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## Effect of Ga content on defect states in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ photovoltaic devices

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Defects in the band gap of  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  have been characterized using transient photocapacitance spectroscopy. The measured spectra clearly show response from a band of defects centered around 0.8 eV from the valence band edge as well as an exponential distribution of band tail states. Despite Ga contents ranging from  $\text{Ga}/(\text{In} + \text{Ga}) = 0.0$  to 0.8, the defect bandwidth and its position relative to the valence band remain constant. This defect band may act as an important recombination center, contributing to the decrease in device efficiency with increasing Ga content. © 2002 American Institute of Physics. [DOI: 10.1063/1.1485301]

Transient photocapacitance spectroscopy (TPC) has been used to study defect state distributions in the band gap of  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS). This technique is sensitive to optical absorption in the active layer of a complete  $p^+n, n^+p$ , or Schottky device, provided that one contact is partially transparent. Because this is the natural configuration for a photovoltaic device, TPC is ideal for studying photovoltaic materials like CIGS.

Photovoltaic devices based on thin polycrystalline CIGS absorbers have achieved record lab efficiencies of 18.8%.<sup>1</sup> The Ga content in this material can be adjusted to vary the band gap, with optimum band gaps for single junction solar cells expected to be around 1.4 eV.<sup>2</sup> This corresponds to a Ga fraction  $x \approx 0.6$ , with  $x = \text{Ga}/(\text{In} + \text{Ga})$ . Higher Ga material would also be useful as a component of multi-junction or graded band gap cells. However, the best devices to date contain material with  $x = 0.2$ , and it is difficult to obtain high-efficiency devices when  $x$  exceeds 0.4. One study has shown this to be due to a reduced minority carrier mobility in the higher Ga materials.<sup>3</sup> In this letter, we identify a previously unobserved deep defect lying in the upper part of the energy gap which may be responsible for a reduction in the minority carrier mobility-lifetime product  $(\mu\tau)_e$ . We believe this defect is likely to be a more significant minority carrier trap than the 0.3 eV defect commonly identified using admittance spectroscopy.<sup>4,5</sup>

The polycrystalline devices discussed here were grown at the Institute of Energy Conversion at University of Delaware (IEC). CIGS films were grown about 2  $\mu\text{m}$  thick using four-source elemental evaporation, which has been discussed previously.<sup>6</sup> Films were deposited on soda-lime glass which had been coated with a 1  $\mu\text{m}$  Mo layer. To form devices, chemical bath deposition was used to deposit 30–40 nm of CdS, then ZnO:Al was sputtered to form the top contact, with evaporated Ni/Al grids. Samples were prepared with  $x$

ranging from 0.0 to 0.8, as determined by energy dispersive x-ray spectroscopy. Auger depth profiles on devices grown using this process have shown uniform Ga profiles.<sup>6</sup>

An additional epitaxial single crystal sample was also studied. This film was grown at University of Illinois on a (110) oriented GaAs substrate as is discussed in detail elsewhere.<sup>7,8</sup> The CdS and ZnO top contacts were added at IEC using the same methods as for the polycrystalline samples. This single crystal sample has  $x \approx 0.3$ .

Device performance parameters for all samples are listed in Table I, along with the diode quality factor  $A$  and forward current  $J_0$ . The range of  $A$  values (1.5–1.8) is consistent with Shockley–Read–Hall recombination in the CIGS absorber through a distribution of deep defects such as those identified later in this letter.

The TPC technique has been discussed in detail elsewhere.<sup>9</sup> This technique is based on detection of the transient capacitance response to a voltage filling pulse. The capacitance transient arises from the release of trapped carriers out of defect levels within the depletion region. This response is represented as a single number by integrating over a fixed time window. The difference between transient signals measured in the presence of weak monochromatic light and those in the dark, normalized by the photon flux, gives the photocapacitance signal.

The interpretation of a TPC signal at first glance resembles that for optical absorption. One contribution to the signal  $P$  can be written

$$P(E_{\text{opt}}, T) = K_P(T) \int_{E_V + E_e}^{E_V + E_{\text{opt}}} \langle i | e x | f \rangle^2 g(E) g_V(E - E_{\text{opt}}) dE, \quad (1)$$

where  $\langle i | e x | f \rangle$  represents the optical matrix element,  $g(E)$  is the density of defect states,  $g_V(E)$  is the density of states in the valence band,  $E_{\text{opt}}$  is the optical excitation energy, and  $E_V$  is the energy at the valence band edge.  $E_e$  is the thermal escape depth of trapped holes for the time window used,

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TABLE I. Summary of device results. All samples listed are polycrystalline, except for the last entry which is a single crystal device. Values of  $A$  and  $J_0$  were calculated from dark  $J$ - $V$  measurements, except as marked.

Ga/(In+Ga)	$E_g$ (eV)	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	eff (%)	$A$	$J_0$ (mA/cm <sup>2</sup> )	$n/p$	$N_D$ (a.u.)	$E_U$ (meV)
0.0	1.0	36.7	0.46	66.5	9.5	1.7 <sup>a</sup>	$6.2 \times 10^{-5a}$	0.97	2	18
0.3	1.18	30.0	0.63	77.3	14.7	1.5	$3.8 \times 10^{-7}$	0.99	0.4	23
0.45	1.29	29.1	0.72	72.5	15.2	1.7	$2.5 \times 10^{-7}$	0.97	0.3	19
0.65	1.42	23.5	0.80	68.7	12.9	1.6	$6.2 \times 10^{-9}$	0.65	0.4	21
0.8	1.53	16.3	0.82	65.9	8.8	1.8	$3.3 \times 10^{-8}$	0.63	0.7	24
0.3 (crys)	1.18	27.7	0.42	55.0	6.3	...	...	...	...	26

<sup>a</sup>These data were calculated from  $J$ - $V$  measurements under illumination.

$E_e = k_B T \ln(\nu\tau)$ , with temperature  $T$ , delay time  $\tau$ , and attempt to escape frequency  $\nu$ . The proportionality constant,  $K_p$ , is temperature and time-window dependent, and also incorporates sample-dependent variations in signal magnitude including effects of the carrier mobilities and the electric field distribution. Note that (1) only takes into account transitions between the valence band and empty defect levels. A complete formula for  $P$  would also contain analogous terms for transitions between filled defect levels and the conduction band.

Two important differences should be noted between the expression for the TPC signal and that for optical absorption. The first is the dependence on  $E_e$ , due to the thermal escape of carriers in shallow traps before the time window commences. Since the corresponding portion of the response is absent from the TPC spectrum, a comparison of spectra taken over a range of temperatures can simultaneously yield the optical and thermal activation energies for a particular defect band. Although this aspect of the technique has been demonstrated, such changes in the spectra can be difficult to interpret.<sup>10</sup>

A second important difference between optical absorption and TPC spectra is the dependence of  $P$  on  $\mu\tau$ . Since changes in capacitance are due to *net* charge change within the sample, in  $p$ -type material  $P$  will be proportional to the *difference*  $p-n$ , where  $p$  is the number of holes collected and  $n$  the number of electrons. Thus, the TPC signal will be small when pairs of majority and minority carriers are optically excited, and  $\mu\tau$  is similar for both carrier types.

A complimentary measurement to TPC, transient photocurrent spectroscopy (TPI) is based on the detection of a current, instead of capacitance, transient. The TPI signal is proportional to *total* collected carriers  $p+n$ . Comparisons of TPI and TPC spectra can thus yield the ratio  $n/p$ , which, assuming that all optically generated holes are collected, corresponds to the fraction of optically generated minority carriers which are collected. From this value and the magnitude of charge density in the depletion region,  $(\mu\tau)_e$  can be estimated. This technique has been utilized previously in  $a$ -Si:H.<sup>9</sup>

The data included in the figures were all recorded at 150 K under similar conditions. Samples were held at 1 V reverse bias, and subjected to 50 ms filling pulses to 0 V bias. The transient response to this voltage pulse was integrated over a boxcar of width 250 ms, centered 275 ms from the start of the transient. Since the capacitance transient response is enhanced by the presence of light (the TPC signal is positive), the observed transitions result from the optical excitation of

trapped holes from the defects to the valence band. Spectra have also been collected using a range of reverse biases and filling pulses. By studying the effect of these parameters on TPC signal magnitude, we have verified that the subband gap response does not originate from the thin, fully depleted CdS layer.

A comparison between TPC spectra of the single crystal device and the polycrystalline device of comparable Ga content is shown in Fig. 1. These spectra are remarkably similar despite the differences in substrate and growth technique. Clearly, the deep defect response does not originate solely from grain boundaries, but is characteristic of the bulk material. However, the single crystal sample does show an additional defect response in the energy regime near 1.0 eV, which is not observed in polycrystalline material. The band-tail slope in CIGS materials, as characterized by the Urbach energy  $E_U$ , has been linked to the degree of structural disorder including disorder due to deviations from stoichiometry.<sup>11</sup> The value of  $E_U$  measured by TPC and TPI corresponds to the broader of the conduction or valence band edges. In these devices,  $E_U$  does *not* seem to be strongly affected by the grain boundaries.

By obtaining TPC spectra over a range of temperatures we have verified that the 0.8 eV defect is unlikely to correspond to the predominant hole trap observed using admittance techniques, which has a thermal activation energy between 0.1 and 0.3 eV. Such trap states are indeed observed in the admittance spectra of all of our samples.<sup>5</sup> However, TPC spectra obtained at 250 K, which should not contain response from this defect, are identical to those taken at 110 K, which certainly should. Moreover, the relative magnitudes of the

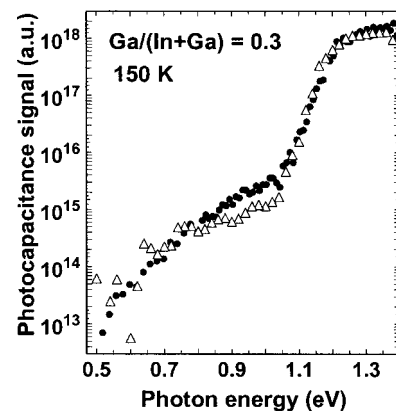


FIG. 1. Transient photocapacitance spectra for single crystal (closed symbols) and polycrystalline (open symbols) devices show a similar deep defect response.

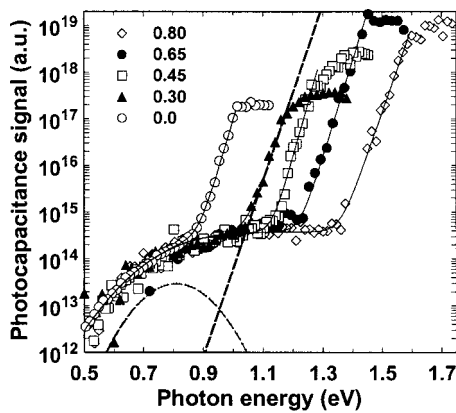


FIG. 2. Transient photocapacitance spectra from polycrystalline samples with Ga contents ranging from  $\text{Ga}/(\text{In}+\text{Ga})=0$  to 0.8 have been aligned to emphasize the similarity of the deep defect response. Fits (solid lines) are obtained from integrating, using Eq. (1), over a single Gaussian defect band, centered at 0.8 eV, plus an exponential band of tail states. These are shown in dashed lines for the  $\text{Ga}/(\text{In}+\text{Ga})=0.3$  sample.

two defects are not correlated. One might wonder why the defect observed by admittance spectroscopy is not also detected by TPC. Most likely, the optical energy to excite holes from this trap into the valence band lies below 0.4 eV, further into the infrared than we are currently able to observe.

TPC spectra for devices with a range of Ga contents are shown in Fig. 2. These spectra have been aligned to emphasize the similarity of the deep defect response. They have all been fit using the same Gaussian deep defect band, centered at  $0.8 \pm 0.05$  eV with width 0.13 eV, plus an exponential distribution of tail states.

The fact that this transition is independent of Ga fraction is consistent with the behavior predicted for many classes of defects in CIGS, including metal vacancies and metal antisite defects.<sup>12</sup> However, the observed 0.8 eV transition energy does not match any of the theoretical predictions. In photoluminescence studies of  $\text{CuInS}_2$  and  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  a similar defect transition, near 0.86 eV, has been detected.<sup>13</sup>

By taking values of  $n/p$  into account and assuming that the optical cross section and densities of states for the band-to-band transition are similar for all samples, relative values of the defect density,  $N_D$ , can be estimated. These are listed in Table I. Using values of charge density in the depletion region measured by drive level capacitance profiling,<sup>5</sup>  $(\mu\tau)_e$  has been estimated to be within a factor of three of  $2 \times 10^{-9}$   $\text{cm}^2/\text{V}$  for all the polycrystalline samples.<sup>14</sup> Unfortunately, a TPI spectrum could not be obtained for the single crystal sample due to excessive dark current.

Although the defect density associated with the 0.8 eV transition does not change systematically with Ga content, it approaches midgap in the high Ga material as illustrated in Fig. 3. This means it would become a much more efficient

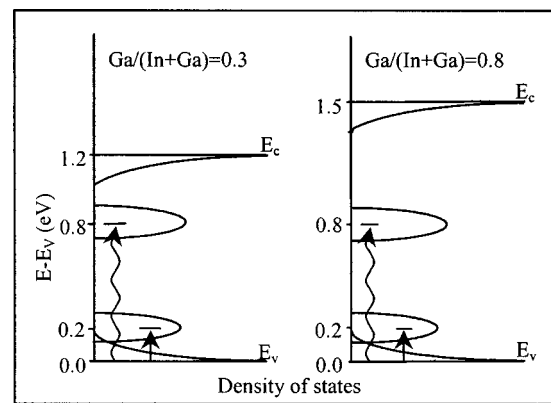


FIG. 3. Schematic of observed defect bands in low and high Ga alloys. Optical transitions are shown with wavy lines and thermal transitions with straight lines. The thermal transition, shown here at 0.2 eV, actually varies from 0.1 to 0.3 eV depending on the sample.

recombination center in the high Ga alloys. A study currently underway focuses on a series of samples all with  $x=0.3$  but with varying device performance. Hopefully this will help us better understand the impact of this deep defect on devices.

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