp-up speed with $Zn_{1-x}Mg_xO$ buffer layer, respectively. Higher V_{oc} was achieved by higher ramp-up speed during sulfurization, with drastically improved V_{oc} deficit ($E_g/q - V_{oc} = \Delta V$). In addition, the V_{oc} improvement was confirmed by applying the $Zn_{1-x}Mg_xO$ buffer layer. This result suggests that both the absorber quality and the interface between the buffer and the absorber layers are among the key factors to enhance V_{oc} , and it is very effective to apply $Zn_{1-x}Mg_xO$ buffer layer into the Se-free CIGS cells for V_{oc} improvement. Finally, the lowest V_{oc} deficit of 595mV was achieved with absorber's E_g of 1.57eV. It has much better V_{oc} deficit compared with the other Se-free chalcogenide solar cell such a Cu_2ZnSnS_4 cell[6].

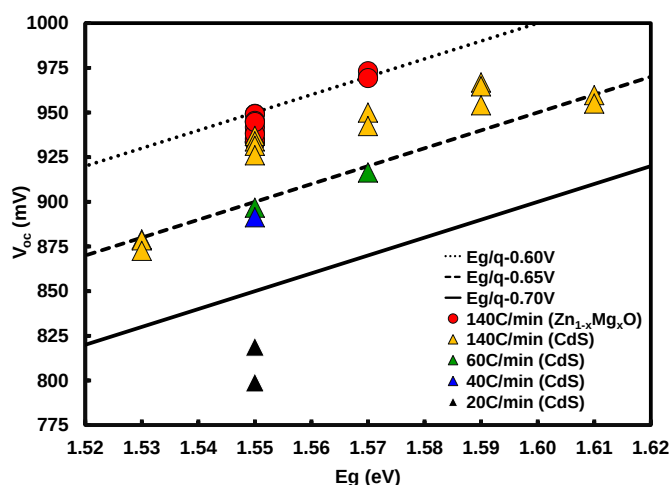


Fig. 8. Correlation between V_{oc} and E_g on our Se-free CIGS cells fabricated via four kinds of ramp-up speed (20, 40, 60, 140C/min) with CdS and with $Zn_{1-x}Mg_xO$ buffer layers.

IV. CONCLUSION

The V_{oc} of 973mV was achieved on chalcopyrite solar cell thanks to the Se-free CIGS fabrication via RTA and the application of Cd-free $Zn_{1-x}Mg_xO$ buffer layer. The higher ramp-up speed was effective to reduce Ga/(Ga+In) ratio of the absorber's surface and to produce steeper Ga grading at the back. In addition, V_{oc} was boosted by optimizing Mg content of $Zn_{1-x}Mg_xO$ buffer layer. We believe that further research based on these results will boost the V_{oc} of chalcopyrite solar cells toward 1000mV, and we are now intensively developing the Se-free CIGS solar cells.

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REFERENCES

- [1] H. Hiroi, Y. Iwata, S. Adachi, H. Sugimoto, and A. Yamada, "New World-Record Efficiency for Pure-Sulfide $Cu(In,Ga)S_2$ Thin-Film Solar Cell With Cd-free Buffer Layer via KCN-Free Process", *IEEE J. Photovoltaics*, vol.6, no. 3, pp. 760-763, May 2016, DOI: 10.1109/JPHOTOV.2016.2537540.
- [2] H. Hiroi, Y. Iwata, K. Horiguchi, and H. Sugimoto, "960-mV Open-Circuit Voltage Chalcopyrite Solar Cell", *IEEE J. Photovoltaics*, vol.6, no. 1, pp. 309-312, Jan. 2016, DOI: 10.1109/JPHOTOV.2015.2479470.
- [3] W.K. Metzger, J.M. Burst, D.S. Albin, E. Colegrove, J. Moseley, J. Duenow, A. Kanevce, S.B. Farrell, H. Moutinho, M.O. Reese, S. Johnston, T. Barnes, C. Perkins, H. Guthrey, S.H. Wei, and M. Al-Jassim, "Resetting the Defect Chemistry in CdTe", presented at 42nd IEEE Photovoltaic Specialists Conference, New Orleans, Louisiana, USA, June 14-19, 2015.
- [4] Noh JH, Im SH, Heo JH, Mandal TH, and Seok SI. "Chemical Management for Colorful, Efficient, and Stable Inorganic–Organic Hybrid Nanostructured Solar Cells", *Nano Letters*. 2013; 13; 1764–1769.
- [5] T. Minemoto, T. Negami, S. Nishiwaki, H. Takakura, and Y. Hamakawa, "Preparation of $Zn_{1-x}Mg_xO$ Films by RF Magnetron Sputtering", *Thin Solid Films* 372 (2000) 173-176.
- [6] O. Gunawan, T. Gokmen, B. S. Shin, and S. Guha, "Device characteristics of high performance Cu_2ZnSnS_4 solar cell", presented at 38th IEEE Photovoltaic Specialists Conference, Austin, Texas, USA, June 3-8, 2012.



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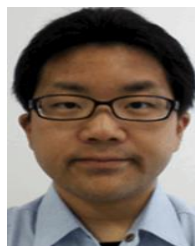
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