April 2003 • NREL/CP-520-33953

Conference Paper

A Barrier to Trap Filling in $CuIn_{1-x}Ga_xSe_2$

Preprint

D.L. Young, K. Ramanathan, M. Contreras, J. AbuShama, and R.S. Crandall

To be presented at the 2003 Materials Research Society Spring Meeting
San Francisco, California
April 21-25, 2003

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

A Barrier to Trap Filling in $CuIn_{1-x}Ga_xSe_2$

David L. Young, Kannan Ramanathan, Miguel Contreras, Jehad AbuShama, Richard S. Crandall
National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401

ABSTRACT

Voltage pulses of variable length were applied to $CuIn_{1-x}Ga_xSe_2$/CdS ($0 < x < 1$) junction solar cells. The resulting transient capacitance emission signal was recorded for several minutes. The amplitude of the capacitance emission signal increased linearly with the log of pulse time. These data do not follow the standard model for trap capture and emission of carriers. Instead they follow a simple electrostatic model based on electrostatic charging of traps.

INTRODUCTION

The $CuIn_{1-x}Ga_xSe_2$ material system is one of the leading candidates for low-cost absorbers for thin-film solar cells achieving efficiencies over 19% [1]. Device performance correlates with the density [2,3] and energy [4] of defect levels detected by capacitance techniques with a maximum efficiency occurring at $x \sim 0.3$. Theoretical studies have assigned defect transition energy levels in the bandgap to specific crystalline defects[5]. However, metastabilities in the material system complicate the assignments of experimental and theoretical defect levels [6-10].

The nature of electronic traps is commonly studied using deep-level transient spectroscopy (DLTS) methods. DLTS approaches can determine defect energy levels relative to band edges (majority or minority trap), as well their trapping cross-section (σ) [11,12]. The charge emission-rate and σ are important quantities for determining whether a defect functions as a recombination center or a shallow trap. This knowledge is especially important for photovoltaic (PV) materials because recombination limits the available photocurrent of the solar cell.

The most reliable method to determine σ is to measure the density of trapped charge as a function of trap-filling pulse time (t_p) in a junction device structure. The density of filled traps (N_f) should increase linearly with time at short t_p and finally saturate when charge is being emitted as fast as it is being captured. This process should obey the following equation [11]: $N_f(t) = N_o\left(1 - e^{-\frac{t_p}{\tau_c}}\right)$, where N_o is the saturated defect density and τ_c is the characteristic time containing σ.

This paper outlines a failed attempt to determine σ in $CuIn_{1-x}Ga_xSe_2$ using the above equation. Instead we find that $N_s(t)$ obeys the expression: $N_s(t) = A_o \ln\left(1 + \frac{t_p}{t_o}\right)$, where A_o is a constant and t_o is a characteristic time. Similar behavior was observed in a-Si [13], GaAs [14], and $Ge_{0.3}Si_{0.7}$/Si [15]. A model [13] explaining these results is based on the realization that the traps are clustered, rather than uniformly distributed. Trap-filling charges these regions thus producing a potential barrier to further filling.

MATERIAL PREPARATION

Thin films of p-type $CuIn_{1-x}Ga_xSe_2$ were grown by co-evaporation using a "3-stage" process [16] onto molybdenum-coated, soda-lime glass substrates. Diodes were formed by depositing a thin film of n-type CdS by chemical-bath deposition onto the $CuIn_{1-x}Ga_xSe_2$ layer. Devices were completed with an intrinsic ZnO layer and a conducting ZnO:Al layer, followed by Ni/Al contact grids. Isolation of individual cells was achieved by mechanical scribing to define an active region of about 0.43 cm^2.

CAPACITANCE MEASUREMENT

The junction of a $CuIn_{1-x}Ga_xSe_2$/CdS solar cell device is thought to be p^-/n^+, thus confining the depletion region mainly to the $CuIn_{1-x}Ga_xSe_2$ layer. To determine the charge trapped on metastable defects in the $CuIn_{1-x}Ga_xSe_2$ material, we apply the familiar junction-capacitance method [11]. The experimental procedure is as follows: First, a reverse bias of - 0.5 V is applied for several hours to allow the device to come to a steady state. Next, a - 0.1 V bias pulse of varying length (t_p = 10^{-6} - 10^3 s) injects charge into the depletion width. Following the pulse, the - 0.5 V bias is immediately reapplied. Immediately following the bias pulse, the capacitance (C(t)) is recorded for five to seven decades of time until C(t) returns to its initial value, C_o. The voltage, acquisition triggering, and time are computer controlled. The capacitance is determined using a lock-in amplifier (Stanford Instruments Model 850) calibrated with a standard capacitor in place of the sample. Usually, the applied ac test signal is 10 kHz at 0.03 V rms. The initial capacitance is recorded before each pulse, giving the baseline value C_o. Data were collected at a rate of 50,000 samples/second. Signal averaging and storing data only at logarithmic time intervals reduces the data set to a more manageable size. For the data presented here, devices were measured in the dark at room temperature. The capacitance change during the transient ($\Delta C = C(t)-C_o$) is converted to trap density (N_s) by using the relation [11] $N_s = 2N_o\Delta C/C_o$, with N_o the total defect density.

DATA

Figure 1 shows a series of ΔC transients with t_p ranging from 10^{-6} to 10^3 s for an x ~ 0.3 device. The dominant feature in Fig. 1 is the increasing amplitude of the majority-carrier [11] emission transient with increasing t_p. The data were fit with two stretched exponentials with characteristic time constants of milliseconds and seconds at room temperature. Figure 2 shows the initial amplitude of the change in capacitance following the filling pulse divided by the initial capacitance, C_o, versus the pulse time, t_p. The initial amplitude of the change in the capacitance was measured 10^{-3} s after the end of the pulse to

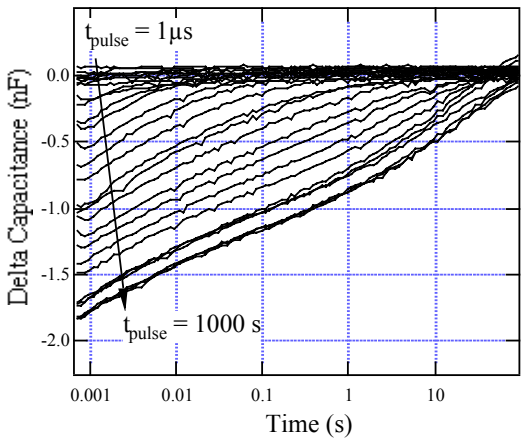

Figure 1. Change in capacitance vs. time following a voltage pulse. t_{pulse} varies from 1 µs to 1000 s, with three logarithmically separated pulse times per decade of time.

ensure lock-in amplifier recovery. Note that each factor of 10 increase in t_p results in the same linear increase in capacitance amplitude. The increasing amplitude with pulse width is likely due to partial filling of the states with short pulse times. An apparent saturation of the signal occurs only for pulse times $t_p > 10^2$ s. Samples with x = 1, 0 also show the log(t_p) dependence and apparent saturation behavior.

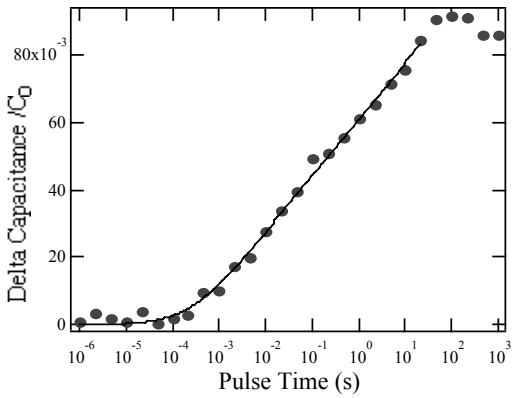

Figure 2. $\Delta C/C_o$ vs voltage pulse time. Circles are data points. The dark line is a fit to the data by equation 3.

THEORY

Following the work with a-Si [13] we assume the $CuIn_{1-x}Ga_xSe_2$ material is inhomogeneous and filled with a random distribution of clustered traps. During the filling pulse, these traps acquire charge that increases with time. However, a Coulomb repulsion energy barrier builds over time, which hinders further trapping of charge. The potential of the trap is $\Phi = N_s f$, where N_s is the density of the carriers captured by the trap during the filling time, t_p, and f is a model-dependent coupling factor. N_s varies with time for the filling of traps according to the first-order rate equation,

$$\frac{dN_s}{dt} = nW_{filling}\langle N_o - N_s(t)\rangle, \qquad (1)$$

where n in the density of valence-band holes, N_o is the total density of traps, and $W_{filling}$ is the filling probability having units of cm^3/s and related to σ via $W_{filling} = \sigma\langle v_T\rangle$, where $\langle v_T\rangle$ is the average thermal velocity of the carriers. The equilibrium defect levels, N_o, were measured by drive-level capacitance profiling [17] at the equilibrium bias used for the voltage pulse experiments (-0.5 V). If n is a constant, eqn (1) has a trivial solution. However, as the traps become charged, n is reduced in the vicinity of the charge distribution. If we assume the carrier density follows a Boltzmann distribution with n_o the carrier density far from the trap, then eqn (1) reduces to

$$\frac{dN_s(t)}{dt} \approx W_{filling}N_o n_o \exp\left(-\frac{e\Phi}{k_B T}\right) = W_{filling}N_o n_o \exp\left(\frac{-eN_s f}{k_B T}\right), \qquad (2)$$

where k_B is Boltzmann's constant and T is absolute temperature. Forcing all traps to be empty at $t = 0$ ($N_s(0) = 0$) and relating $N_s(t)$ to capacitance via the depletion-width approximation [11,18] gives

$$\frac{\Delta C}{C_o} = A_o Ln\left(1 + \frac{t_p}{t_o}\right), \qquad (3)$$

with constants

$$A_o = \frac{k_B T}{2 N_o e f} \quad \text{and} \quad t_o = \frac{2 A_o}{n_o W_{filling}}. \tag{4}$$

DISCUSSION

Figure 2 shows the fit to the data by eqn. (3). Similar excellent fits are common for both $CuInSe_2$ and $CuGaSe_2$ samples. Table I gives fit parameters for several $CuIn_{1-x}Ga_xSe_2$ samples. Clearly, the amplitude of the change in capacitance varies as the natural log of the voltage pulse length. This same relationship was found by Crandall on a-Si solar cells [13] and by Wosinski et al. [14] in plastically deformed GaAs, but without the saturation in signal at long pulse times. Grillot *et al.* [15] found that $Ge_{0.3}Si_{0.7}$/Si heterostructures followed eqn. (3), with signal saturation strongly dependent on sample preparation. However, this trend is in clear contrast to similar data taken on Ge bicrystals, where the amplitude of the change in capacitance varied according to a power law of t_p, and did saturate at long pulse times [19]. It is interesting to note the greater similarity of our polycrystalline material data to that of the amorphous material and the deformed GaAs, as opposed to the Ge bicrystal. Perhaps a comparison of the defects in each of these materials to those in $CuIn_{1-x}Ga_xSe_2$ [5] will shed light on the origin of the observed traps in this material system.

Table I. Fit and calculated parameters

Sample ($CuIn_{1-x}Ga_xSe_2$)	A_o	t_o	N_o (cm^{-3}) (-0.5 V)	Radius (nm)	n_o (cm^{-3})	σ (cm^2)
S2051 (x = 0.3)	7.34×10^{-3}	3.86×10^{-4}	5×10^{16}	18	5×10^{16}	8×10^{-23}
S2038 (x = 0.3)	9.68×10^{-3}	9.89×10^{-3}	4.2×10^{15}	55	4×10^{14}	4×10^{-22}
Sc1391 (x = 1.0)	7.28×10^{-3}	2.36×10^{-4}	2.2×10^{17}	9	8×10^{16}	7×10^{-23}
S2044 (x = 0.0)	1.70×10^{-2}	6.81×10^{-3}	1.57×10^{16}	22	2×10^{16}	3×10^{-23}

If we assume the charging centers are spherical (as opposed to say, parallel cylinders), then the coupling factor becomes, $f = eR^2/3\varepsilon$, where e is the elemental charge, R is the radius of the sphere, and ε is the dielectric constant of the material. With f so defined the constant A_o may be related to the radius of the spherical traps. Table I gives the calculated radii of these hypothetical traps. The calculated radial dimensions of the hypothetical charging spheres are of the same order of magnitude as the smallest polycrystalline "grains" seen by Romero *et al*. using scanning electron microscopy images and by spectrally resolved cathodoluminescence data [20]. Their data show a shallow defect concentrated on the outer "skin" of the grains. This dimensional coincidence may imply that the charging is taking place at the surface of the grains. Single-crystal samples need to be tested to verify this.

Capture cross-sections for the observed traps may be calculated from the fit parameters A_o and t_o ((eqn (4)) and the definition of $W_{filling}$ given earlier. Table I gives the calculated cross-sections of the samples. Obviously, they are surprisingly small, but do agree somewhat with DLTS data [21]. Perhaps either the meaning of cross-section for this trap needs to be reconsidered or the small cross-sections for the capture of carriers on these traps may imply they

are benign in terms of device performance. Alternatively, the small, calculated cross-section could be due to a repulsive barrier superimposed onto the charging barrier from the traps [22]. More detailed study of this effect is ongoing.

Finally, the data of Figs. 1 and 2 have significant implications for the applicability of the traditional DLTS technique for the $CuIn_{1-x}Ga_xSe_2$ material system. The decays of Fig. 1 are neither exponential nor do they represent a single defect. A single exponential decay is a main assumption in DLTS theory. The data of Fig. 2 imply that the traps are not saturated during typical DLTS pulse lengths. Nonsaturation of traps during a DLTS "filling pulse" gives erroneous trap densities.

REFERENCES

1 K. Ramanathan et al. Accepted for publication, Progress in Photovoltaics, 2003.
2 G. Hanna, A. Jasenek, U. Rau, and H. W. Schock, Thin Solid Films 387, 71-73 (2001).
3 R. Herberholz, M. Igalson, and H. W. Schock, J. Appl. Phys. 83, 318-325 (1998).
4 J. T. Heath, J. D. Cohen, W. N. Shafaman, D. X. Liao, and A. A. Rockett, Appl. Phys. Lett. 80, 4540-4542 (2002).
5 S. B. Zhang, S.-H. Wei, and A. Zunger, Physical Review B 57, 9642-9656 (1998).
6 M. Igalson and P. Zabierowski, Thin Solid Films 361-362, 371-377 (2000).
7 V. Nadazdy, M. Yakushev, E. H. Djebbar, A. E. Hill, and R. D. Tomlinson, J. Appl. Phys. 84, 4322-4326 (1998).
8 U. Rau, M. Schmitt, and J. Parisi, Appl. Phys. Lett. 73, 223-225 (1998).
9 A. E. Delahoy, A. Ruppert, and M. Contreras, Thin Solid Films 361-362, 140-144 (2000).
10 J. Abushama, S. Johnston, R. Ahrenkiel, and R. Noufi, in *Deep level transient spectroscopy and capacitance-voltage measurements of Cu(In,Ga)Se$_2$*, New Orleans, LA, 2002 (IEEE), p. 740-743.
11 D. V. Lang, in *Thermally Stimulated Relaxation in Solids*, edited by P. Braunlich (Springer-Verlag, New York, 1979).
12 D. V. Lang, J. Appl. Phys. 45, 3014-3022 (1974).
13 R. S. Crandall, Journal of Electronic Materials 9, 713-726 (1980).
14 T. Wosinski, A. Morawski, and T. Figielski, Appl. Phys. A 30, 233-235 (1983).
15 P. N. Grillot, S. A. Ringel, E. A. Fitzgerald, G. P. Watson, and Y. H. Xie, J. Appl. Phys. 77, 3248-3256 (1995).
16 U.S. Patent No. 5,436,204 (1995).
17 C. E. Michelson, A. V. Gelatos, and J. D. Cohen, Appl. Phys. Lett. 47, 412-414 (1985).
18 G. L. Miller, D. V. Lang, and L. C. Kimerling, in *Annual Review of Materials Science*; *Vol. 7*, edited by R. A. Huggins, R. H. Bube, and R. W. Roberts (Annual Reviews, Palo Alto, 1977), p. 377.
19 A. Broniatowski and J.-C. Bourgoin, Physical Review Letters 48, 424-427 (1982).
20 M. J. Romero, K. Ramanathan, M. A. Contreras, M. M. Al-Jassim, J. Abushama, and R. Noufi, in *Mesoscopic fluctuation in the distribution of electronic defects near the surface layer of Cu(In,Ga)Se$_2$*, Solar Program Review Meeting, Denver, CO, 2003 (U.S. Department of Energy).
21 J. A. AbuShama, Thesis, Colorado School of Mines, 2003.
22 R. S. Crandall, Spring MRS Symp. B, B2.5 (2003).

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 2003	Conference paper

4. TITLE AND SUBTITLE
A Barrier to Trap Filling in $CuIn_{1-x}Ga_xSe_2$: Preprint

5. FUNDING NUMBERS
PVP34901

6. AUTHOR(S)
D.L. Young, K. Ramanathan, M. Contreras, J. AbuShama, and R.S. Crandall

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

8. PERFORMING ORGANIZATION REPORT NUMBER
NREL/CP-520-33953

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words):* Voltage pulses of variable length were applied to $CuIn_{1-x}Ga_xSe_2$/CdS ($0 < x < 1$) junction solar cells. The resulting transient capacitance emission signal was recorded for several minutes. The amplitude of the capacitance emission signal increased linearly with the log of pulse time. These data do not follow the standard model for trap capture and emission of carriers. Instead they follow a simple electrostatic model based on electrostatic charging of traps.

14. SUBJECT TERMS: PV; voltage pulses; trap filling; deep-level transient spectroscopy (DLTS); chemical-bath deposition; junction-capacitance; spectrally resolved cathodoluminescence (SRCL);

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL