Area: Thin-Film Compound Semiconductor PV

OPTICAL PROPERTIES OF $Cu_2ZnGeSe_4$ WITH VERY LOW URBACH ENERGY: COMPARISON WITH Cu-Se-BASED MATERIALS

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When a $Cu_2ZnSnSe_4$ (CZTSe) semiconductor is alloyed with $Cu_2ZnGeSe_4$ (CZGSe) with a Ge composition of ~20 at.%, the conversion efficiency has been reported to show a relatively high value of 12.3% due to the increase in the band gup (E_g) [1]. In this study, the optical properties of co-evaporated CZGSe polycrystalline layers have been determined accurately from spectroscopic ellipsometry (SE). As a result, we find superior optical properties of CZGSe kesterite with a very low Urbach energy (E_U) of ~25 meV.

The CZGSe layers were prepared on crystalline Si substrates by a co-evaporation process at a low temperature of ~200 °C. These samples were further annealed at temperatures of 500-550 °C in [$GeSe_2$+Se] atmosphere [1]. From EPMA, we have confirmed the stoichiometric composition of the CZGSe (Cu:Zn:Ge:Se = 2.00:1.11:0.96:3.93). The Raman measurement confirmed the kesterite crystal structure. To eliminate SE analysis errors induced by rough surface, quite thin CZGSe layers (<50 nm) have been characterized using a global error minimization scheme [2]. Figure 1 shows the absorption coefficient (α) of CZGSe, together with the results for Cu_2SnSe_3 (CTSe) [3], CZTSe [3], Cu_2ZnSnS_4 (CZTS) [4], $CuInSe_2$ (CISe) [5], $CuGaSe_2$ [5] reported previously. The solid lines show the result of E_U analysis. It can be seen that CZGSe shows high α comparable to the other materials. The E_g of the CZGSe layer is determined to be 1.39±0.01 eV from the critical point analysis. Figure 2 shows E_U as a function of E_g. We find that the CZGSe shows a very low E_U of 25 meV, which is similar to those of CISe and CGSe. In contrast, the CTSe, CZTSe, CZTS materials that contain Sn atoms indicated by the yellow region in Figure 2 exhibits quite high E_U values. The above results show that the CZGSe has ideal optical properties for solar cells with E_g of ~1.4 eV and a sharp absorption edge with low E_U.

[1] Kim et al. Appl. Phys. Express **9**, 102301 (2016), [2] Fujiwara et al. Rhys. Rev. **61**, 10832 (2000), [3] Hirate et al. J. Appl. Phys. **117**, 015702 (2015), [4] Li et al. Opt. Express **20**, A327 (2012), [5] Minoura et al. J. Appl. Phys. **117**, 195703 (2015).

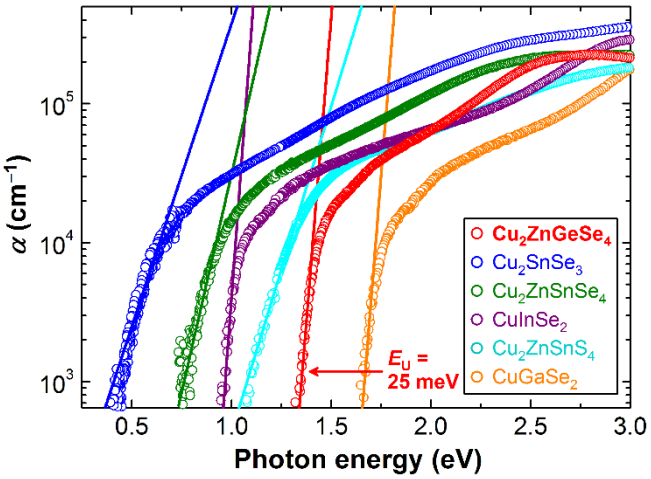

Figure 1: α spectra of $Cu_2ZnGeSe_4$, Cu_2SnSe_3 [3], $Cu_2ZnSnSe_4$ [3], Cu_2ZnSnS_4 [4], $CuInSe_2$ [5] and $CuGaSe_2$ [5] (open circles). The solid lines indicate the result of the Urbach energy analysis.

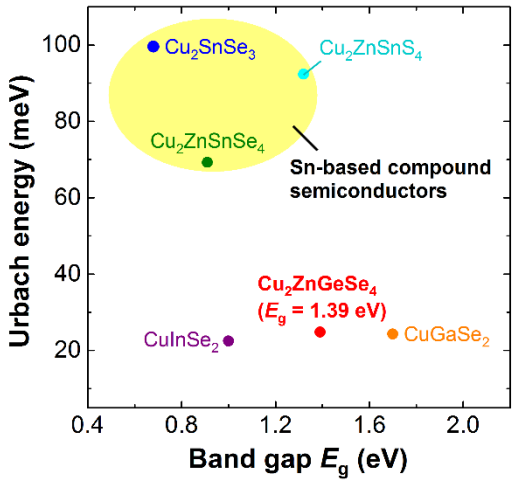

Figure 2: Urbach energy of the Cu-Se compounds, plotted as a function of the band gap.