Study of time-resolved photoluminescence (TR-PL) in Cu$_2$ZnSn(S,Se)$_4$ thin films with different Cu/Sn ratio.

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Introduction: The earth abundant and non-toxic kesterite Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) alloys are promising as absorber materials for a high efficiency thin film solar cell. The maximum reported conversion efficiency for CZTSSe solar cells is 12.6%, but this is much lower than the theoretical limited value. The main concern is that, the open circuit voltage ($V_{oc}$) is much lower than that expected. One of the possible reasons is the recombination of photo generated carriers. Time-resolved photoluminescence (TR-PL) is useful for the estimation of minority carrier lifetime from the decay time of band-to-band recombination. In this study we have shown the variation of lifetime measured by TR-PL with different Cu/Sn ratio for bare CZTSSe, CdS/CZTSSe and ZnO/CdS/CZTSSe samples. In addition, in order to study surface recombination, penetration depth dependence TR-PL was performed on bare CZTSSe thin films by using two different excitation wavelengths (420 nm and 750 nm).

Results and Discussion: A mode-locked titanium:sapphire laser of wavelength 750 nm and 420 nm with a pulse width and repetition rate of ~80 fs and 10 MHz, respectively, was used for excitation in the TR-PL measurements. Fig. 1 shows PL decay curves for a set of CdS covered CZTSSe thin films. All PL decay curves have been measured at the peak energy of the corresponding PL band. A double exponential function, $I(t) = C_1 \exp(-t/\tau_1) + C_2 \exp(-t/\tau_2)$, where $t$ is the time after a laser pulse excitation, $I(t)$ is the luminescence intensity at time $t$, $C_1$ and $C_2$ are PL intensities of the corresponding PL components, and $\tau_1$ and $\tau_2$ are the fast and slow decay lifetimes, respectively, could be fitted to the experimental curve, and we derive the longer lifetime of $\tau_2$. The highest lifetime of 18 ns is found at the Cu/Sn of 1.75 and correspondingly we have found the best efficiency 8.7% from the current-voltage (I-V) measurement. For all structure of CZTSSe, it is observed that longer minority carrier lifetime is associated with lower Cu/Sn compositions; this can be attributed to the decrease of non-radiative native defects at the Cu poor condition. Lifetime for bare samples is low maybe due to surface degradation and surface states. Surface recombination plays an important role in the bare sample. Fig. 2 shows the TR-PL decays at the excitation wavelength of 420 and 750 nm. Unlike low-energy (750 nm) excitation, the PL intensity falls rapidly with time for high-energy excitation (420 nm). All uncovered samples show the same tendency. For 420 nm excitation, most of the carrier injection occurs very near the surface. PL intensity abruptly falls because of non-radiative carrier recombination via surface states rather than radiative recombination. For 750 nm excitation, only a small amount of photons are absorbed near the surface and relatively high absorption occurs deep inside the material and consequently produce higher carrier lifetime with slow PL decay.

![Fig. 1 TR-PL decay curves for CdS covered CZTSSe for three different Cu/Sn ratios under the excitation wavelength of 750 nm.](image1)

![Fig. 2 TR-PL decay curves for bare CZTSSe sample with Cu/Sn ratio of 1.75 at two different excitation wavelength of 420 nm and 750 nm.](image2)