Observation of unusual optical transitions in thin-film $Cu(In,Ga)Se_2$ solar cells

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Abstract: In this paper, we examine photoluminescence spectra of $Cu(In,Ga)Se_2$ (CIGS) via temperature-dependent and power-dependent photoluminescence (PL). Donor-acceptor pair (DAP) transition, near-band-edge transition were identified by their activation energies. S-shaped displacement of peak position was observed and was attributed to carrier confinement caused by potential fluctuation. This coincides well with the obtained activation energy at low temperature. We also present a model for transition from V_{Se} to V_{In} and to V_{Cu} which illustrates competing mechanisms between DAPs recombinations.

OCIS codes: (160.5335) Photosensitive materials; (350.6050) Solar energy.

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1. Introduction

Lately, Cu(In,Ga)Se_2 (CIGS) has been proposed as a promising material for thin film solar cells with potential to replace silicon-based solar cells. CIGS solar cells have achieved a high photovoltaic efficiency of 20.3% in laboratory experiments [1]. This is the highest among all types of thin film solar cells. There are abundant point defects in the CIGS absorber layer which behave as acceptor/donor sites dominating the electrical characteristics [2]. To improve the film quality and reduce carrier recombination, understanding of these point defects in CIGS is required [3]. A great deal of work on defect properties in CIGS has been carried out in this decade. However, defect features in CIGS films are not yet clearly understood owing to the fluctuation in its optoelectronic properties, complex device structures, and complex composition of CIGS solar cells. Therefore, investigating fundamental physics of defects in CIGS is crucial to understand the carrier transport mechanism in CIGS solar cells and make improvement in cell efficiency.

Among available characterization techniques, photoluminescence (PL) is a technique commonly used for the analysis of crystal quality, impurity, alloy composition and intrinsic

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recombination in semiconductors. PL spectrum is extremely sensitive to point defects and deviation of stoichiometry making it suitable to analyze the defects in the absorber layer [4,5]. In this study, we have examined and characterized a CIGS thin film via temperature-dependent and power-dependent PL measurements. A model of emission competition between donor-acceptor pairs has been proposed.

2. Experiments

The CIGS thin film was prepared on a Mo-coated soda-lime glass (SLG) substrate via three stage co-evaporation method with [Cu]/[Ga] + [In] ratio around 0.7 and [Ga]/([Ga] + [In]) (GGI) ratio around 0.2. Gradient Ga-concentration was applied for a conventional v-shaped gradient bandgap of CIGS [6,7]. One as-deposited CIGS thin film had been further fabricated into a CIGS solar cell with structure of ZnO:Al (AZO)/ZnO/CdS/CIGS/Mo/SLG and an efficiency of 12%. More details of CIGS thin film deposition can be found elsewhere [8]. A 635 nm diode laser was used for PL measurements. Temperature-dependence PL measurements were made over the range 10 K to 300 K under a constant excitation power of 50 mW. Power dependent PL was measured at a constant temperature of 10K with excitation powers ranging from 5 mW to 50 mW. The PL signal emitted from the CIGS sample was transferred to a monochromator with a 600 groove/mm grating and detected by an infrared photomultiplier tube. All PL measurements were taken from a bare CIGS absorber layer.

3. Carrier localization

Figure 1(a) shows the PL spectra of the CIGS thin film in the temperature range 10-260K, where four individual emission peaks were observed. These four peaks are labeled P1, P2, P3 and P4 from low photon energy to high photon energy as indicated in Fig. 1(a). Four distinguishable peaks exist across all temperatures, implying that there are different recombination processes in the CIGS film. The inset of Fig. 1(a) shows the experimental data (black line) and the results of fitting to Gaussian distribution at 10K (green lines). According to the Gaussian fitting results, the photon energies of these PL emission peaks related to P1, P2, P3 and P4 are 0.974 eV, 1.054 eV, 1.130 eV and 1.191 eV respectively. Due to the 0.2 GGI ratio of our CIGS thin film, a bandgap of 1.14 eV was expected and accords with the 1.130 eV photon energy of P3 [9]. Additionally, photon energy of P3 was found to be very sensitive to variation of temperature and is possibly a response to bandgap shrinkage. It is therefore very likely to be due to band-to-band transition. P1 and P2 are consequently assigned to the donor–acceptor pair (DAP) transition [10,11]. P4 is related to a consequent result of v-shaped gradient bandgap, in which a PL emission with larger photon energy can be observed due to the wider part of gradient bandgap [12,13]. The corresponding PL emission shift of P1, P2, P3 and P4 are illustrated in Fig. 1(b). S-shaped emission shift, a behavior deviates from bandgap shrinkage upon temperature rise illustrated by Varshni empirical Eq [14], has been revealed from all recombination processes, indicating localization of carrier occurring upon both DAPs recombination and band-to-band transition, which is caused by bandgap fluctuation and is very much possible to be observed in CIGS due to its characteristic of highly-compensated semiconductor [15–17].

Fluctuation of band gap energy is particularly of interest in this study, since it is an important factor limiting the efficiency of a CIGS solar cell: energy difference smaller than the average bandgap can locally construct band tail and induce recombination current and limits device performance [16,18]. The PL peak position dependence of P3 on temperature between 10K to 270K is shown in Fig. 2(a). Sixteen temperatures were chosen for PL measurements: 10K, 20K, 30K, 40K, 50K, 60K, 80K, 100K, 120K, 140K, 160K, 180K, 200K, 220K, 240K and 260K. Intensity of PL at temperatures above 260K was too weak for analysis. It shows redshift in the temperature range of 10–70K, blueshifts in 70–120K, and then redshifts as temperature increased to 260K. The S-shaped peak position was attributed to the recombination of excited electron-hole pair on the fluctuation band edge [19]. The redshift

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in the range of 10-70K was affected by energy gap shrinkage as carriers become confined at potential minimum in band tail. As the rising temperature exceeded 70K, localized carriers obtained enough thermal energy to cause band-filling within the band tail and resulted in recombination of degenerate electrons that leaded to a greater energy of emitted photons [20]. Band-filling became more severe as the temperature kept rising and resulted in the observed blueshift over the range 70-120K. As the temperature exceeds 120K, most excited carriers acquired adequate thermal energy to overcome the potential barrier and escaped from confinement. Therefore the luminescence emission was once again dominated by bandgap shrinkage and showed the observed redshift in 120K-260K. The anomalous S-shaped temperature-induced emission shift is attributed to the inhomogeneous composition over the CIGS thin film [17]. The inhomogeneous distribution of In and Ga atoms or point defects can lead to the band fluctuation and consequently resulted in localization phenomenon.

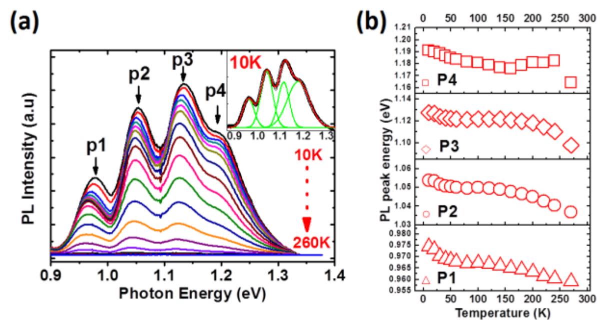

Fig. 1. (a) The PL spectra of the CIGS thin film under temperatures from 10 K to 300 K. Inset is the fitting result of PL spectrum at 10 K using Gaussian distribution, and (b) plots of the four PL emission peak positions at different temperatures.

In order to confirm whether P3 is band-to-band recombination and the existence of localization, we fitted the temperature-dependent PL peak position as a function of temperature for the case of fluctuation potential illustrated below [15,21]:

$$E_{peak}(T) = E_g(0) - \frac{\alpha T^2}{\beta + T} - \frac{\sigma^2}{k_B T}, \quad (1)$$

where $E_g(0)$ is the bandgap energy at 0K, α and β are Varshni thermal coefficients for bandgap shrinkage with temperature, and σ is a standard deviation of the most probable Gaussian distribution of potential fluctuations. Here, we've dropped the PL intensity above 260K as it was too weak for analysis. The above equation measures potential fluctuation by assuming carrier localization effect dominates. Fitting range was chosen to start at the point where blueshift first occurred [15,21]. The fitting curve is shown in Fig. 2(a). The resultant values of fitting parameters are $\alpha = 1.02 \times 10^{-4}$ eV/K, $\beta = 272$ K and $\sigma = 7.7$ meV. The values of α and β are close to those reported by T. Yamaguchi et al. [22] and Yoshino et al [23] that shows certain accuracy of fitting results. The slight deviation might be due to a difference in film quality and deposition method. A PL emission of P3 due to band-to-band transition with fluctuation of band edge is consequently confirmed.

Furthermore, the temperature-dependent integrated PL intensity of P3 (band-to-band recombination), as shown in Fig. 2(b), can be fitted by the two-channel model of Arrhenius plot function [24]:

$$I(T) = \frac{I(0)}{1 + A\exp\left(\frac{-E_a}{k_B T}\right) + B\exp\left(\frac{-E_b}{k_B T}\right)}, \quad (2)$$

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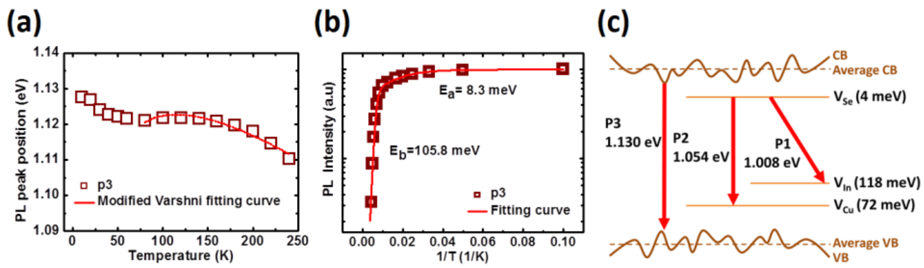

Fig. 2. (a) Peak position versus temperature of p3 with result of fitting to modified Varshni Eq. and (b) the Arrhenius plot of p3 and both of their corresponding fitting curves. (c) The energy level diagram of the CIGS thin film.

where I(0) is the PL intensity at 0 K, the coefficients A and B are related to the strengths of two quenching mechanisms, k_B is Boltzmann constant, E_a and E_b are the thermal activation energies in the low temperature and high temperature regions, respectively. The red line in Fig. 2(b) shows the fitting result which corresponds well with the experimental data. The values of activation energy were found to be 8.3 meV and 105.8 meV for E_a and E_b respectively. In particular, E_a is correlated to photoluminescence under low temperature therefore presents the thermal energy for carriers to escape from band tail. This value of E_a well-agreed with σ = 7.7 meV acquired from Eq. (1) which represents the average depth of band tail. According to these results, we speculate that the nonuniform composition in CIGS results in carrier localization with confinement energy of about 8 meV in the CIGS thin film.

According to activation energies of P1 (E_a = 4 meV, E_b = 199 meV) and P2 (E_a = 5 meV, E_b = 76 meV), and also the bandgap value obtained from analysis of temperature dependent PL, the donor level shared by transitions of DA_1P and DA_2P was found to be located at around 5 meV below conduction band, while A_1 and A_2 located at 195 meV and 71 meV above valence band, respectively [25]. The donor at 5 meV is very likely to be V_{Se}, of which the value is smaller than what commonly observed (10 meV) is due to fluctuation of conduction band edge. As for the acceptors, A_1 and A_2 are V_{In} and V_{Cu}, respectively [26–28]. An energy level diagram is shown in Fig. 2(c) for interpretation. The observed photon energy 0.974 eV of P1 related to V_{Se}-V_{In} transition is of 43 meV larger than the difference between energy levels of V_{Se} and V_{In} obtained from activation energy, which is 0.931 eV. The blueshift is attributed to Coulomb interaction of DAP, which can be interpreted as below [29]:

$$\hbar\omega = E_g - \left(E_A + E_D\right) + \frac{e^2}{4\pi\varepsilon_0 \varepsilon R}, \tag{3}$$

where E_g is band gap, E_A and E_D are acceptor and donor energy level respectively, R is the distance between the ionized DAP. Meanwhile, the difference between energy levels of V_{Se} and V_{Cu} corresponds well with the observed photon energy of P2.

4. Unusual photoluminescence emission

Power-dependent PL spectrum with variation of excitation power from 1 mW to 50 mW at 10K is shown in Fig. 3(a). It is noteworthy that the intensity of P1 first *increases* with the increasing excitation power and then started to *decrease* as the excitation power goes above 5 mW up to 50mW. The intensity of P2 increases monotonically with the rising excitation power. The evolution in PL intensity of P1 and P2 according to the deconvolution results are displayed in Fig. 3(b). This phenomenon is significantly distinct from the general knowledge, and implies competition between recombination mechanisms of P1 and P2. To clarify the transition mechanisms, we propose a model taking consideration of a competition in transitions between DA_1P and DA_2P due to their different transition rates under different excitation conditions, which is caused by a great difference in concentration of A_1 and A_2 acceptors and a limited concentration of donors, as schematically illustrated in inset of Fig. 3(b).

When the excitation power is weaker than 5 mW, (as shown in region I of Fig. 3(b)), acceptor A_1 dominates DAP recombination with the single-existing donor so that P1 is the main PL emission peak under this condition. Consequently a Coulomb interaction was observed in DA_1P recombination, which was absent in DA_2P recombination. Therefore the transition tendency of carriers from ionized donors toward acceptor A_1 may be attributed to an enhanced transition rate of DA_1P due to Coulomb force.

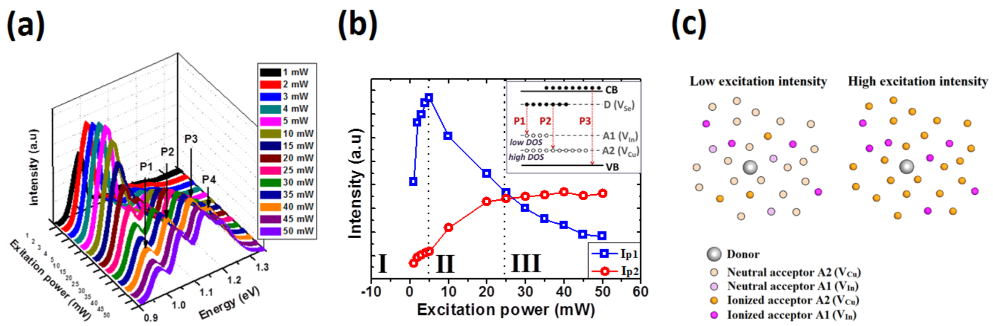

Fig. 3. (a) The PL spectrum of the CIGS thin film under excitation powers from 1 mW to 50 mW. (b) PL intensity of p1 (blue line) and p2 (red line) with temperature. Inset shows the schematic representation of proposed DAP transition. (c) A schematic illustration for conditions under low excitation and high excitation.

When the rising excitation power exceeds 5 mW, P1 and P2 show an unusual rise and fall in their intensity: the intensity of P1 decreases dramatically while the intensity P2 continues rising, as shown in region II of Fig. 3(b). We have deduced that this is due to a larger concentration of acceptor A_2 which significantly surpasses that of acceptor A_1. Such difference results in a rising transition rate of DA_2P and a falling transition rate of DA_1P and therefore switches the carrier transition tendency around.

Fermi's golden rule has been utilized to describe the transition rate of spontaneous emission:

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} \left| \left\langle f \left| \vec{d} \bullet \vec{E}(\vec{r}_e) \right| i \right\rangle \right|^2 \rho_f , \tag{4}$$

where ρ_f is the density of state (DOS) of the final state in transition, here namely DOS belonging to one certain kind of acceptor among two, and $\langle f |\vec{d} \cdot \vec{E}(\vec{r}_e)| i \rangle$ is the dipole emission matrix element. We have assumed that acceptors of the same kind possess an identical energy level. For acceptor A_2, its higher DOS at its own energy level caused a higher transition rate of DA_2P than that of DA_1P. As the excitation power exceeded 5 mW, the transition rate of DA_2P become more dominant compared to Coulomb interaction of DA_1P. Consequently, the limited donor electrons were being removed more and more severely by acceptor A_2. The transition tendency of carriers from the limited donors had been turned to acceptor A_2 rather than acceptor A_1 so that the PL intensity of P2 had gradually grown stronger and eventually surpassed the decreasing PL intensity of P1 (see region III in Fig. 3(b)). Due to the reason that the PL intensity of P1 showed decline rather than saturation, the donor must be insufficient for fulfilling both transitions to acceptor A_1 and to acceptor A_2 so that either one of them can be suppressed under different conditions. This is quite reasonable since CIGS is a p-type semiconductor. Another schematic diagram (Fig. 3(c)) indicates that difference in concentrations of the two acceptors could be more significantly affected under high excitation intensity since each acceptor has equal chance to be excited at all excitation intensities.

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CIGS thin films providing good efficiency (including our sample), are of Cu-poor type. V_{Cu} is therefore expected to be abundant, as widely reported [25–28]. On the contrary, V_{In} is not much expected in our sample due to its GGI ratio of 0.2, which is pretty much an In-rich type. Moreover, the formation energy of V_{Cu} is very low, whereas the formation energy of V_{In} is a lot larger than that of V_{Cu} [2]. These facts reflect that the concentration of V_{Cu} is significantly higher than that of V_{In}.

An as-deposited CIGS thin film was fabricated into a CIGS solar cell and found to possess an efficiency of 12%, which is adaptable for applications. Although composition of point defects in CIGS thin films varies widely across literature, the characteristic of highly-compensated semiconductor remains universal, which has a good chance of inducing competition between optical transitions. CIGS-based solar cells can be affected by such phenomenon in performance especially as a concentrated photovoltaic. As the intensity of incident light can induce selective recombination between DAPs and results in significant change in their recombination rate, extraction of photo-current can be severely affected due to DAP-related carrier dynamics in CIGS, such as carrier extraction from ionized donors/acceptors, or tunneling-enhanced recombination in CIGS [30,31].Further study in competition between optical transitions is needed, yet it may be important for understanding CIGS-based solar cells.

5. Conclusion

In this work, we have measured PL of a CIGS thin film at different temperatures and excitation powers. According to the temperature-dependence PL spectra, we have identified these emission peaks as DA transitions and band-to-band transitions. Furthermore, we have observed obvious S-shape displacement of peak position in both DA transition and band-to-band transition. Analysis shows the parameter σ in modified Varshni empirical Eq. measuring potential fluctuation has found to be 7.7 eV, and is very close to the activation energy of 8.3 meV obtained from Arrhenius plot. The consistence strongly shows the existence of band fluctuation with potential depth around 8 meV which causes localization effect at low temperature. In addition, an unusual rise and fall has been observed in photoluminescence emission, and we conclude that this is due to transition competition between two DAPs, which are correlated to V_{Se} – V_{Cu} transition and V_{Se} – V_{In} transition. It is caused by concentration difference of the two acceptors and Coulomb force in between. Carrier localization and the new-discovered recombination competition may be affected to recombination current in a CIGS solar cell such as tunneling-enhanced recombination. Therefore they can be affected to efficiency as well and is important for understanding a CIGS solar cell.

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