

Deep Level Transient Spectroscopy and Capacitance-Voltage Measurements of Cu(In,Ga)Se₂

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DEEP LEVEL TRANSIENT SPECTROSCOPY AND CAPACITANCE-VOLTAGE MEASUREMENTS OF Cu(In,Ga)Se₂

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ABSTRACT

The electronic properties of ZnO/CdS/Cu(In,Ga)Se₂ (CIGS)/Mo/SLG polycrystalline thin-film solar cells with compositions ranging from Cu-rich to In-rich were investigated by deep level transient spectroscopy and capacitance-voltage (C-V) measurements. This compositional change represents the evolution of the film during growth by the three-stage process. Four thin-film CIGS samples with different Cu content were obtained. The Cu/(In+Ga) ratio ranges from 1.24 (Cu-rich) to 0.88 (In-rich), whereas the Ga/(In+Ga) ratio ranges from 0.19 (Cu-rich) to 0.28 (In-rich). The Cu-rich sample exhibits a shallow majority-carrier trap with an activation energy of 0.12 eV and another deeper trap with an activation energy of 0.28 eV, whereas the In-rich sample has a shallow minority-carrier trap with an activation energy of 0.12 eV. The two samples show evidence of a deeper trap at higher temperature. C-V measurements showed that the average carrier concentration (N values) around the junction of the cell changed as the film transitions from Cu-rich to In-rich. DLTS shows that acceptor-like traps are dominant in samples where CIGS grains did not go through the Cu-rich to In(Ga)-rich transition. While donor-like traps are dominant in the In(Ga)-rich samples.

INTRODUCTION

Polycrystalline thin-film solar cells based on Cu(In,Ga)Se₂ (CIGS) have the highest conversion efficiencies for both small laboratory devices and large modules—18.8% [1] and 12.1% [2]—respectively, of any thin-film photovoltaic technology. The four elements of this multinary polycrystalline film may form different components as dictated by the phase equilibria. Even though this multiplicity makes the material complicated, CIGS nevertheless tolerates defects and impurities by self-adjusting its chemistry and microstructure [3]. In our laboratory, we are investigating the thin-film growth mechanisms using our so-called “three-stage process.” The electronic properties of thin-film CIGS devices made from films as they transition from Cu-rich to In(Ga)-rich, and for low Ga contents, are the subject of this work. Devices made from these films were analyzed using deep level transient spectroscopy (DLTS) and capacitance-voltage measurements (C-V).

EXPERIMENTAL

The CIGS thin films were deposited by physical vapor deposition in a multisource bell jar system. A three-stage growth process was used for this deposition (see Fig. 1). This process consists of: (1) the formation of an (In,Ga)₂Se₃ layer on Mo-coated soda-lime glass substrates heated to 400°C; followed by (2) the deposition of Cu and Se at about 550°C, at which point the compound formation and crystallization of Cu(In,Ga)Se₂ takes place with the additional formation of Cu_{2-x}Se as a secondary phase; and (3) the addition of more In, Ga, and Se at the same temperature, so that the final composition expected is slightly Cu-poor.

Our approach is to interrupt the film growth at predetermined points along the film growth pathway. The thin-film samples from which the devices were made are labeled **a** through **d** and are indicated in Fig. 1. Sample **a** is Cu-rich and Sample **d** is In(Ga)-rich. The compositions are given in Table 1. The thin-film samples **a**, **b**, **c**, and **d** were treated by NaCN for about 5 min to remove the Cu_{2-x}Se secondary phase [4,5]. Devices were made from these NaCN-treated thin-film samples. CdS was deposited by CBD and ZnO, and the front contacts were deposited by sputtering. Another device was made from the untreated In-rich thin-film sample (which will be referred to as **d'**).

RESULTS AND DISCUSSION

The electronic properties of ZnO/CdS/Cu(In,Ga)Se₂ (CIGS)/Mo/SLG polycrystalline thin-film solar cells made from samples **a** through **d** (where the film transitions from Cu-rich to In(Ga)-rich) were investigated by DLTS and C-V measurements. In our p-type CIGS material, an electron (minority-carrier) trap is defined as the one tends to be empty of electrons (minority carriers), and thus capable of capturing them [6]. Similarly, a hole (majority-carrier) trap is one that tends to be full of electrons (minority carriers), and thus capable of having a trapped electron recombine with a hole, i.e., capture a hole [6]. For DLTS measurements, carriers are introduced using a bias pulse, changing the electron occupation of a trap. The junction capacitance increases as the electron occupation of the trap increases [6]. In this study, we used the DLTS

technique to measure the activation energy (which is approximately the energy distance from the conduction or the valance band to the trap level) and the trap concentration. The DLTS spectra measured with a reverse voltage $V=-0.4$ V; trap-filling pulses of amplitude V of 0.5 V; and a saturation pulse width of 1 ms are shown in Fig. 2. Figure 2a shows the DLTS data for samples **a-d'**. Table 2 summarizes the DLTS and C-V data. For sample **a**, the signal shows a negative peak (at a temperature of about 120 K), identifying the defect A_1 as a hole trap in the bulk of the Cu-rich CIGS. Also, it shows a beginning of a positive peak (at a temperature of about 300 K), identifying a defect D_1 as a deeper electron trap in the bulk of the Cu-rich sample. For sample **b**, the signal shows a negative peak (at a temperature of about 210 K), identifying a defect A_2 as a hole trap in the bulk of the near-stoichiometry CIGS sample. For sample **c**, the signal shows a positive peak (at a temperature of about 230 K), identifying a defect D_2 as an electron trap in the bulk of the less stoichiometric CIGS. For sample **d**, the signal has two positive peaks (at temperatures of about 120 and 260 K, respectively), identifying the defects D_3 and D_4 as electron traps in the bulk of In(Ga)-rich CIGS. For sample **d'**, the signal shows a positive peak (at a temperature of about 230 K), identifying a defect D_5 as an electron trap in the bulk of the untreated In-rich CIGS. The heights of the peaks in Fig. 2 are proportional to their respective trap concentration [6]. Trap A_1 in Fig. 2a (sample **a**) with a concentration of about $2.1 \times 10^{14} \text{ cm}^{-3}$ yields the dominant emission in Cu-rich CIGS in the observed temperature and frequency range. However, trap D_1 could not be resolved without heating the sample above room temperature and possibly changing its properties. Traps A_2 (sample **b**), D_2 (sample **c**), and D_5 (sample **d'**) in Fig. 3a, with concentrations of 1.1×10^{13} ,

6.6×10^{11} , and $1.4 \times 10^{13} \text{ cm}^{-3}$, respectively, yield the dominant emission in the observed temperature and frequency range.

Trap D_3 (sample **d**) in Fig. 2a, with a concentration of about $7.2 \times 10^{13} \text{ cm}^{-3}$, yields the dominant emission in In(Ga)-rich CIGS in the observed temperature and frequency range. Trap D_4 (sample **d**) has a concentration of $2.1 \times 10^{12} \text{ cm}^{-3}$, which is small compared to the concentration of trap D_3 . From Fig. 2b, traps A_1 , and A_2 exhibit activation energies of 0.12 and 0.28 eV (from the valance band), respectively, whereas traps D_2 , D_3 , D_4 , and D_5 exhibit activation energies of 0.47, 0.12, 0.25, and 0.63 eV (from the conduction band), respectively. Figure 3a shows the C-V measurements for samples **a-d'**. The average carrier concentrations (N values) for the four samples were deduced from Fig. 2b. These concentrations were found to be: 4.8×10^{16} , 7.5×10^{15} , 4.8×10^{15} , 7.9×10^{16} , $1.4 \times 10^{16} \text{ cm}^{-3}$ (for samples **a**, **b**, **c**, **d**, and **d'** respectively-see Fig. 1). We see that the N values change as the film transitions from Cu-rich (sample **a**) to In(Ga)-rich (sample **d**).

Table 1. Compositions for Samples **a-d'**, (') before NaCN Treatment.

Sample #	Cu/(In+Ga)	Ga/(In+Ga)
a'	1.24	0.19
a	1.02	0.19
b	0.95	0.24
c	0.93	0.26
d'	0.90	0.28
d	0.90	0.28

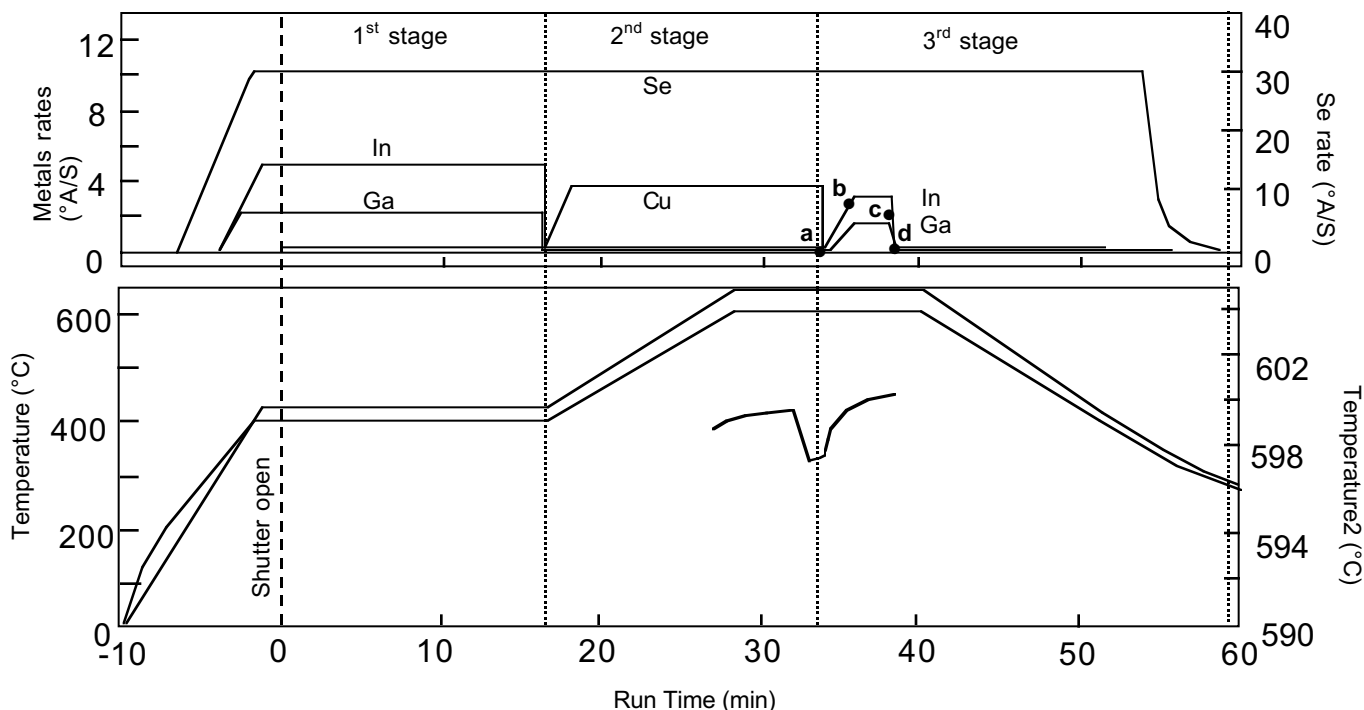


Fig. 1. Schematic Profile of the 3-stage Growth Process.

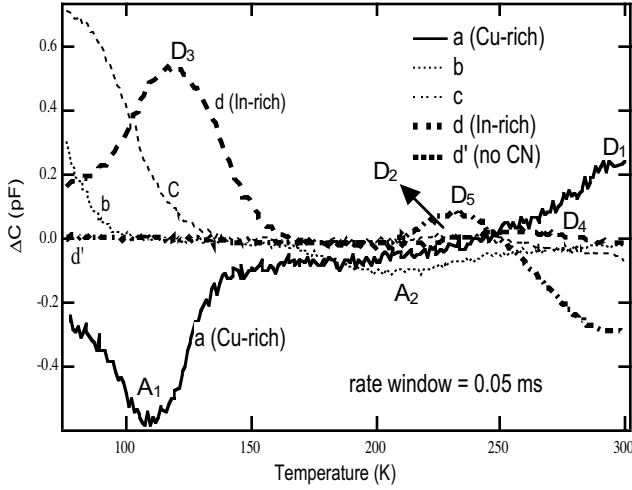


Fig. 2a. DLTS data for samples (a-d'). (') before NaCN treatment.

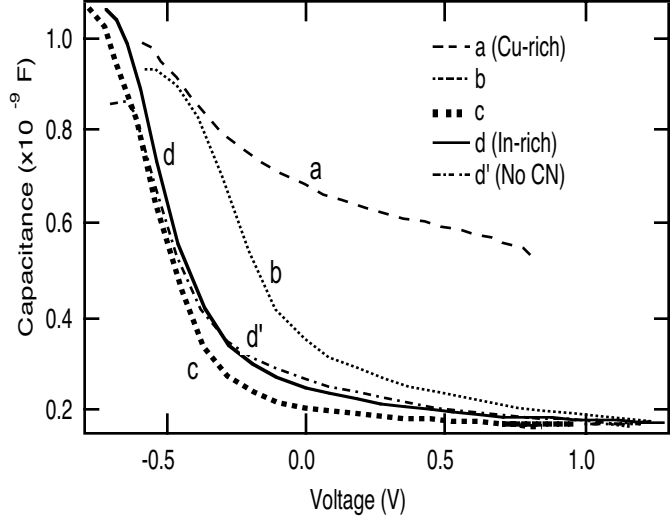


Fig. 3a. C-V data for samples a-d'.

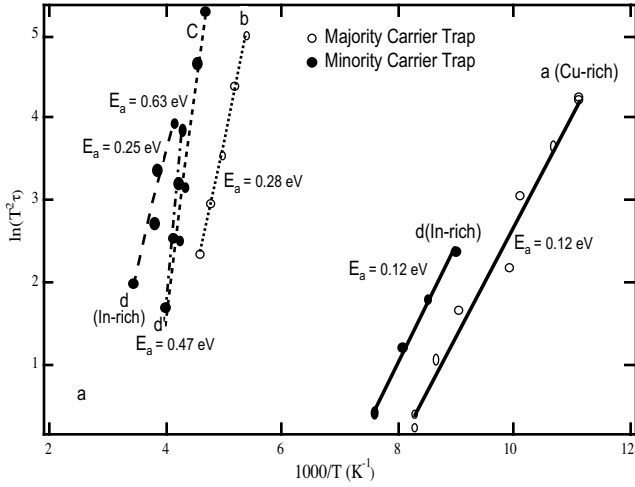


Fig. 2b. Arrhenius plots of $\ln(T^2\tau)$ vs. $1000/T$ for samples (a-d'). (T: temperature, τ : time constant).

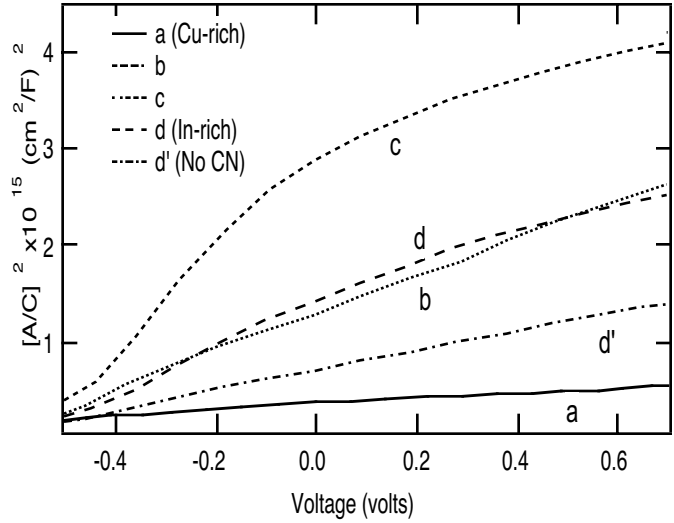


Fig 3b. $[A/C]^2$ vs. applied voltage for samples (a-d'). (A: area, C: capacitance)

Table 2. Summary of DLTS and C-V Data for Samples (a-d').

Sample #	Trap Label	Approximate Peak Temperature (K)	Activation Energy (eV)	DLTS Peak	Trapped Carrier Type	N (cm ⁻³) (from C-V)	# of Traps (cm ⁻³)
a	A ₁	110	0.12	negative	Majority	4.8e+16	2.0e+14
b	A ₂	210	0.28	negative	Majority	7.5e+15	1.1e+13
c	D ₂	230	0.47	positive	Minority	4.8e+15	6.6e+11
d	D ₃	120	0.12	positive	Minority	7.9e+15	7.2e+13
	D ₄	260	0.25	positive	Minority		2.1e+12
d'	D ₅	230	0.63	positive	Minority	1.4e+16	1.4e+13

From the discussion above, we see that acceptor-like traps are dominant in samples **a** and **b**, while donor-like traps are dominant in samples **c**, **d**, and **d'**. In samples **a** and **b**, the Cu_{2-x}Se phase exists on the surface and between the grains of the CIGS before the NaCN treatment [4,5]. We believe that the presence of this phase triggers the generation of the majority of the acceptor-like traps in these samples [4,5]. The transition from Cu-rich to In(Ga)-rich causes an extensive transformation of intrinsic defects such that donor-like traps become dominant in the In(Ga)-rich films; **c**, **d**, and **d'**. This transformation is manifested in the switching of the DLTS peaks from negative ΔC in sample **a** to positive ΔC in sample **d**.

SUMMARY

We find that in the "three-stage process," the growth kinetics, substrate temperature profile, and reaction time will make the outcome of local equilibria unique to the growth process. Cu content in CIGS thin films is important for defect dynamics. Evolution of the intrinsic native defects depends on the dynamics of the reaction pathway, i.e., the compositional changes that occur when the film transitions from Cu-rich to In(Ga)-rich. This method of fabricating CIGS thin films in our laboratory and others, has demonstrated CIGS-based thin-film devices with efficiencies approaching 19%. From this study, we conclude that acceptor-like traps are dominant in samples where CIGS grains did not go through the Cu-rich to In(Ga)-rich transition. While donor-like traps are dominant in the In(Ga)-rich samples.

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