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The investigation of Ge substitution effects in $Cu_2ZnSnSe_4$ Thin film solar cells

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The kesterite solar cells such as $Cu_2ZnSnSe_4$ and $Cu_2ZnSn(S_xSe_{1-x})_4$ have been attracting much attention because each materials are composed by earth abundant elements so they are expected to decrease the solar cell cost efficiently. Although their recent successful results, the kesterite solar cells are still suffering the low efficiency compared to $CuIn_{1-x}Ga_xSe_2$ solar cells [1]. One possible way to improve efficiency is the band gap engineering of the absorption layer using substitution of effective doping elements [2, 3].

In this study, we prepared Ge substituted $Cu_2ZnSnSe_4$ (CZTGSe) thin film solar cell using a two-step process. The CZTGSe precursors were prepared by the co-evaporating each elements and followed by annealed at various temperature and atmosphere conditions either [$GeSe_2$ + Se] or [$GeSe_2$ + $SnSe_2$ +Se]. The samples were characterized by electron probe micro analyzer (EPMA), X-ray diffraction (XRD), I-V measurement and external quantum efficiency (EQE) measurement. EPMA analysis showed composition of the CZTGSe precursors were not stoichiometry. After annealing, composition of the CZTGSe shifted to near stoichiometry at the annealing temperature over 500℃ and the Ge substitution rate (Ge/Ge+Sn) was approximately 10.0 ~ 40.0 %. The best power conversion efficiency (PCE) of the CZTGSe solar cell (active area = 0.515 cm^2) was obtained 7.13 % with the Ge substitution rate of 29 %. However, the PCE and V_{oc} of the CZTGSe solar cell was deteriorated with decreasing the Ge content, while the short circuit current was almost same (Fig. 1). In addition, EQE revealed that the band gap of each solar cell absorption layer decreased with the reduction of Ge substitution rate (Fig. 2). It is seemed that the increase of band gap by the Ge substitution improved V_{oc} with an increase of PCE. Therefore, the Ge substitution rate played the most important role in the band gap engineering of absorption layer as well as improvement in the solar cell properties [2, 3]. This study will present the comprehensive evaluation of Ge substitution effect in CZTSe films and its solar cell properties.

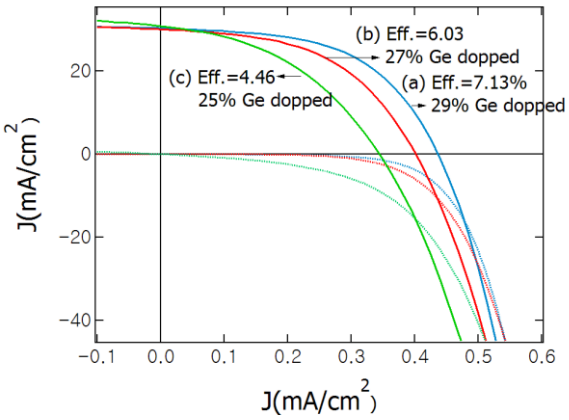

Fig. 1. J−V characteristics of the CZTGSe solar cells with different Ge contents.

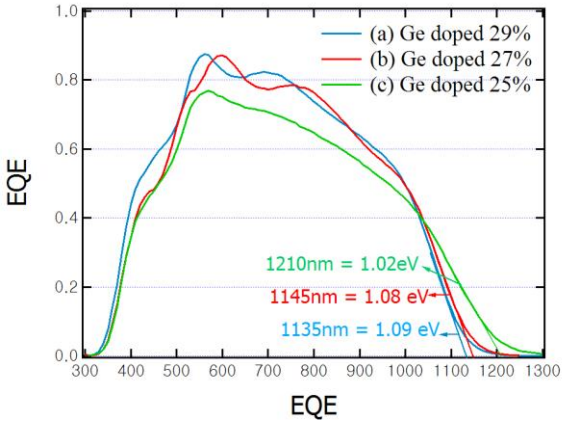

Fig. 2. EQE of the CZTGSe solar cell with the different Ge substitution rate.

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