

# Application of sputtered $\text{ZnO}_{1-x}\text{S}_x$ buffer layer for $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ solar cells

Akira Okamoto<sup>1</sup>, Takashi Minemoto<sup>2</sup> and Hideyuki Takakura<sup>1</sup>

<sup>1</sup>Ritsumeikan University, College of Science and Engineering  
1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan

Phone: +81-77-561-3065, E-mail: ro001067@ed.ritsumei.ac.jp

<sup>2</sup>Ritsumeikan University, Ritsumeikan Global Innovation Research Organization

## 1. Introduction

$\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$  (CIGS) solar cells are a representative of the high efficiency thin film solar cells. Currently, a CdS thin film is utilized as a buffer layer in high efficiency CIGS solar cells [1-3]. The CdS film is prepared by chemical bath deposition (CBD). However, in the view of the environmental impact of cadmium, there is a need to find an alternative to CdS films. Although many interests and efforts are concentrated on the developments of CIGS solar cells using Cd-free buffer layers, it has not been reported that the performances of solar cells with Cd-free buffer layers exceed those with CdS. We have proposed (Zn,Mg)O buffer layers as Cd-free buffer layers [4]. The (Zn,Mg)O films are prepared by co-sputtering of ZnO and MgO. The band gap energy ( $E_g$ ) of (Zn,Mg)O films can be controlled by changing the Mg content. But the CIGS solar cells using the (Zn,Mg)O buffer layers have not achieved a higher conversion efficiency than those using CdS. This would be due to the sputtering damage on the CIGS surface. On the other hand,  $\text{ZnO}_{1-x}\text{S}_x$  films are considered as alternative buffer layers [5-7]. The band gap of  $\text{ZnO}_{1-x}\text{S}_x$  can be controlled by changing the S content. Also, the S in the  $\text{ZnO}_{1-x}\text{S}_x$  films may passivate the defects on the CIGS surface. In this study, we have applied the  $\text{ZnO}_{1-x}\text{S}_x$  by co-sputtering of ZnO and ZnS, which should have high controllability of the compositional ratios of O and S. The  $E_g$  of the  $\text{ZnO}_{1-x}\text{S}_x$  films was compared with that of the CdS thin films, and the performance of CIGS solar cells with the  $\text{ZnO}_{1-x}\text{S}_x$  and CdS buffer layers are discussed.

## 2. Experimental

The  $\text{ZnO}_{1-x}\text{S}_x$  thin films were prepared by a radio frequency (RF) magnetron sputtering from ZnO and ZnS targets. The S content in the thin film was controlled by varying the sputtering power applied to each target to control the sputtering rates. The CdS thin film was prepared by CBD. Fig. 1 shows the band alignments of (a) CIGS and  $\text{ZnO}_{1-x}\text{S}_x$  and (b) CIGS and CdS layers. The  $E_g$  of  $\text{ZnO}_{1-x}\text{S}_x$  can be controlled from 2.8 eV to 3.7 eV. The  $E_g$  of the  $\text{ZnO}_{1-x}\text{S}_x$  and CdS thin films were derived from a plot of  $(\alpha h\nu)^2$  as a function of photon energy ( $h\nu$ ). The  $\text{ZnO}_{1-x}\text{S}_x$  thin film with the S content ( $x$ ) of 0.18 was used. Fig. 2 shows the structures of CIGS solar cells with (a)  $\text{ZnO}_{1-x}\text{S}_x$  and (b) CBD-CdS buffer layers. The CIGS solar cells consisting of Al/NiCr/ITO/ $\text{ZnO}_{1-x}\text{S}_x$ /CIGS/Mo/soda-lime glass (SLG) and Al/NiCr/ITO/ZnO/CdS/CIGS/Mo/SLG structures were fabricated [1]. The CIGS layer by three stage process [8] had the Cu/(In+Ga) ratio of 0.91 and the

Ga/(Ga+In) ratio of 0.29. The  $E_g$  of the CIGS layer was about 1.1 eV. The current-voltage ( $J$ - $V$ ) characteristics of the CIGS solar cells were measured under 100 mW/cm<sup>2</sup>, AM 1.5G illumination at 25°C. The external quantum efficiency (EQE) of the CIGS solar cells was also measured.

## 3. Results and discussions

Fig. 3 shows the  $(\alpha h\nu)^2$  plots of the  $\text{ZnO}_{1-x}\text{S}_x$  and CdS thin films as a function of photon energy ( $h\nu$ ) to measure the  $E_g$ . The absorption coefficient ( $\alpha$ ) was obtained from the transmittance. The  $E_g$  of the  $\text{ZnO}_{1-x}\text{S}_x$  and CdS thin films were 2.9 eV and 2.6eV, respectively. The  $\text{ZnO}_{1-x}\text{S}_x$  film had a wider band gap than CdS. Fig. 4 shows  $J$ - $V$  curves of the CIGS solar cells with (a)  $\text{ZnO}_{1-x}\text{S}_x$ /CIGS and (b) ZnO/CdS/CIGS structures. The CIGS solar cell with the  $\text{ZnO}_{1-x}\text{S}_x$  buffer layer had a higher short-circuit current density ( $J_{sc}$ ), and a lower open-circuit voltage ( $V_{oc}$ ) and a fill factor ( $FF$ ). Thus, the efficiency of 11.1% approaching to that of the CdS/CIGS solar cell was obtained. Fig. 5 shows the EQE of the CIGS solar cells with the  $\text{ZnO}_{1-x}\text{S}_x$  and CdS buffer layers. This result indicates that the CIGS solar cell with the  $\text{ZnO}_{1-x}\text{S}_x$  buffer layer showed significantly enhanced EQE in the spectral region between 300 and 500 nm than that with the CdS buffer layers. The CIGS solar cells with the  $\text{ZnO}_{1-x}\text{S}_x$  buffer layers can decrease the absorption loss than the cells with the CdS buffer layer.

## 4. Conclusions

The  $\text{ZnO}_{1-x}\text{S}_x$  thin films were prepared by co-sputtering of ZnO and ZnS targets. The  $E_g$  of the  $\text{ZnO}_{1-x}\text{S}_x$  and CdS thin films were 2.9 eV and 2.6eV, respectively. The  $\text{ZnO}_{1-x}\text{S}_x$  film had a wider band gap than CdS. The CIGS solar cells with the  $\text{ZnO}_{1-x}\text{S}_x$  buffer layer showed the efficiency approaching to that of the cell with the CdS buffer layer. The CIGS solar cell with the  $\text{ZnO}_{1-x}\text{S}_x$  buffer layer had a higher  $J_{sc}$  than that with the CdS buffer layer. The CIGS solar cells with the  $\text{ZnO}_{1-x}\text{S}_x$  buffer layers can decrease the absorption loss than the cells with the CdS buffer layer. The  $\text{ZnO}_{1-x}\text{S}_x$  has a wider band gap than CdS and can be expected to provide a useful buffer layer of solar cells that improves the overall efficiency by decreasing the absorption loss.

## Acknowledgements

The authors would like to thank Kobelco Research Institute for the chemical composition ratios analysis of  $\text{ZnO}_{1-x}\text{S}_x$ . The authors would like to thank Dr. T. Negami of Panasonic Electric Works Co. Ltd. for useful discussion.

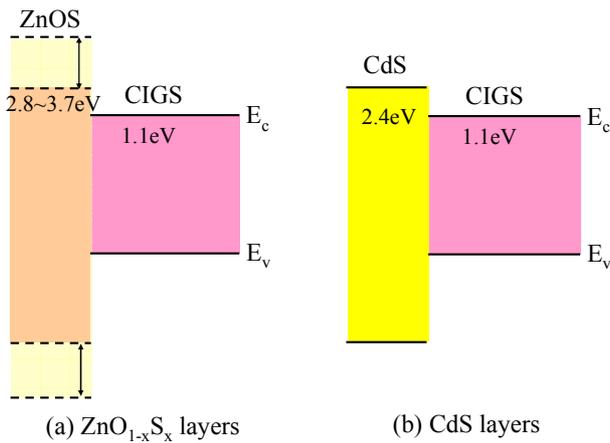


Fig. 1 Schematics band diagrams of  $\text{ZnO}_{1-x}\text{S}_x/\text{CIGS}$  and  $\text{CdS}/\text{CIGS}$  layers.

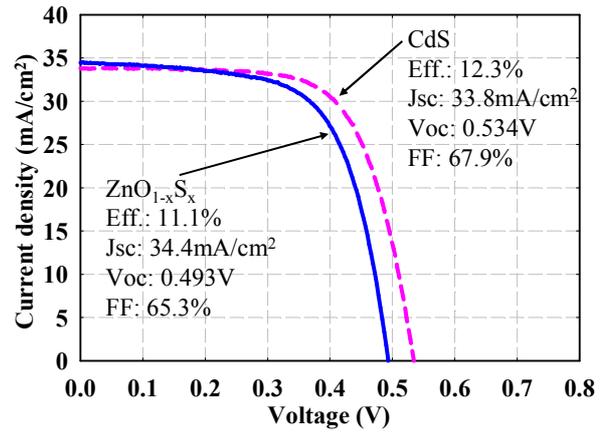


Fig. 4  $J$ - $V$  curves of CIGS solar cell with  $\text{ZnO}_{1-x}\text{S}_x$  and  $\text{CdS}$  buffer layers.

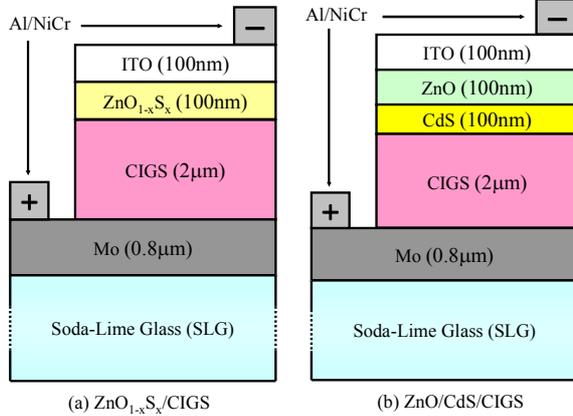


Fig. 2 Schematic structure of CIGS solar cells.

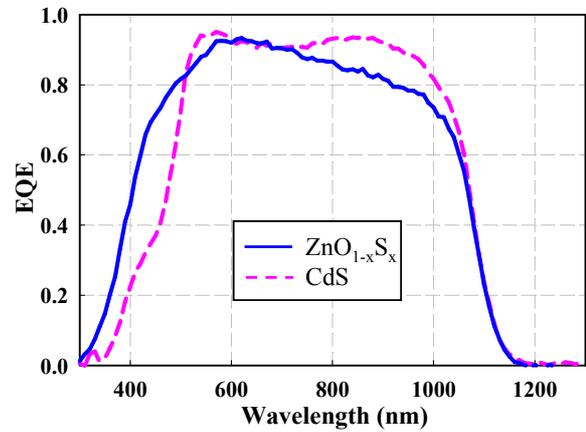


Fig. 5 EQE of CIGS solar cell with the  $\text{ZnO}_{1-x}\text{S}_x$  and  $\text{CdS}$  buffer layers.

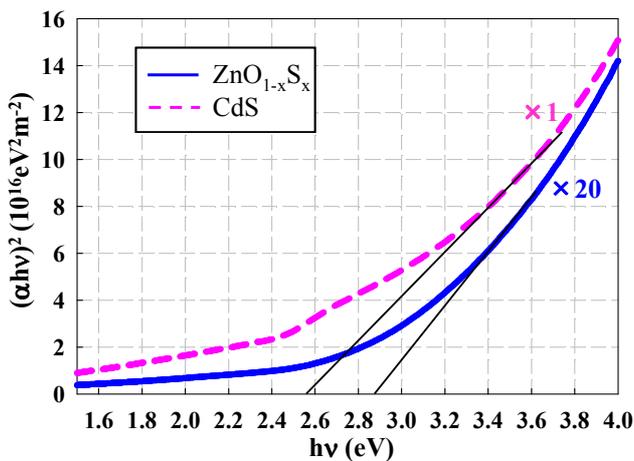


Fig. 3  $(\alpha h\nu)^2$  of  $\text{ZnO}_{1-x}\text{S}_x$  films ( $x=0.18$ ) and  $\text{CdS}$  as a function of photon energy( $h\nu$ ).

## References

- [1] M.A. Contreras, B. Egaas B, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Haddon and R. Noufi, *Prog. Photovolt. Res. Appl.* **7** (1999) 311.
- [2] F. Engelhardt, L. Bornemann, M. KoÈ ntges, Th. Meyer, J. Parisi, E. Pschorr-Schoberer, B. Hahn, W. Gebhardt, W. Riedl and U. Rau, *Prog. Photovolt. Res. Appl.* **7** (1999) 423.
- [3] D. Hariskos, B. Fuchs, R. Menner, N. Naghavi, C. Hubert, D. Lincot and M. Powalla, *Prog. Photovolt. Res. Appl.* **17** (2009) 479.
- [4] T. Minemoto, Y. Hashimoto, T. Satoh, T. Negami, H. Takakura and Y. Hamakawa, *J. Appl. Phys.* **89**, (2001) 8327.
- [5] C. Platzer-Björkman, T. Törndahl, D. Abou-Ras, J. Malmström, J. Kessler and L. Stolt, *J. Appl. Phys.* **100** (2006) 044506.
- [6] B. K. Meyer, A. Polity, B. Farangis, Y. He, D. Hasselkamp, T. Krämer, C. Wang, U. Haboeck, and A. Hoffmann, *phys. stat. sol. (c)* **1** (2004) 694.
- [7] Y.-Z. Yoo, Z.-W. Jin, T. Chikyow, T. Fukumura, M. Kawasaki and H. Koinuma, *Appl. Phys. Lett.* **81** (2002) 3798.
- [8] T. Negami, T. Satoh, Y. Hashimoto, S. Nishiwaki, S. Shimakawa and S. Hayashi, *Sol. Energy Mater. Sol. Cells* **67** (2001) 1.