Kesterites and Chalcopyrites: A Comparison of Close Cousins

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Ingrid Repins, Nirav Vora, Carolyn Beall,
Su-Huai Wei, Yanfa Yan, Manuel Romero,
Glenn Teeter, Hui Du, Bobby To, Matt Young,
and Rommel Noufi

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Kesterites and Chalcopyrites: A Comparison of Close Cousins

Ingrid Repins, Nirav Vora, Carolyn Beall, Su-Huai Wei, Yanfa Yan, Manuel Romero, Glenn Teeter, Hui Du, Bobby To, Matt Young, Rommel Noufi
National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, U.S.A.

ABSTRACT

Chalcopyrite solar cells based on CuInSe_2 and associated alloys have demonstrated high efficiencies, with current annual shipments in the hundreds of megawatts (MW) range and increasing. Largely due to concern over possible indium (In) scarcity, a related set of materials, the kesterites, which comprise $\text{Cu}_2\text{ZnSnS}_4$ and associated alloys, has received increasing attention. Similarities and differences between kesterites and chalcopyrites are discussed as drawn from theory, depositions, and materials characterization. In particular, we discuss predictions from density functional theory, results from vacuum co-evaporation, and characterization via x-ray diffraction, scanning electron microscopy, electron beam-induced current, quantum efficiency, secondary ion mass spectroscopy, and luminescence.

INTRODUCTION

Chalcopyrite solar cells have progressed from first proof of concept on melt-grown crystals [1] to high-efficiency thin-film laboratory devices [2,3] to manufacturing presently in the hundreds of MW range. Manufacturing volumes are expected to push into the gigawatt (GW) range in coming years due to the combination of relatively high efficiency (compared to CdTe or α -Si) and potentially low processing costs (compared to single-crystal Si).

As production volumes increase, concern has arisen as to whether limits in the world supply of In will restrict the amount of chalcopyrite photovoltaics that can be manufactured at low cost. While the current cost of In adds only 1 to 10 ¢/Watt to the price of module manufacturing [4], a tenfold increase in In price would be problematic for the necessary sub-\$1/W manufacturing cost. Estimates of when In scarcity will become important to module prices range in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) manufacturing volumes from 4 GW/yr to over 100 GW/yr [4,5,6,7]. If estimates of 4 GW/yr are correct, In scarcity could impact the industry within 10 years. If estimates of over 100 GW/yr are correct, and multiple technologies continue to be close in cost, In scarcity may not impact the photovoltaic industry.

To mitigate possible future effects of In scarcity, it has been proposed that CIGS can be replaced by $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ in the kesterite structure, in which every two group III (In or Ga) atoms in chalcopyrite structure are replaced by a Zn (group II) and Sn atom (group IV), thus maintaining the octet rule. To date, solar cells with up to 9.7% efficiency [8] have been made using these In-free kesterite absorbers. In our work with the co-evaporation of chalcopyrites and kesterites, we have observed both similarities and differences between absorbers made using these closely related crystal structures. Several aspects of this comparison are discussed in the sections below.

PREDICTIONS FROM DENSITY FUNCTIONAL THEORY

Structural, electronic, and defect properties of both kesterites and chalcopyrites have been investigated using density functional theory [9] (DFT). These examinations have revealed both similarities and differences between kesterites and chalcopyrites.

Positions of conduction and valence band edges have been calculated for both kesterites and chalcopyrites [10,11,12], as shown in Table I for CuInSe₂ (CISe), Cu₂ZnSnSe₄ (CZTSe), CuInS₂ (CIS), and Cu₂ZnSnS₄ (CZTS). In the table, positions of conduction and valence band edges are shown relative to vacuum, where the relative band offsets have been calculated from DFT, and the experimental value of the electron affinity for CISe, 4.6 eV [13], is taken from experiment. For the selenides and sulfides, the kesterite band gaps are very similar to (slightly less than) the corresponding chalcopyrite band gaps. Furthermore, each material maintains a reasonable alignment with the CdS conduction band at -4.3 eV, explaining the success of the CdS/i-ZnO/ZnO:Al buffer and window layers in finishing both chalcopyrite and kesterite devices. It should be noted that for both the chalcopyrite and the kesterite, other crystal structures with the same stoichiometry exist. For I-III-VI₂ compounds, a chalcopyrite or CuAu-like structure may form. For I₂-II-IV-VI₄ compounds, a kesterite, stannite, or primitive mixed CuAu structure may form. However, DFT calculation predicts that the chalcopyrite and kesterite structures are the lowest energy configuration for the materials considered here [14].

Table I. Calculated band gaps, valence band edges, and conduction band edges (relative to vacuum) for selenide and sulfide chalcopyrites and kesterites.

Material	E _g (eV)	E _v (eV)	E _c (eV)
CISe (chalcopyrite)	1.04	-5.64	-4.60
CZTSe (kesterite)	1.00	-5.56	-4.56
CIS (chalcopyrite)	1.53	-5.92	-4.39
CZTS (kesterite)	1.50	-5.71	-4.21

The stability of single-phase stoichiometric material has been calculated as a function of the chemical potential of constituent atoms for both chalcopyrites [15] and kesterites [16]. For CuInSe₂, single-phase material can occur for Cu chemical potentials $-0.4 < \mu_{\text{Cu}} < 0$ eV and the corresponding In chemical potential $-0.4 < \mu_{\text{In}} < -1.8$ eV. For CZTS, single-phase material occurs only at a much smaller chemical potential space around ($\mu_{\text{Cu}} = -0.20$ eV, $\mu_{\text{Zn}} = -1.23$ eV, and $\mu_{\text{Sn}} = -0.50$ eV). It is thus predicted that constraints on forming stoichiometric CZTS are more strict for kesterites than for chalcopyrites.

Chemical defects impose further limits on compositions or reaction paths that may yield high-efficiency solar cells. Because there is one more element in the kesterite structure than in the chalcopyrite structure, there are a larger number of possible intrinsic defects for CZTS and related compounds than for CIS. Formation energies and transition energy levels within the gap have been calculated for the 13 dominant defects that do not involve the unlikely situation of a

cation on an anion lattice site or vice versa [11]. Of these 13 defects, five have relatively low formation energy for Cu-poor kesterite. These five low-formation-energy defects are, in order of increasing formation energy: copper on zinc site (denoted Cu_{Zn}), copper vacancy (denoted V_{Cu}), Zn_{Sn} , V_{Zn} , and Cu_{Sn} . The formation energy of Cu_{Zn} is significantly lower than that of V_{Cu} and Zn_{Sn} , predicting that Cu_{Zn} should be the dominant intrinsic defect for CZTS. The predicted abundance of Cu_{Zn} is a different situation than for the chalcopyrite, where V_{Cu} is the lowest formation energy defect [15] and is responsible for the p-type doping. The Cu_{Zn} acceptor level is predicted to lie about 0.1 eV above the valence band maximum (VBM), as opposed to the shallower acceptor V_{Cu} (0.02 or 0.03 eV above the VBM in the kesterite or chalcopyrite, respectively). Since $kT \approx 0.025$ eV at room temperature, the fraction of the dominant acceptors ionized may be significantly different in the kesterite than in the chalcopyrite. For both the chalcopyrite [17] and the kesterite [11], n-type doping is predicted to be unlikely due to the high formation energy of the donor defects and low formation energy of acceptor defects.

For both chalcopyrites and kesterites, low-formation-energy defects with energy levels deep within the gap exist, but may be largely benign due to the formation of defect complexes. For CISE, the most important defect for carrier recombination is predicted to be In_{Cu} due to both its low formation energy and its predicted level 0.34 eV below the CBM [15]. However, the electronic activity of this defect is to some extent passivated by the formation of $[\text{2V}_{\text{Cu}} + \text{In}_{\text{Cu}}]$ defect complexes [15]. Of the five low-formation-energy defects previously mentioned for CZTS, Cu_{Sn} is expected to be the most active recombination center, with an energy level close to mid-gap, ~ 0.6 eV above the VBM [11]. As is the case for CISE, DFT calculations predict that charge-compensated defect complexes such as $[\text{Cu}_{\text{Sn}} + \text{Sn}_{\text{Cu}}]$ are likely to form and passivate deep levels in the kesterites [11]. The dominant defect complex in CZTS is $[\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}]$. However, unlike in CISE, where the formation of $[\text{2V}_{\text{Cu}} + \text{In}_{\text{Cu}}]$ defect complexes leads to charge-separated α and β phases [17], the formation of $[\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}]$ does not have this possibly beneficial effect observed in chalcopyrite compounds.

The effects of alloying CZTS and CZTSe have also been investigated using DFT calculations [18]. It is shown that the enthalpy of formation for the $\text{CZT}(\text{S}_{1-x}\text{Se}_x)$ is very small, indicating that the mixed-anion alloys are highly miscible, and that the cations maintain the same ordering preferences as in pure kesterites. The band gaps of the random alloy decrease with Se content almost linearly. The conduction band down-shift contributes more to the gap decrease than the valence band up-shift. The shift of the band edges makes the $\text{CZT}(\text{S}_{1-x}\text{Se}_x)$ alloys with high Se concentration easier to be doped both n-type and p-type. The balance between the band gap size and the doping ability may therefore be important in determining the optimal alloy composition to achieve high-efficiency $\text{CZT}(\text{S}_{1-x}\text{Se}_x)$ -based solar cells.

FILM DEPOSITION

Co-evaporation of CIGS films at the National Renewable Energy Laboratory (NREL) and their incorporation into device structure has been previously discussed in detail [19]. To make kesterite films and devices, identical procedures were followed, except that In and Ga shot were replaced in the evaporator by Zn and Sn shot, and appropriate optical filters (202.55 nm for Zn and 284.0 nm for Sn) were substituted for the Ga and In filters in the electron impact emission spectrometer rate monitor. For devices discussed in this study, anti-reflective coating was *not* applied.

The two types of CZTSe recipes used for films in this study are shown in Figure 1. In all depositions, rates and temperatures were stabilized, then a substrate shutter was opened at time = 0. Substrate temperature was held constant in the range of 470-500°C throughout the deposition. Temperature variations within this range are noted in the text when discussing different samples. Deposition temperatures are relatively low, due to decomposition of the kesterite at temperatures typically used during CIGS formation [20]. Depositions lasted about 20 minutes. In all cases, Se and Sn were supplied in overpressure throughout the deposition, similar to the conditions for Se flux during CIGS deposition. Cu and Zn fluxes were supplied in two variations. In the first variation, shown in Figure 1a, Cu and Zn fluxes are constant throughout the deposition period. Thus, the Cu/Zn and Cu/(Zn+Sn) atomic ratios in the film are constant with time. This type of deposition is analogous to “one-stage” depositions used for CIGS. In the second type of recipe, shown in Figure 1b, the Cu rate is increased so that Cu/Zn and Cu/(Zn+Sn) can be greater than one during most of the deposition, and yet the final film can be Cu-poor. We observe during such depositions that the Cu-rich or Cu-poor character of the film is indicated by emissivity signature [21], in much the same way as for CIGS films, presumably due to the effects of excess copper selenide.

Figure 1. Schematic representation of recipes used for samples in this study. For CIGS, these types of recipes are commonly called a) “one-stage” and b) “two-stage.”

A summary of the composition measurements for the samples described in this paper is shown in Table II. Compositions are shown in terms of atomic ratio. Film compositions were measured by x-ray fluorescence (XRF) calibrated against inductively coupled plasma optical emission spectrometry (ICP-OES). The table also shows the recipe type for each sample (either one-stage or two-stage) and the figure in which data for each sample is presented. X-ray diffraction, Raman spectroscopy, energy dispersive spectroscopy, and resistance measurements were used to confirm that the films in this paper are kesterites, with the occasional ZnSe precipitate in Zn-rich samples. The results and application of these phase identification techniques to co-evaporated CZTSe will be discussed in a separate publication [22].

Table II. Summary of compositions and recipe types for films used in this study.

Sample	Zn/Sn	Cu/(Zn+Sn)	Cu/Sn	Recipe type	Figure in which sample is characterized
M3214	1.2	1.0	2.15	One-stage	Figure 3a
M3250	1.35	0.8	1.9	One-stage	Figure 3b
M3253	1.0	0.85	1.7	Two-stage	Figure 2a
M3251	1.2	0.95	2.0	Two-stage	Figure 2b
M3272	1.1	0.95	2.0	Two-stage	Figure 2c
M3268	1.2	0.85	1.8	Two-stage	Figure 2d
M3257	1.05	0.9	1.9	Two-stage	Figure 4
M3215	0.75	1.2	2.1	One-stage	Figure 5
M3244	1.1	0.9	1.9	Two-stage	Figure 6, Figure 8

MORPHOLOGY

Parallels are observed in the morphology versus vacuum growth conditions of chalcopyrites and kesterites. These similarities include increasing grain size with both temperature and occurrence of a Cu-rich growth period.

Grain size in CIGS films increases with temperature [23]. CZTSe films in this study have shown a similar trend. Figure 2 shows scanning electron micrograph (SEM) images of CZTSe films grown under nearly identical conditions, except for increasing substrate temperature. The compositions for these films, as measured by x-ray fluorescence (XRF), are also listed in Table I. Feature size in the SEM images increases with substrate temperature. Note that the temperature range in Figure 2 is considerably narrower than that which has been examined for CIGS [23]. The films of Figure 2b and Figure 2d, with the highest Zn/Sn ratios in the sample set, begin to show segregation of ZnSe, which is evident as the bright spots near the Mo in the SEM images. Energy dispersive spectroscopy (EDS), used to examine these bright spots while the films are mounted in the electron microscope, confirms that the bright spots are mostly Zn and Se. For the films in this study, the increase in grain size with temperature did not yield an increase in device performance.

Figure 2. SEM cross-sections of CZTSe films grown under nearly identical conditions, except for varying substrate temperatures of a) 468°C , b) 486°C , c) 492°C , or d) 502°C .

Chalcopyrite films have been documented to exhibit increased grain sizes when a period of Cu-rich (i.e., $\text{Cu}/(\text{In}+\text{Ga}) > 1$) growth is included in the deposition [24,25,26]. This improved grain growth has been associated with a flux recrystallization of chalcopyrite grains by a liquid Cu_xSe phase. In the present work, kesterite films have been observed to exhibit a similar dependence on Cu-rich vs. Cu-poor growth. Figure 3 shows two kesterite films made under nearly identical conditions. For both, the substrate temperature was about 490°C , and a one-stage recipe was utilized. However, for the film in Figure 3a, Cu rate was chosen such that the $\text{Cu}/(\text{Zn}+\text{Sn})$ ratio just exceeds one. For the film in Figure 3b, Cu rate was chosen such that the $\text{Cu}/(\text{Zn}+\text{Sn})$ ratio was always below one. The film grown under Cu-rich conditions exhibits considerably larger grain size. Other researchers have also observed large grain sizes under Cu-rich growth conditions [27,28]. For the film in Figure 3a, a sodium cyanide etch was used to remove excess copper selenide prior to acquiring the SEM image.

The relationship between Cu ratio and grain size for CZTSe films is likely multi-variate and should be investigated more fully. It has been shown for CIGS that the amount of benefit obtained via a Cu-rich growth period is a function of deposition temperature [23]. Furthermore,

a marked dependence of CZTSe grain size on temperature is demonstrated in Figure 3. Variations in composition other than Cu excess may also have an effect on morphology.

Figure 3. SEM cross-section of CZTSe films grown at the same temperature and constant deposition fluxes, except Cu rates were adjusted to produce only a) Cu-rich growth or b) Cu-poor growth.

COMPOSITION PROFILES

Figure 4 shows Auger emission spectroscopy (AES) profiling of a CZTSe film that yielded 4.4% devices. In Figure 4a, the entire film thickness (1.5 μm) is shown. Composition is fairly constant throughout the bulk. Figure 4b expands the near-surface region of the same data, plotted this time in terms of atomic ratio, in order to examine trends in the constituent elements without seeing effects from several atomic percent oxygen or carbon at the surface. It is evident in Figure 4b that, while the amount of Zn and Sn in the film is constant, the amount of Cu drops considerably near the surface. The two minutes of sputtering time over which this drop occurs corresponds to roughly 70 nm. Cu-poor surfaces are also observed in CIGS [29].

Figure 4. AES profile of a) entire film and b) near-surface region.

Secondary ion mass spectrometry (SIMS) profiling was used to compare the amount of Na in standard CIGS with that in the CZTSe films. Na is known to be important in CIGS devices for increasing free carrier density and decreasing recombination [30,31]. Positive secondary data are shown compared for CIGS (thin dashed lines) and CZTSe (thick solid lines) in Figure 5. For both films, Se makes up $\sim 50\%$ of the lattice, and Se counts are normalized to 10^3 to allow for comparison of amounts of other elements. The CZTSe film is only half the thickness of the CIGS film, so the SIMS data is horizontally offset so that the back contact (i.e., the area of Mo signal increase) lines up for both films. The CZTSe film contains much less Na than the CIGS, as might be expected from the necessarily lower deposition temperature, since diffusion through the Mo is the main barrier to Na inclusion in CIGS [32]. Determining from device results whether the optimum amount of Na in CZTSe is the same as that in CIGS should be an area of future examination.

Figure 5. SIMS data comparing CIGS (thin dashed lines) and CZTSe (thick solid lines).

ELECTRO-OPTICAL CHARACTERISTICS

Both CIGS and CZTSe samples have been mapped using electron beam-induced current (EBIC) and cathodoluminescence (CL). The methodology and apparatus used for luminescence microscopy has been described in earlier publications [33].

To examine the effect of morphology on carrier collection, cross-sectional SEM images and cross-sectional electron beam induced current (EBIC) maps were compared between CIGS and CZTSe. Figures 6a and b show typical SEM and EBIC images for a $\sim 16\%$ -efficient CIGS device. The dotted lines in Figures 6a and b are benchmarks to indicate the same physical location on the sample in each image. Also shown in Figure 6b is a linescan, i.e., an x-y representation of the image brightness at the location where the linescan is drawn. The salient feature of Figures 6a and b is that the response is basically constant as the electron beam moves away from the junction, although grain boundaries and an occasional grain show reduced response. Figures 6b and c show the same type of characterization for a 4.1% CZTSe device. Carriers are collected only within tenths of a micron of the junction, and this response length is nonuniform over the sample. The data in Figure 6 imply that improving collection length is extremely important in early work in improving CZTSe devices.

This conclusion is consistent with quantum efficiency (QE) data taken on progressively improving devices in this study. The QE data are shown in Figure 7 and show increasing red collection with improving efficiency. A 20.0%-efficient CIGS device is also shown in Figure 7 for comparison. The minimal red loss (i.e. flat QE from ~ 700 -900 nm) is apparent in the CIGS device, in strong contrast with the kesterite devices shown. Also evident is the difference in band gap between the CIGS and CZTSe (wavelength at which QE approaches 0) and the lack of anti-reflective coating on the CZTSe devices ($\sim 5\%$ reduction in maximum QE).

CL images of the surface of CZTSe films were also compared with those from CIGS. Several aspects of this comparison are consistent with the high recombination center density indicated by the EBIC and the QE. First, the intensity of the luminescence is about two orders of magnitude lower for the CZTSe than for the CIGS. Second, the materials show a different behavior in emitted photon energy with increasing CL current. This comparison is shown in Figure 8. CL as a function of excitation current for CIGS of 1.15 eV band gap is shown in figure 8a, and that for CZTSe is shown in Figure 8b. Figure 8b was taken on the same material used to make the 4.1% device of Figure 6. For both CZTS and CIGSe, the spectrum consists of a broadband luminescence associated with transitions between donor and acceptor defect bands. The electronic states participating in the formation of these bands are deeper for CZTSe (~ 0.2 eV below the band gap) than CIGS (~ 0.1 eV below the band gap). The spectrum shows a significant blueshift with the external excitation (measured by the electron beam current) for both chalcopyrites and kesterites. This blueshift is due to the filling of the bands while increasing the excitation. We observe that (i) the blueshift is much more pronounced for CIGS than CZTSe, and (ii) there is a saturation of the bands at high excitation in CIGS (confirmed by the change in the shape of the peak with the e-beam current for CIGS), which is not observed in CZTSe. Thus, not only are the dominant intrinsic defects leading to the formation of these bands deeper in energy for CZTSe when compared to CIGS but, based on these measurements, the density of these defects is much higher in CZTSe.

Figure 6. a) SEM and b) EBIC cross-sections for CIGS; and c) SEM and d) EBIC cross-sections for CZTSe.

Figure 7. QE for CZTSe devices of various efficiencies.

Figure 8. CL spectrum as a function of CL current for a) CIGS and b) CZTSe.

CONCLUSIONS

A comparison of chalcopyrites and kesterites yields both significant similarities and differences. Theory predicts similar band edge energies, p-type doping, formation of benign defect complexes, and miscibility of alloys. However, theory also predicts differences: a smaller single-phase composition space and a different dominant intrinsic defect. During vacuum co-evaporation, the chalcopyrites and kesterites can be made using nearly identical equipment, recipes, and endpoint detection. However, co-evaporation of the kesterites requires

Sn (not just Se) overpressure and lower temperatures. Kesterites and chalcopyrites both show an increase in grain size with temperature and with a Cu-rich growth period. A Cu-poor surface is observed in both types of film, although the universality of this observation has not been tested for the kesterites. The kesterite deposition recipes used in this study result in much less Na in the absorber than in optimized CIGS films, as might be expected from the necessarily lower deposition temperature. The kesterite films in this study show evidence of short diffusion lengths, in sharp contrast with good CIGS devices. This evidence of increased activity of recombination centers is evident in cross-sectional EBIC, QE, and CL.

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REFERENCES

1. S. Wagner, J. L. Shay, and P. Migliorato, *Appl. Phys. Lett.* **25**(8), 434-435 (1974).
2. P. Jackson, D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, R. Menner, W. Wischmann, M. Powalla, *Prog. Photovoltaics*, DOI: 10.1002 (2011).
3. I. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, B. To, and R. Noufi, *Prog. Photovoltaics* **16**, 235–239 (2008).
4. V. Fthenakis, *Renew. Sust. Energ. Rev.* **13**, 2746–2750 (2009).
5. T. Sullivan, W.H. Kuo, P. Karayan, M. LoCascio, M. Holman, S. Udupa, B. Hilman, A. Stuk, “Solar State of the Market Q3 2008: The Rocky Road to \$100 Billion,” *LRSI-SMR-08-02*, (Lux Research, 2008).
6. A. Feltrin, A. Freundlich, *Renew. Energ.* **33**, 180–185 (2008).
7. B.A. Andersson, *Prog. Photovoltaics* **8**, 61-76 (2000).
8. T. K. Todorov, K. B. Reuter, D. B. Mitzi, *Adv. Mater.* **22**, 1-4 (2010).
9. G. Kresse, J. Furthmuller, *Comp. Mater. Sci.* **6**(1), 15-50 (1996).
10. S. Chen, X.G. Gong, A. Walsh, S.H. Wei, *Appl. Phys. Lett.* **94**, 041903 (2009).
11. S. Chen, J.H. Yang, X.G. Gong, A. Walsh, S.H. Wei, *Phys. Rev. B* **81**, 245204 (2010).
12. S.H. Wei, A. Zunger, *J. Appl. Phys.* (6), 3846-3856 (1995).
13. N. Romeo, *Jpn. J. Appl. Phys.* **19-3**, 5-13, (1980).
14. D.S. Su, S.H. Wei, *Appl. Phys. Lett.* **74**(17), 2483-2485 (1999).
15. S. B. Zhang, S.H. Wei, A. Zunger, H. K. Yoshida, *Phys. Rev. B* **57**(16), 9642-9656 (1998).
16. S. Chen, X.G. Gong, A. Walsh, S.H. Wei, *Appl. Phys. Lett.* **96**, 021902 (2010).
17. S.H. Wei, B. Zhang, *J. Phys. Chem. Solids* **66**, 1994 (2005).
18. S. Chen, A. Walsh, J.-H. Yang, X.-G. Gong, L. Sun, P.-X. Yang, J.-H. Chu, and S.-H. Wei, *Phys. Rev. B* **83**, 125201 (2011).
19. A.M. Gabor, “The conversion of (In,Ga)₂Se₃ thin films to Cu(In,Ga)Se₂ for application to photovoltaic solar cells,” *PhD thesis*, (University of Colorado, 1995), pp. 42-49.
20. A. Weber, R. Mainz, H.W. Schock, *J. Appl. Phys.* **107**, 013516 (2010).
21. J. Kessler, J. Scholdstrom, L. Stolt, *IEEE Phot. Spec. Conf.* **28**, 509-512(2000).

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22. N. Vora et al, in progress.
 23. W.N. Shafarman, J. Zhu, *Mater. Res. Soc. Symp. P.* **668**, H2.3.2-H2.3.6 (2001).
 24. A.M. Gabor, J.R. Tuttle, D.S. Albin, M.A. Contreras, R. Noufi, *Appl. Phys. Lett.* **65** (2), 198-200 (1994).
 25. R.A. Mickelsen, W.S. Chen, Y.R. Hsiao, V.E. Lowe, *IEEE Transactions on Electron Devices* **ED-31** (5), 542-546 (1984).
 26. J.R. Tuttle, M.A. Contreras, M.H. Bode, D. Niles, D.S. Albin, R. Matson, A.M. Gabor, A. Tennant, A. Duda, R. Noufi, *J. Appl. Phys.* **77** (1), 153-161 (1995).
 27. B.A. Schubert, B. Marsen, S. Cinque, T. Unold, R. Klenk, S. Schorr, H.W. Schock, *Prog. Photovoltaics* **19** (1), 93-96 (2011).
 28. T. Tanaka, A. Yoshida, D. Saiki, K. Saito, Q. Guo, M. Nishio, T. Yamaguchi, *Thin Solid Films* **518**, S29-S33 (2010).
 29. S.H. Han, F.S. Hasoon, A.M. Hermann, D.H. Levi, *Appl. Phys. Lett.* **91**, 021904 (2007).
 30. J.E. Granata, J.R. Sites, *World Conf. Photo. Sol. Energ. Conv.* **2**, 604-607 (1998).
 31. D. Rudmann, "Effects of sodium on growth and properties of Cu(In,Ga)Se₂ thin films and solar cells," *PhD thesis*, (Swiss Federal Institute of Technology, 2004).
 32. M.B. Zellner, R.W. Birkmire, E. Eser, W.N. Shafarman, J.G. Chen, *Prog. Photovoltaics* **11**, 543-548 (2003).
 33. M.J. Romero, M.A. Contreras, I. Repins, C.S. Jiang, M.M Al-Jassim, *Mater. Res. Soc. Symp. P.* **1165**, 419-424 (2010).