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Identification of Defect Levels in Copper Indium Diselenide ($CuInSe_2$) Thin Films via Photoluminescence Studies

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Photoluminescence (PL) spectroscopy has been used to study the defect levels in thin film copper indium diselenide ($CuInSe_2$, CIS) which we are developing as the absorber layer for the bottom cell of a monolithically grown perovskite/$CuInSe_2$ tandem solar cell. Temperature and laser power dependent PL measurements of thin film CIS for two different Cu/In ratios (0.66 and 0.80) have been performed. The CIS film with Cu/In = 0.80 shows a prominent donor-to-acceptor peak (DAP) involving a shallow acceptor of binding energy ~22 meV, with phonon replica at ~32 meV spacing. In contrast, PL measurement of CIS film for Cu/In = 0.66 taken at 20 K exhibited an asymmetric and broad PL spectrum with peaks at 0.845 eV and 0.787 eV. Laser intensity dependent PL revealed that the observed peaks 0.845 eV and 0.787 eV shift towards higher energy (aka j-shift) at ~11.7 meV/decade and ~ 8 meV/decade with increase in laser intensity respectively. The asymmetric and broad spectrum together with large j-shift suggests that the observed peaks at 0.845 eV and 0.787 eV were related to band-to-tail (BT) and band-to-impurity (BI) transition, respectively. Such a band-tail-related transition originates from the potential fluctuation of defect states at low temperature. The appearance of band related transition in CIS film with Cu/In = 0.66 is the indicator of the presence of large number of charged defect states.

INTRODUCTION:

Chalcopyrite-structured copper indium diselenide ($CuInSe_2$, CIS) thin films have been widely used as absorber layers in thin film solar cells because of large absorption coefficient and controllable p-type conduction. [1-4] The CIS or CIGS absorber layers used in CIS or CIGS (copper indium gallium diselenide) solar cells are usually Cu-poor. Lower interfacial recombination sites in Cu-poor CIS or CIGS is the reason behind better performance of the CIS or CIGS solar cells in terms of power conversion efficiency. [5, 6] On the other hand, Cu-poor CIS or CIGS films are highly compensated giving rise to fluctuating defect potentials at low temperature. [7] These fluctuating potentials are the reason behind band-to-tail (BT) and band-to-impurity (BI) transitions in Cu-poor CIS or CIGS. [8-10] An asymmetric and broad photoluminescence spectrum, with a tail on the lower energy side, together with larger blue shift of the peak with laser excitation power (usually expressed as j-shift) are the characteristics of transitions related to the band tail states. [8-10] Identifying such defect-assisted transitions, and exploring their sources, are crucial to further improve the performance of CIS based solar cells. [11, 12] Therefore, we focus on defect analysis of Cu-poor CIS films via photoluminescence (PL) spectroscopy technique. CIS films prepared by a co-evaporation technique were used for temperature and laser power dependent PL measurements. Asymmetric and broad PL spectra were obtained in the case of Cu/In = 0.66 CIS film at low temperature. The observed peaks at 0.845 eV and 0.787 eV show large j-shift of ~11.7 meV/decade and 8 meV/decade with increase in laser intensity and were assigned to BT and BI recombination, respectively. In contrast, a prominent DAP peak and its phonon replica at ~32 meV were observed in case of CIS film for Cu/In = 0.80.

EXPERIMENTAL DETAILS

A 2 µm thick ($CuInSe_2$) CIS thin film was deposited on 3″ x 1″ soda lime glass substrate by using single-stage thermal co-evaporation in a high vacuum chamber maintained at a base pressure of 2 x 10^{-6} Torr. The substrate was maintained at 570 ^{o}C. The Cu, In, and Se were evaporated simultaneously with constant flux. The position of the substrate was placed to ensure an intended spatial variation of the stoichiometry of the CIS film. The sample was cut into pieces and the Cu/In ratio in thin films were analyzed by energy dispersive X-ray spectroscopy (EDS). Temperature dependent PL measurements were carried out by mounting the sample on the cold finger of a He closed-cycle refrigerator system from Advanced Research Systems. PL measurements were conducted using a 532 nm cw excitation laser beam (beam diameter ≈ 90 µm) with intensities ranging from 1.2 to 63 W/cm^2. Samples were excited from the film side, and the PL signal was detected by a liquid nitrogen cooled Ge photodiode from Electro-Optical Systems after a 300 g/mm grating monochromator. For liquid nitrogen cooled photodiodes, noise is minimized by chopping the incident light at 200 Hz and acquiring the signal via a Stanford Research Systems SR510 lock-in amplifier.

RESULTS & DISCUSSION

Figure 1a shows the broad and asymmetric PL spectrum of $CuInSe_2$ film for Cu/In = 0.66 taken at 20 K with its maximum at 0.845 eV. Additionally, a 0.787 eV peak on lower energy side was also observed in the PL spectrum. The former peak is due to the band-to-tail (BT) transition while the lower energy peak corresponds to a band-to-impurity (BI) transition. BT band comes from the recombination of free electrons to the holes localized in the valence band tail while BI transitions take place via recombination of free electrons with holes localized at an acceptor state which is slightly deeper than band tail. [8, 9] The laser intensity dependent PL measurements displayed in figures 1b and 2a revealed that observed peaks shift towards higher energy with increasing laser intensity, the so-called j-shift. The j-shift values were determined by fitting emission peak energy vs. laser intensity using the equation $I_{ex} = I_o \, exp(E_p/\beta)$, where I_{ex} be excitation intensity, E_p emission peak energy and β the rate of energy shift (meV/decade). [13] The rates of such shifts were 11.7 meV/decade for 0.845 eV peak and 8 meV/decade for 0.787 eV peak

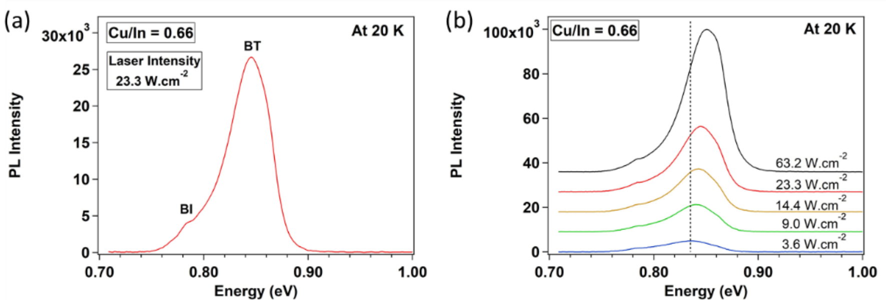

Figure 1. PL spectra of $CuInSe_2$ film with Cu/In = 0.66 taken at 20 K (a) showing BT and BI band (b) for various intensities of laser.

respectively. Such a large j-shift at lower temperature along with asymmetric spectra are the characteristic of emission arising from band – to - tail recombination (BT). [8, 9] The reason behind large j-shift is the potential fluctuation of defect states that form localized deep hole states within the gap, which act as acceptors. Such a transition is referred to as a band-tail recombination event and is common in highly compensated semiconductors.

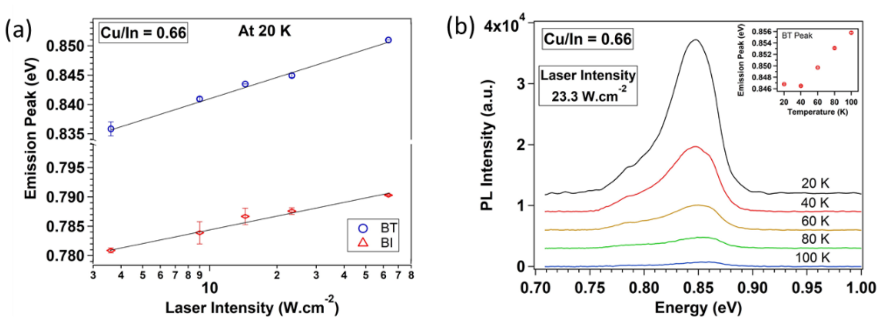

Figure 2. (a) Peak emission vs. laser intensity at 20 K and (b) temperature dependence of PL intensity of $CuInSe_2$ film with Cu/In = 0.66.

The blue shift of the BT peak with increase in laser intensity is caused by flattening of the potential fluctuation due to increase in neutralization of charged defect states by increasing free carriers with laser intensity. [12] Yakushev *et al.* and Krustok *et al.* independently reported the existence of such band tail related transitions in nearly ideal stoichiometric $CuInSe_2$ single crystals and $CuIn_{0.5}Ga_{0.5}Se_2$, respectively. [8, 9]

Figure 2b shows the temperature dependent PL spectra of $CuInSe_2$ film for Cu/In = 0.66. The temperature-dependent emission peak energy (inset, Fig. 2b) indicates a redshift of the BT peak at 40 K, which is one of the characteristic features for a BT transition. While additional data points would clarify the behavior, these data are consistent with a red-shift over the range below 40 K. At low temperatures, increasing thermal energy allows the localized holes to sample nearby lower-potential sites, thereby reducing their energy. The energy distribution of holes establishes the quasi-Fermi level that yields a decrease in the peak energy of the BT band. [12] The nature of the blue shift evident for T > 40 K has been assigned to thermal activation of bound holes back to the valence band. [8] Since a BT transition involves the recombination of a free electron to a hole localized

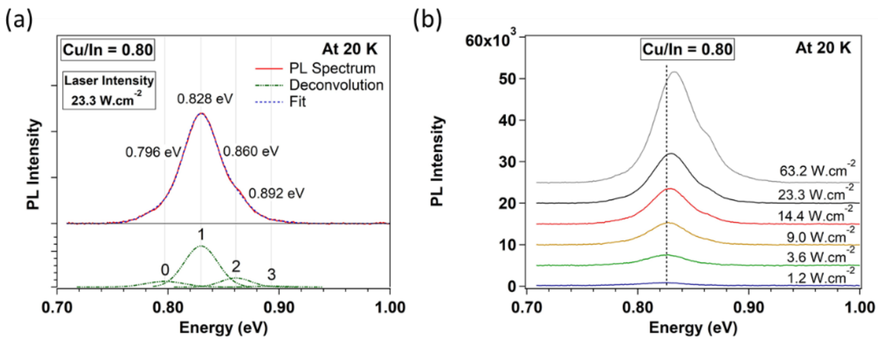

Figure 3. (a) PL spectrum along with multi-gaussian fits and (b) laser excitation dependent PL of $CuInSe_2$ films with Cu/In = 0.80.

in the valence band tail, we can not consider the activation energy related to this transition. However, for a BI band which originates from the recombination of a free electron with a hole localized at an acceptor state deep enough not to overlap with the valence band tail, we can estimate the activation energy once we know the band gap of the film at that temperature at which the BI band appears. The value of the activation energy can be determined by subtracting BI band peak position energy from the band gap energy of the film. [14] Since we do not know the band gap energy of $CuInSe_2$ film with Cu/In = 0.66 at 20 K, we were not able to estimate the activation energy of BI band.

In contrast, a nearly symmetric PL spectrum was obtained for the higher Cu/In ratio (Cu/In = 0.80). Multi-peak fitting of the observed PL spectrum revealed the existence of longitudinal optical phonon replica with a zero-phonon line at 0.892 eV as shown in Figure 3a. The observed value of the phonon energy was ~32 meV, very close to the reported value by the previous researchers. [1, 4, 15, 16] The intensity-dependent PL follows a power law $I_{PL} = I^{k}_{Laser}$ with a value of $1 < k < 2$ for band-to-band (BB) and excitonic recombination, and $k < 1$ for free-to-bound (FB) and donor-to-acceptor (DAP) recombination. [17, 18] The intensity-dependent PL displayed in figures 3b and 4a confirm that the observed peaks relate to a defect-assisted transition. Furthermore, the observed defect emission peaks shift towards higher energy with increasing laser intensity as shown

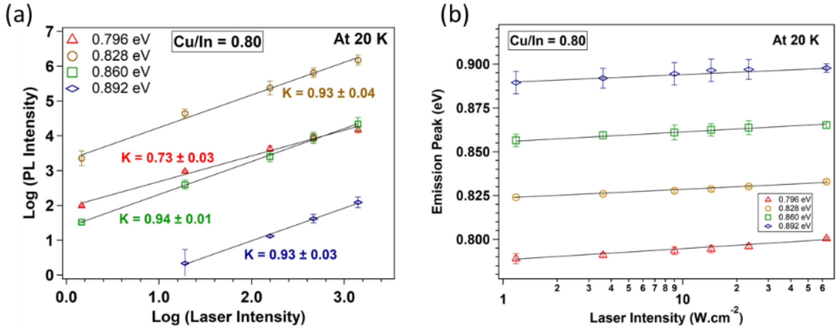

Figure 4. (a) Power law dependence for observed peaks and (b) emission peak vs. laser intensity in $CuInSe_2$ film with Cu/In = 0.80.

in figures 3b and 4b. The measured j-shift was ~ 5 meV/decade. Such a small value of j-shift with laser excitation intensity is characteristic of donor-to-acceptor pair (DAP) recombination mechanism. [4] The DAP peak at ~0.89 eV has also been reported by Dagan *et al.* and Niki *et al.*, respectively, in single crystal CIS for Cu/In = 0.85 and in CIS film for Cu/In = 0.81. [11, 19]

PL spectra of $CuInSe_2$ film with Cu/In = 0.80 at various temperatures were presented in figure 5a. The emission peak vs. temperature plotted in the inset of Figure 5a shows the blue shift of the DAP with increase in temperature. The blue shift occurred at slower rate over the temperature range studied – this is commonly the case for published reports of the study of the temperature dependent blue shift of DAP peaks. [20, 21] The temperature-dependent PL intensity of observed peaks in $CuInSe_2$ film with Cu/In = 0.80 was used to determine their thermal quenching behavior as depicted in figure 5b. The values of thermal activation energy of the DAP peak and its phonon replica obtained by using equation [21, 22] were ~ 22 meV. Here A, B and I_0 are the fitting parameter, and E is the activation energy. The obtained value of thermal activation energy indicates that the same shallow acceptor state having binding energy of ~22 meV was involved in recombination process of all the observed transitions. The binding energy of ~22 meV has been previously attributed to a copper vacancy (V_{Cu}) defect level in CIS. [23-25]

$$I(t) = \frac{I_o}{1 + A\,T^{3/2} + B\,T^{3/2}\,e^{-E/_{KT}}} \qquad (1)$$

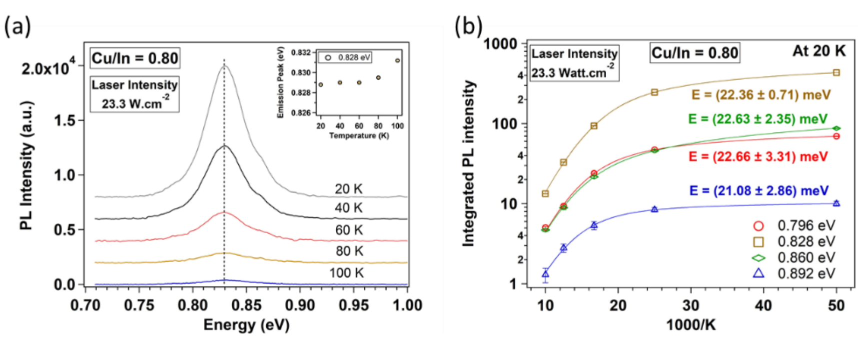

Figure 5. (a) Temperature dependent PL spectra and (b) temperature dependence of PL intensity of observed peaks for the $CuInSe_2$ film with Cu/In = 0.80.

CONCLUSIONS

Temperature and laser power dependent PL measurements of CIS films with two different Cu/In ratios (0.66 and 0.80) were performed. Low temperature PL measurement of a CIS film for Cu/In = 0.66 revealed the asymmetric and broad PL spectrum, while also showing large j-shift of 11.7 meV/decade and 8 meV/decade for 0.845 eV and 0.787 eV peaks respectively. Therefore, the observed peaks at 0.845 eV and 0.787 eV were assigned to BT and BI transition, respectively, originating from the fluctuation of the potential of the defect states. On the other hand, a DAP peak and its phonon replica at ~32 meV spacing were observed when Cu/In ratio increased to 0.80. The temperature dependent PL intensity shows that the DAP transition involves a shallow acceptor, possibly a Cu-vacancy, with binding energy ~ 22 meV.

ACKNOWLEDGEMENTS

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