The investigation of Ge incorporation effects in Cu$_2$ZnSnSe$_4$ thin-film solar cells (2)

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Kesterite thin-film solar cell, Cu$_2$ZnSn(S$_x$Se$_{1-x}$)$_4$ (CZTSSe), have been attracting attention because its absorption layer comprise earth-abundant elements, and is therefore expected to substantially decrease the costs of solar cells. The CZTSSe absorption layer exhibits a direct band-gap ($E_g$) in the range of ~1.0–~1.5 eV; this gap is controlled by the S/(Se+S) ratio. However, the ability to control the $E_g$ on the basis of the S/(Se+S) ratio is limited because of the high volatility of the anionic components and consequent difficulty in controlling the film composition. In the previous study, we presented Ge incorporated CZTSe (CZTGSe) thin films and its device properties. The $E_g$ of CZTGSe thin films were increased with increasing amount of incorporated Ge. Also, increased band gap led to the improvement of open circuit voltage ($V_{OC}$) and efficiency of CZTGSe thin film solar cells. We exhibited the 7.13% CZTGSe thin-film solar cell with Ge/(Sn+Ge) ratio of 0.29.

In this study, we provide a further detailed and improved experimental results for Ge incorporation effects in CZTSe thin film and its device. The CZTGSe thin films were prepared using a two-step process comprising co-evaporation of each element and a subsequent annealing step at various temperature in the range of 450–530 °C. Ge atoms were successfully incorporated into the Cu$_2$ZnSnSe$_4$ thin films, and the $E_g$ of CZTGSe was controlled via the full Ge/(Sn+Ge) ratio range of 0–1. In addition, the annealing environment containing GeSe$_2$ led to CZTGSe thin films with flat surfaces, dense morphologies, and large grains comparable to their thickness. The highest efficiency achieved with the fabricated CZTGSe solar cells was 10.03%, with an $V_{OC}$ of 0.54 V (Fig. 1(a)). The $E_g$ of absorption layer was controlled to 1.19 eV (Fig. 1(b)) and its device exhibited an improved $V_{OC}$ deficit ($E_g/q - V_{OC}$, $q$: electron charge) of 0.647 V, which is comparable to that of high-efficiency Cu$_2$ZnSn(S$_x$S$_{1-x}$)$_4$ solar cells.

Figure 1. (a) I–V measurement results for the CZTGSe thin-film solar cell and (b) its EQE results. Plot of [E ln(1 − EQE)]$^2$ vs. E used to determine the band-gap is inset into the EQE figure.