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

Akira Okamoto$^1$, Takashi Minemoto$^2$ and Hideyuki Takakura$^1$

$^1$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
$^2$Ritsumeikan University, Ritsumeikan Global Innovation Research Organization

1. Introduction
Cu(In,Ga)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, ZnO$_{1-x}$S$_x$ films are considered as alternative buffer layers [5-7]. The band gap of ZnO$_{1-x}$S$_x$ films can be controlled by changing the S content. Also, the S in the ZnO$_{1-x}$S$_x$ films may passivate the defects on the CIGS surface. In this study, we have applied the ZnO$_{1-x}$S$_x$ buffer layer 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 ZnO$_{1-x}$S$_x$ films was compared with that of the CDS thin films, and the performance of CIGS solar cells with the ZnO$_{1-x}$S$_x$ and CdS buffer layers are discussed.

2. Experimental
The ZnO$_{1-x}$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 ZnO$_{1-x}$S$_x$ and (b) CIGS and CdS layers. The $E_g$ of ZnO$_{1-x}$S$_x$ can be controlled from 2.8 eV to 3.7 eV. The $E_g$ of the ZnO$_{1-x}$S$_x$ and CdS thin films were derived from a plot of ($ahv$)$^2$ as a function of photon energy ($h\nu$). The ZnO$_{1-x}$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) ZnO$_{1-x}$S$_x$ and (b) CdS/CdS buffer layers. The CIGS solar cells consisting of Al/NiCr/ITO/ZnO$_{1-x}$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$^2$, 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 ($ahv$)$^2$ plots of the ZnO$_{1-x}$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 ZnO$_{1-x}$S$_x$ and CdS thin films were 2.9 eV and 2.6 eV, respectively. The ZnO$_{1-x}$S$_x$ film had a wider band gap than CdS. Fig. 4 shows $J$-V curves of the CIGS solar cells with (a) ZnO$_{1-x}$S$_x$/CIGS and (b) ZnO/CdS/CIGS structures. The CIGS solar cell with the ZnO$_{1-x}$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 ZnO$_{1-x}$S$_x$ and CdS buffer layers. This result indicates that the CIGS solar cell with the ZnO$_{1-x}$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 ZnO$_{1-x}$S$_x$ buffer layers can decrease the absorption loss than the cells with the CdS buffer layer.

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

Fig. 2 Schematic structure of CIGS solar cells.

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

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

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

References