Investigation of Deep-level Defects in CuGaSe$_2$ Thin-film Solar Cells by Transient Photo-capacitance Spectroscopy

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Abstract. Properties of deep-level defects in CuGaSe$_2$ thin-film solar cells were investigated using transient photo-capacitance (TPC) spectroscopy. Two Gaussian-shaped deep-level defects centered at around 0.8 eV and 1.54 eV above the valence band were identified. The electronic structure of the two defects was illustrated by a configuration coordinate model to explain the thermal quenching effect in the two defects, which considered a large lattice distortion for the 0.8 eV defect while no distortion for the 1.54 eV defect.

1. Introduction
Chalcopyrite Cu(In$_{1-x}$Ga$_x$)Se$_2$ (CIGS) is one of the most promising materials for use in thin-film solar cells. CIGS-based solar cells have attained the highest efficiency (>20%) among all photovoltaic thin film technologies [1]. However, these high-efficiency solar cells are typically made from CIGS alloys with low Ga content (x~0.3), corresponding to bandgap energy of about 1.15 eV [2]. The developing of CIGS films with higher bandgap energy is also desirable since the optimum bandgap for the highest efficiency of solar cell is around 1.4 eV as theoretically predicted which means there is still much space to improve the efficiency [3], and also they are promising candidates as intermediate or top layers for application in the tandem solar cells which should attain higher efficiency than single-junction solar cells [4]. Especially, CuGaSe$_2$ (x =1.0) with a band gap of 1.68 eV would represent an ideal partner for CuInSe$_2$ in an all-chalcopyrite tandem structure [4]. However, the present efficiency of CuGaSe$_2$ is still much lower than theoretical predictions and needs further improved [5].

It is commonly recognized that formation of various point defects and defect phases in the films is considered as important factor limiting the efficiency since they are good candidates as effective carrier recombination centers and could directly induce the higher open-circuit voltage loss and poor carrier life-time compared to the CIGS solar cells with low bandgap energy [6]. Thus, a complete understanding of the deep-level defects is very useful to improve the performance of CuGaSe$_2$ solar
cells. Transient photo-capacitance (TPC) spectroscopy is a powerful tool for the analysis of deep levels in the photo-absorber layer because of the very low detection limit [7]. Much has been done in studying CIGS solar cells by employing TPC spectroscopy in our previous work [8,9], however, these work were studied based on CIGS solar cells with Ga content 0.3~0.8, and studies on CIGS with higher Ga content such as CuGaSe$_2$ has not been reported.

In this study, transient photocapacitance (TPC) spectroscopy were used to investigate the properties of optically active deep-level defects in CuGaSe$_2$ solar cells.

2. Experimental
Polycrystalline CuGaSe$_2$ thin films were grown on Mo-coated soda-lime glass substrates by a three-stage process using a molecular beam epitaxy (MBE) system. The detailed deposition conditions and processes for the CuGaSe$_2$ solar cell have been described elsewhere [10]. The device parameters of CuGaSe$_2$ thin-film solar cells used in this study were measured under AM1.5 illumination at 25 °C, with short-circuit current of 14.49 mA/cm$^2$, open-circuit voltage of 0.818 V, fill factor of 0.643 and efficiency of 7.624%, respectively.

The TPC measurements were carried out from 100 K to 300 K by setting the samples in a cryostat chamber. The experimental conditions were the same as our previous work described [8,9]. During the photo-capacitance measurements, a halogen lamp was used as the monochromatic probe light source (700~1800 nm). The detail timing chart for the measurements is described in ref [11]. The transient response, which arises after the pulse, was integrated over a fixed time window (0.75 s) by using an analog-to-digital converter with the rate window fixed at 2s$^{-1}$.

3. Results and discussion
The TPC spectrum of the CuGaSe$_2$ sample measured at 100 K was shown in figure 1 (a). The spectrum shows three optical absorption features: one kind of interband absorption for photon energies ranging from about 1.6 to 1.8 eV, and two kinds of sub-bandgap absorption from 0.8 to 1.2 eV and from 1.2 to 1.6 eV caused by deep-level defects in the CuGaSe$_2$ cell. Regarding the interband absorption, we observed a steep increase in the intensity of the TPC signal with increasing photon energy due to the large cross section of the direct interband transition, this could be fitted by an exponential band tail as figure 1 (a) shows. With regard to the sub-bandgap absorption, the intensity of the TPC signal was lower than that of the interband absorption by one to two orders of magnitude, and two Gaussian shaped bands were used to fit the defect signal which considered two defects locating at around 0.8 eV and 1.54 eV above valence band respectively.

Figure 1 (b) shows the temperature dependence of the TPC spectrum measured in the temperature range from 100 to 300 K. The intensity of sub-bandgap TPC signal decreased with increasing temperature while significant variation in the inter-band signal was not observed with temperature. The decreasing of TPC intensity with temperature can be attributed to the thermal de-trapping of charges in defect levels with temperature. The inset shows the relation between the temperature and logarithm of TPC signal measured under monochromatic band gap light irradiation (at 0.8 eV and 1.54 eV as the inset shows). The variation of the TPC signal $S(T)$, with the temperature $T$ was described by the thermal quenching model commonly used for the photoluminescence study [12], $S(T)=S(0)/[1+C\exp(-E_a/kT)]$ where C is a constant and $E_a$ is the activation energy of thermal quenching.
The activation energy was obtained as 0.20 eV for the 0.8 eV defect and 0.13 eV for the 1.54 eV defect, respectively, as the inset shows.

The mechanism of thermal quenching has been interpreted by using a discrete energy model [6]. In this model, the thermal excitation of the electrons trapped in deep defects to the conduction band leads to the quenching of the TPC signal. By using this model, the thermal quenching activation energy $E_a$ is the difference between the bandgap energy and the optical transition energy. Thus, the activation energies of quenching are expected to be approximately 0.88 eV and 0.14 eV for the 0.8 eV defect and 1.54 eV defect ($E_g=1.68$ eV). For the 1.54 eV defect, the discrete model could explain the thermal activation energy properly since the experimentally obtained $E_a=0.13$ eV coincides well with the predicted 0.14 eV; however, for 0.80 eV defect, the value is considerably larger than that observed in the experiment as figure 1 (b) shows.

This could be interpreted using a configuration coordinate (CC) diagram, as shown in figure 2.

For the 0.8 eV defect, the optical process and thermal quenching process can be explained based on the CC model as follows: $A \rightarrow B$: optical transition without changing configuration coordinate; $B \rightarrow C$: 

Figure 1. (a) TPC spectrum of the CuGaSe$_2$ sample measured at 100 K; (b) Temperature dependent of TPC spectrum of the CuGaSe$_2$ sample from 100 K to 300 K.

Figure 2. Configuration coordinate diagram describing the optical transition process for the defect 0.8 eV and 1.54 eV.
lattice relaxation with multi-phonon emissions; C→D: atomic vibrations by changing configuration coordinate, at low temperatures, the charged defects retain their configuration at position C due to lower vibration energy, however, when temperatures increases, atomic vibrations can shift their configuration from C to D, the energy difference between C and D is defined as the activation energy $E_{a1}$. D→A: non-radiative transition by shifting configuration coordinate. For the 1.54 eV defect, the thermal quenching process can be easily explained by the direct transition of electrons from B’ to C’ without atomic vibration, with the energy difference between B’ to C’ is defined as the activation energy $E_{a2}$. The CC model could also explain the spectrum broadening which was thought to be caused by the strong electron–phonon interaction between the valence band and the deep defect as the dash arrow shows in figure 2.

4. Conclusion
The deep-level defects in CuGaSe$_2$ thin film were investigated through transient photo-capacitance (TPC) technique. A 0.8 eV defect and a 1.54 eV above valence band maximum (VBM) were identified, and a configuration coordinate model was proposed to explain the thermal quenching effect for the two defects.

References
[1] Green M A, Emery K, Hishikawa Y, Warta W, and Dunlop E D 2016 Prog. Photovolt: Res. Appl. 24 3–11
[2] Repins I, Contreras M A, Egaas B, DeHart C, Scharf J, Perkins C L, To B, and Noufi R 2008 Prog. Photovolt: Res. Appl. 16 235–9
[3] Werner J H, Mattheis J, and Rau U 2005 Thin Solid Films 480 399–409
[4] Nishiwaki S, Siebentritt S, Walk P, and Lux-Steiner M C 2003 Prog. Photovolt: Res. Appl. 11243–8
[5] Ishizuka S, Yamada A, Fons P J, Shibata H and Niki S, 2014 Prog. Photovolt: Res. Appl. 22 821–9
[6] Sakurai T, Uehigashi H, Islam M M, Miyazaki T, Ishizuka S, Sakurai K, Yamada A, Matsubara K, Niki S, and Akimoto K 2009 Thin Solid Films 517 2403–6
[7] Cohen J D, Unold T and Gelatos A V 1992 J. Non-Cryst. Solids 141 142–54
[8] Hu X B, Sakurai T, Yamada A, Ishizuka S, Niki S, and Akimoto K, Appl. Phys. Lett. 2013 103 163905
[9] Hu X B, Sakurai T, Yamada A, Ishizuka S, Niki S, and Akimoto K 2014 Jpn. J. Appl. Phys. 53 068008
[10] Islam M M, Yamada A, Sakurai T, Kubota M, Ishizuka S, Matsubara K, Niki S and Akimoto K 2012 J. Appl. Phys. 112 103707
[11] Siebentritt S and Rau U 2006 Wide-Gap Chalcopyrites ( Berlin: Springer Verlag) p 69
[12] Pankove J I 1971 Optical Processes in Semiconductors (New York: Dover)

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