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A PL and PLE study of high Cu content $\text{Cu}_2\text{ZnSnSe}_4$ films on Mo/glass and solar cells *

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$\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) is amongst leading candidates for the absorber layer in sustainable solar cells. We examine CZTSe thin films with $[\text{Cu}]/[\text{Zn} + \text{Sn}]$ of 0.99 and $[\text{Zn}]/[\text{Sn}]$ of 1.07, deposited on Mo/glass substrates, and solar cells fabricated from these films. The bandgap (E_g) of the as deposited films and solar cells was examined by photoluminescence excitation (PLE) whereas the temperature and excitation intensity dependence of photoluminescence (PL) spectra was used to examine the nature of radiative recombination. The 6 K PL spectra of CZTSe/Mo exhibit an intense broad and asymmetrical band P1 at 0.822 eV and a lower intensity band P2 at 0.93 eV. The shape of this band, high rates of blue shift with excitation intensity rise (j -shift) $j(\text{P1}) = 14$ meV and $j(\text{P2}) = 8$ meV per decade, and red shifts of both bands with increasing temperature suggest that both bands are associated with valence band tails due to potential fluctuations caused by high populations of charged defects. The mean depth of such fluctuation γ of 24 meV was estimated from the low energy side of P1. Device processing increased E_g , blue shifted P1, decreased its width, j -shift and the mean depth of potential fluctuations. These can be due to the annealing and/or can partly be related to KCN etching and the chemical effect of Cd, from CdS replacing copper at the CdS–CZTSe interface layer. Processing induced a new broad band P3 at 1.3 eV (quenching with $E_a = 200$ meV). We attributed P3 to defects in the CdS layer.

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