Why can CuInSe₂ be readily equilibrium-doped n-type but the wider-gap CuGaSe₂ cannot?

Yu-Jun Zhao, Clas Persson, a) Stephan Lany, and Alex Zunger b)
National Renewable Energy Laboratory, Golden, Colorado 80401
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The wider-gap members of a semiconductor series such as diamond → Si → Ge or AlN → GaN → InN often cannot be doped n-type at equilibrium. We study theoretically if this is the case in the chalcopyrite family CuGaSe₂ → CuInSe₂, finding that: (i) Bulk CuInSe₂ (CIS, $E_g = 1.68$ eV) can be doped at equilibrium n-type either by Cd or Cl, but bulk CuGaSe₂ (CGS, $E_g = 1.68$ eV) cannot; (ii) result (i) is primarily because the Cu-vacancy pins the Fermi level in CGS farther below the conduction band minimum than it does in CIS, as explained by the “doping limit rule”; (iii) Cd doping is better than Cl doping, in that CdCu yields in CIS a higher net donor concentration than ClSe; and (iv) in general, the system shows massive compensation of acceptors (CdIn⁺, VCu) and donors (ClSe, Cu₂⁺, InCu⁺). © 2004 American Institute of Physics. [DOI: 10.1063/1.1830074]

Solar cells based on CuInSe₂ are highly successful (approaching 20% efficiency), even in polycrystalline form, because of their remarkable electronic tolerance to a high concentration of stoichiometric defects to and to the presence of surprisingly benign grain boundaries. To achieve higher efficiencies, however, wider-gap absorber materials are needed, the primary candidate being alloying of CuGaSe₂ (CGS, $E_g = 1.04$ eV at room temperature) into CuInSe₂ (CIS, $E_g = 1.68$ eV). However, the device need for a region of normally p-type absorber becoming n-type (“type inversion”) poses a severe restriction on alloying CIS with CGS, for while CIS can be made n-type (via InCu⁺, ZnCu and Cu₂⁺ or ClSe⁺), it proved difficult to do so for CGS. The difficulty to n-dope CGS is another example of the general trend [11,12] that wider-gap members of a semiconductor series often resist n-type doping. Well-known examples [11] being the difficulty to n-dope diamond, but not Si or Ge; the difficulty to n-dope AIN, but not GaN or InN, etc. It was recently discovered [11,13] (“doping-limit rule”) that on a fundamental level this trend reflects the position of a material-intrinsic “n-type pinning level” $E_{\text{pin}}^n$, rather than the band gap itself. Using first-principles total energy calculations, we study here the microscopic mechanism limiting n-type doping in CGS/CIS. We consider both cation-site donors CdCu and anion-site donors ClSe.

We start by describing qualitatively the appropriate doping rules. They are based on the observation that the concentrations of either intrinsic defects such as $D = V_{\text{Cu}}$, $\text{In}_{\text{Cu}}$ or of dopant impurities, $D = \text{CdCu}$ or $\text{ClSe}$, depend on their formation energies $\Delta H_{D,q}$ for charge state $q$, and that the latter depends both on Fermi level $E_F$ and the chemical potentials $\Delta \mu_a$ of all species $a$ present:

$$\Delta H_{D,q}(E_F, \mu) = (E_{D,q} - E_H) + q(E_V + E_F) + \sum_a n_a \mu_a. \quad (1)$$

The first term is the change in total energy due to the defect formation calculated here as a total-energy difference of a large supercell with versus without the defect; all atoms are relaxed. The second term describes the carrier reservoir in equilibrium: It shows that $\Delta H$ of ionized donors ($q > 0$) increases as $E_F$ rises in the gap, since electrons are added to the Fermi reservoir, whereas $\Delta H$ of ionized acceptors ($q < 0$) decreases as $E_F$ rises in the gap, since electrons are removed from the Fermi reservoir. The third term describes the chemical reservoir in equilibrium, where the chemical potential $\mu_a = \Delta \mu_a + \mu_a^{\text{elem}}$ of the atomic species $a$ is given with respect to the elemental phase of $a$. We see that $\Delta H$ of Cu vacancies increases as the Cu chemical potential $\mu_{\text{Cu}}$ rises since the removed Cu atoms are added ($n_a = +1$) to the Cu reservoir; on the other hand, $\Delta H$ of Cd substitution decreases as $\mu_{\text{Cd}}$ rises since the incorporated Cd atoms are removed ($n_a = -1$) from the Cd reservoir.

Figure 1 details for chalcopyrites the basic “doping rules” [11] for n-type doping either via cation-site or anion-site substitution. These rules determine which growth conditions, according to Eq. (1), minimize the formation energies $\Delta H$ of wanted defects, and maximize $\Delta H$ of unwanted defects. We illustrate in the following these rules for Cd doping of CIS: (1) Solubility. Maximal incorporation of Cd into the CIS lattice requires lowering $\Delta H_{\text{CdCu}}$. This means, according to...
Eq. (1), Cu-poor (i.e., low $\Delta \mu_{\text{Cd}}$) and dopant-rich (i.e., maximal $\Delta \mu_{\text{Cd}}$) growth conditions.

2. Competing phases. The formation of unwanted dopant-host atom compounds, such as CdSe, lowers $\Delta \mu_{\text{dopant}}$ by consuming Cd. To maintain maximal $\Delta \mu_{\text{Cd}}$ needed in rule (1), one needs host-anion-poor conditions, i.e., low $\Delta \mu_{\text{e}}$.

3. Killer defects. The Cu vacancy $V_{\text{Cu}}$ is an acceptor, which compensates the intended donor doping. By Eq. (1), its formation energy $\Delta H[V_{\text{Cu}}]$ is lowered as the Fermi energy rises in the band gap. At the Fermi energy denoted as $E_{\text{F}}^{\text{site}}$ in Figs. 2 and 3, where $\Delta H[V_{\text{Cu}}]=0$, any further donor doping is compensated by the spontaneous formation of $V_{\text{Cu}}$ [Figs. 2(a) and 3(a)]. For successful doping $E_{\text{F}}^{\text{site}}$ needs to be as high as possible in the gap. This requirement of minimizing the concentration of $V_{\text{Cu}}$ requires Cu-rich growth conditions ($\Delta \mu_{\text{Cd}}=0$).

4. Assisting defects. The antisite In$_{\text{Cu}}^{++}$ or Ga$_{\text{Cu}}^{++}$ is a (double) donor which, when formed, assists the intended n-type doping. By Eq. (1), its formation energy $\Delta H[\text{In}_{\text{Cu}}^{++}]$ is lowered as the Fermi energy moves down in the gap. At the Fermi energy denoted $E_{\text{F}}^{\text{comp}}$ in Fig. 2 we have $\Delta H[V_{\text{Cu}}]+\Delta H[\text{In}_{\text{Cu}}^{++}]$, at which point the intrinsic acceptors tend to compensate the intrinsic donors [see Fig. 2(a)]. For successful n-type doping, $E_{\text{F}}^{\text{comp}}$ needs to be as high as possible in the gap. This requires Cu-poor and In-rich conditions; i.e., low $\Delta \mu_{\text{Cu}}$ and high $\Delta \mu_{\text{In}}$. Figure 2 shows that the energy to form In$_{\text{Cu}}$ in CIS is much lower than the energy to form Ga$_{\text{Cu}}$ in CGS. This reflects the larger gap of CGS, and leads to fewer n-type assisting defects in CGS.

5. Wrong-site substitution. n-type doping by divalent cation requires Cd-on-Cu substitution (a donor), but is hampered by Cd-on-In substitution (an acceptor). Thus, one needs low $\Delta H[\text{Cd}_{\text{Cu}}]$ (low $\Delta \mu_{\text{Cd}}$) and high $\Delta H[\text{Cd}_{\text{In}}]$ (high $\Delta \mu_{\text{In}}$). The Fermi level denoted $E_{\text{F}}^{\text{site}}$ in Fig. 3(a) is the point where $\Delta H[\text{Cd}_{\text{Cu}}]=\Delta H[\text{Cd}_{\text{In}}]$. For successful n-type doping, $E_{\text{F}}^{\text{site}}$ needs to be as high as possible in the gap.

In order to study the limitations of n-type doping, we first determine the optimum growth conditions for n-type doping in CIS and CGS. We note that, considering a broad range of chemical potentials, rules (1)–(5) impose intrinsically conflicting requirements; for example, the Cu-rich conditions required by rule (3) conflict with rules (1), (4), and (5) in case of Cd doping. However, only a limited range of chemical potentials of the host atoms is allowed thermodynamically. Figure 4 shows the phase stability diagram of CIS and CGS, where the outer triangle corresponds to all the $\Delta \mu$ values that satisfy the stability condition for CIS, that is, $\Delta \mu_{\text{Cu}}+\Delta \mu_{\text{Se}}=\Delta H[\text{CuInSe}_2]$ where $\Delta H[\text{CuInSe}_2]$ is the calculated compound formation energy of CIS. The real allowed range (shaded area in Fig. 4) of the $\Delta \mu$ is further narrowed by the formation of competing compounds that can form from the host atoms; for example CuSe and In$_2$Se$_3$. In addition, the maximum dopant chemical potential depends on the host chemical potentials; for example, $\Delta \mu_{\text{Cd}}+\Delta \mu_{\text{Se}}=\Delta H[\text{CdSe}]$ is required by rule (2). Taking into account these restrictions and using maximal $\Delta \mu_{\text{Cd}}$ under these restrictions, we find that maximally Se-poor conditions (denoted “point N” in Fig. 4), fulfill all requirements in case of Cd-doping: (1) $\Delta H[\text{Cd}_{\text{Cu}}]$ is minimal; (2) $\Delta \mu_{\text{Cu}}$ is maximal as allowed by $\Delta \mu_{\text{Cd}}+\Delta \mu_{\text{Se}}=\Delta H[\text{CdSe}]$; (3) $\Delta H[V_{\text{Cu}}]$ is maximal; (4) $\Delta H[\text{In}_{\text{Cu}}]$ is minimal; and (5) $\Delta H[\text{Cd}_{\text{In}}]$ is minimal and $\Delta H[\text{Cd}_{\text{In}}]$ is maximal. Thus, these Se-poor conditions satisfy all doping rules (1)–(5), and resolve the conflicts indicated by the broader chemical potential range of Cu.
tial range of Fig. 1. The “point $N$” conditions are defined by $\Delta \mu_{\text{Cu}} = 0$, $\Delta \mu_{\text{C}} = -0.07$ eV, and $\Delta \mu_{\text{Se}} = -0.83$ eV in CIS, and by $\Delta \mu_{\text{Cu}} = 0$, $\Delta \mu_{\text{Ga}} = -0.21$ eV, and $\Delta \mu_{\text{Se}} = -0.86$ eV. The maximal Cd chemical potentials under these conditions are $\Delta \mu_{\text{Cd}} = -0.21$ eV in CIS, and $\Delta \mu_{\text{Cd}} = -0.18$ eV in CGS. In the case of anion doping, some of the conflicting requirements noted in Fig. 1 do remain: for example, rules (1), (2), and (4) conflict even if we consider the restricted chemical potential range (shaded area in Fig. 4). For Cl doping, the best growth conditions are also those described by “point $N$” in Fig. 4, minimizing $\Delta H$ of In$_{\text{Cu}}$ according to rule (4). Under these conditions, the maximal CI chemical potentials are limited by InCl and GaCl$_3$ formation ($\Delta \mu_{\text{Cl}} = -1.74$ eV in CIS, and $\Delta \mu_{\text{Cl}} = -1.47$ eV in CGS, given with respect to the diatomic Cl molecule; that is, $\mu_{\text{Cl}} = \frac{1}{2} \mu_{\text{Cl}_2}$). In the following, we consider only the “point $N$” growth conditions, which correspond to Cu-rich (equilibrium with metallic Cu), In- or Ga-rich (equilibrium with InSe or GaSe), and Se-poor.

$\Delta H_D$ are determined from Eq. (1), where total energies are calculated within a fully relaxed 64-atom supercell approach, using the pseudopotential-momentum space formalism,\textsuperscript{14}–\textsuperscript{15} projective augmented wave potentials\textsuperscript{15} and the local density approximation (LDA). The underestimate of the CIS and CGS band gap in the LDA has been remedied by adjusting both the energy of the VBM ($E_V$) and that of the conduction band minimum ($E_C$). Here, $E_V$ is shifted down by using the LDA+U method,\textsuperscript{16} which corrects for the underbinding of the Cu–d electrons by fitting U to place the Cu–d band at the photoemission value $E_{\text{V}} = 2.5$ eV, whereas $E_C$ is shifted up by the remaining band-gap error. In addition, the total energies have been corrected for cell-size-dependent effects, as will be described in more detail in a forthcoming paper.\textsuperscript{17} We do not use the truncated multipole expansion of Ref. 18 for image charge correction.

From the defect formation energies, the equilibrium defect concentration is calculated according to $c_{D_{\text{ad}}}(E_F, \mu_{\text{ad}}, T) = N \times \exp(-\Delta H_{D_{\text{ad}}}(E_F, \mu_{\text{ad}})/kT)$, where $N$ is the concentration of atomic sites that are substituted by the defect, the chemical potentials $\mu_{\text{ad}}$ correspond to the growth conditions described earlier (“point $N$”), and $T = 800$ K is a temperature used in the growth of solar cell devices.\textsuperscript{19} Since the defect concentrations depend on $E_F$, and, in turn, $E_F$ depends on the concentrations of both the charged defects and the carriers (electrons and holes), via the requirement of overall charge neutrality, we determine the self-consistent solution that comprises $c_{D_{\text{ad}}}(E_F)$, and the carrier concentration. Using the self-consistently calculated defect concentrations, we define the “net doping balance” $\Delta c = c_{\text{Cu}} + 2c_{\text{Ga}} - c_{\text{Cd}}$ in case of Cl doping, and $\Delta c = c_{\text{Cd}_3} + 2c_{\text{In}_2} - c_{\text{Cd}_2} - c_{\text{Cd}}$ in case of Cd doping. The doping balance $\Delta c$ indicates whether net donor doping ($\Delta c > 0$) or net acceptor doping ($\Delta c < 0$) is obtained.

Figure 2(a) shows, for Cl doping, the calculated defect formation energies as a function of $E_F$ for “point $N$” growth conditions, while Fig. 2(b) shows the ensuing equilibrium defect concentrations at $T = 800$ K. We see that in CIS, $E_F^{\text{nd,comp}}$ and $E_F^{\text{nd,exp}}$ both lie in the upper part of the band gap, thus, a net donor doping $\Delta c > 0$ can be achieved in CIS as shown in Fig. 2(b); $\Delta c = 1 \times 10^{18}$ cm$^{-3}$. In contrast, in CGS, the positions of $E_F^{\text{nd,comp}}$ and $E_F^{\text{nd,exp}}$ are closer to the VBM. This results in a net acceptor doping [Fig. 2(b); $\Delta c = -5 \times 10^{18}$ cm$^{-3}$]. Note that the contribution of ClSe to the net $\Delta c$ is rather small. Figure 3(a) shows $\Delta H_F$ versus $E_F$ for Cd doping in CIS and CGS, again under “point $N$” growth conditions. We see that the equilibrium Fermi level lies higher in the gap compared to Cl. The corresponding defect concentrations [Fig. 3(b)] in CGS show, despite the higher $E_F$, still a negative doping balance $\Delta c = -1 \times 10^{18}$ cm$^{-3}$, indicating a net acceptor excess and the failure of $n$-type doping. In CIS, Cd doping yields a higher net donor concentration $\Delta c = 10^{18}$ cm$^{-3}$ (Ref. 20) than Cl doping [Fig. 3(b)]. We also see from Figs. 2(b) and 3(b) that a high compensation ratio is present in all cases; that is, $\Delta c$ is much lower than the total defect concentration. It is also noted that the defect concentrations depend strongly on growth temperature; for example, for CIS grown under “point $N$” conditions without extrinsic dopants, $\Delta c$ increases from $1 \times 10^{18}$ to $7 \times 10^{18}$ cm$^{-3}$ when $T$ (growth) increases from 800 to 1000 K. At the same time, the calculated electron density at 300 K increases from $2 \times 10^{14}$ to $5 \times 10^{14}$ cm$^{-3}$ as the growth temperature increases from 800 to 1000 K.

In conclusion, in CIS, Cd doping outperforms Cl doping, yielding a higher electron concentration. In CGS, however, $n$-type doping under equilibrium conditions is achieved neither by Cl nor Cd doping, since $n$-type doping is intrinsically hampered by the low formation energy of the electron-killer $V_{\text{Cu}}$.

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