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Why can CuInSe$_2$ be readily equilibrium-doped *n*-type but the wider-gap CuGaSe$_2$ cannot?

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The wider-gap members of a semiconductor series such as diamond$\rightarrow$Si$\rightarrow$Ge or AlN$\rightarrow$GaN $\rightarrow$InN often cannot be doped *n*-type at equilibrium. We study theoretically if this is the case in the chalcopyrite family CuGaSe$_2$$\rightarrow$CuInSe$_2$, finding that: (i) Bulk CuInSe$_2$ (CIS, E_g=1.04 eV) can be doped at equilibrium *n*-type either by Cd or Cl, but bulk CuGaSe$_2$ (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 Cd$_{Cu}$ yields in CIS a higher net donor concentration than Cl$_{Se}$; and (iv) in general, the system shows massive compensation of acceptors (Cd$_{III}$, V$_{Cu}$) and donors (Cl$_{Se}$, Cd$_{Cu}$, In$_{Cu}$). © *2004 American Institute of Physics*. [DOI: 10.1063/1.1830074]

Solar cells based on CuInSe$_2$ are highly successful (approaching 20% efficiency),[1] even in polycrystalline form, because of their remarkable electronic tolerance to a high concentration of stoichiometric defects[2] and to the presence of surprisingly benign[3] grain boundaries. To achieve higher efficiencies, however, wider-gap absorber materials are needed, the primary candidate being alloying of CuGaSe$_2$ (CGS, E_g=1.68 eV at room temperature) into CuInSe$_2$ (CIS, E_g=1.04 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 In$_{Cu}$,[4,5] Zn$_{Cu}$ and Cd$_{Cu}$,[5,6] or Cl$_{Se}$[7]), it proved difficult to do so for CGS.[8–10] 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 AlN, 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" $E_F^{n,pin}$, rather than the band gap itself. Using first-principles total energy calculations,[14] we study here the microscopic mechanism limiting *n*-type doping in CGS/CIS. We consider both cation-site donors Cd$_{Cu}$ and anion-site donors Cl$_{Se}$.

We start by describing qualitatively the appropriate doping rules.[11] They are based on the observation that the concentrations of either intrinsic defects such as D=V$_{Cu}$, In$_{Cu}$ or of dopant impurities, D=Cd$_{Cu}$ or Cl$_{Se}$, 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 $\Delta\mu_\alpha$ of all species α present:

$$\Delta H_{D,q}(E_F,\mu) = (E_{D,q} - E_H) + q(E_V + E_F) + \sum_\alpha n_\alpha\mu_\alpha. \quad (1)$$

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 ΔH of ionized donors ($q>0$) *increases* as E_F rises in the gap, since electrons are *added* to the Fermi reservoir, whereas ΔH 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 $\mu_\alpha=\Delta\mu_\alpha+\mu_\alpha^{elem}$ of the atomic species α is given with respect to the elemental phase of α. We see that ΔH of Cu vacancies *increases* as the Cu chemical potential μ_{Cu} rises since the removed Cu atoms are *added* (n_α=+1) to the Cu reservoir; on the other hand, ΔH of Cd substitution *decreases* as μ_{Cd} rises since the incorporated Cd atoms are *removed* (n_α=−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 ΔH of wanted defects, and maximize ΔH 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 $\Delta H[Cd_{Cu}]$. This means, according to

	Anion-site doping (e.g. CIS : Cl)	Cation-site doping (e.g. CIS : Cd)
(1) To maximize dopant solubility use:	• Dopant-rich • Anion-poor	• Dopant-rich • Cu-poor
(2) Competing phases are:	Dopant + host-*cation* (e.g. CuCl, InCl)	Dopant + host-*anion* (e.g. CdSe)
To reduce effect use:	• Cation-poor (=Anion-rich)	• Anion-poor (=Cation-rich)
(3) Electron-killer is:	V$_{Cu}^-$	V$_{Cu}^-$
To minimize electron killers V$_{Cu}$ use:	• Cu-rich	• Cu-rich
(4) Assisting intrinsic defect is:	In$_{Cu}^{2+}$	In$_{Cu}^{2+}$
To maximize assisting In$_{Cu}$ use:	• In-rich • Cu-poor	• In-rich • Cu-poor
(5) "wrong site" defects are:	—	Cd$_{Cu}^+$ vs. Cd$_{In}^-$
To minimize "wrong site" defects use:		• Cu-poor • In-rich

FIG. 1. *n*-type doping rules. The terms "anion" and "cation" refer to the *host* atoms: Cu, In, Ga, and Se.

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FIG. 4. Phase diagram indicating the stability region of CIS and CGS (gray), and the respective competing phases. The point N defines the growth conditions optimal for n-type doping.
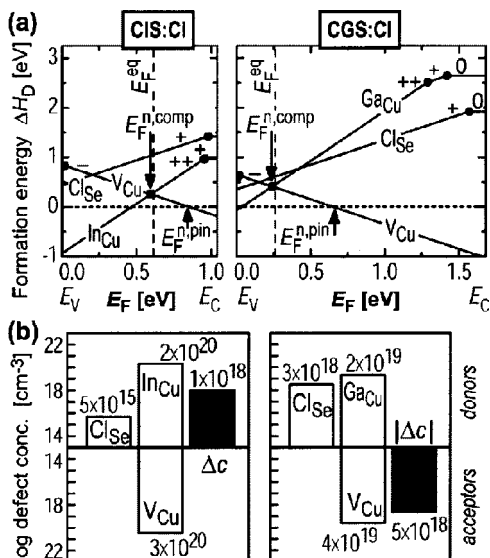
FIG. 2. (a) Cl_{Se} and related defect formation energies in CIS and CGS under growth conditions favorable for n-type doping (point N in Fig. 4). The arrows show the Fermi energy where the concentrations of the charged defects are balanced, $E_F^{n,comp}$ ($\Delta H[V_{Cu}^-]=\Delta H[In_{Cu}^{++}]$), and the maximum Fermi energy $E_F^{n,pin}$ ($\Delta H[V_{Cu}^-]=0$). The vertical line indicates the self-consistenly calculated equilibrium Fermi energy E_F^{eq} at $T=800$ K. (b) The ensuing defect concentrations under these growth conditions ($T=800$ K).

Eq. (1), Cu-poor (i.e., low $\Delta\mu_{Cu}$) and dopant-rich (i.e., maximal $\Delta\mu_{Cd}$) growth conditions.

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

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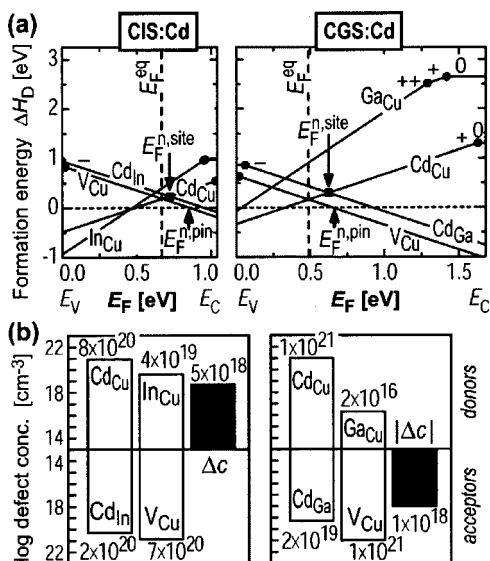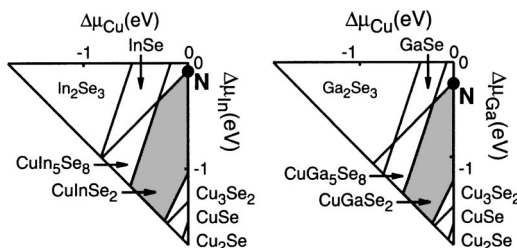
the concentration of V_{Cu} requires Cu-rich growth conditions ($\Delta\mu_{Cu}=0$).

(4) *Assisting defects.* The antisite In_{Cu}^{++} or Ga_{Cu}^{++} is a (double) donor which, when formed, assists the intended n-type doping. By Eq. (1), its formation energy $\Delta H[In_{Cu}^{++}]$ is lowered as the Fermi energy moves down in the gap. At the Fermi energy denoted $E_F^{n,comp}$ in Fig. 2 we have $\Delta H[V_{Cu}^-]=\Delta H[In_{Cu}^{++}]$, at which point the intrinsic acceptors tend to compensate the intrinsic donors [see Fig. 2(a)]. For successful n-type doping, $E_F^{n,comp}$ needs to be as high as possible in the gap. This requires Cu-poor and In-rich conditions; i.e., low $\Delta\mu_{Cu}$ and high $\Delta\mu_{In}$. Figure 2 shows that the energy to form In_{Cu} in CIS is much lower than the energy to form Ga_{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 $\Delta H(Cd_{Cu})$ (low $\Delta\mu_{Cu}$) and high $\Delta H(Cd_{In})$ (high $\Delta\mu_{In}$). The Fermi level denoted $E_F^{n,site}$ in Fig. 3(a) is the point where $\Delta H[Cd_{Cu}^+]=\Delta H[Cd_{In}^-]$. For successful n-type doping, $E_F^{n,site}$ 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, $\Delta\mu_{Cu}+\Delta\mu_{In}+2\Delta\mu_{Se}=\Delta H_f[CuInSe_2]$, where $\Delta H_f[CuInSe_2]$ 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_2Se_3. In addition, the maximum dopant chemical potential depends on the host chemical potentials; for example, $\Delta\mu_{Cd}+\Delta\mu_{Se}\leq\Delta H_f[CdSe]$ is required by rule (2). Taking into account these restrictions and using maximal $\Delta\mu_{Cd}$ 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) $\Delta H[Cd_{Cu}]$ is minimal; (2) $\Delta\mu_{Cd}$ is maximal as allowed by $\Delta\mu_{Cd}+\Delta\mu_{Se}\leq\Delta H_f[CdSe]$; (3) $\Delta H[V_{Cu}]$ is maximal; (4) $\Delta H[In_{Cu}]$ is minimal; and (5) $\Delta H[Cd_{Cu}]$ is minimal and $\Delta H[Cd_{In}]$ is maximal. Thus, these Se-poor conditions satisfy all doping rules (1)–(5), and resolve the conflicts indicated by the broader chemical poten-

FIG. 3. (a) Cd_{Cu} and related defect formation energies under "point N" growth conditions. $E_F^{n,site}$ indicates the Fermi energy where ΔH of the donor Cd_{Cu}^+ and the acceptor Cd_{In}^- (Cd_{Ga}^-) intersect. (b) The ensuing calculated defect concentrations at $T=800$ K.

tial range of Fig. 1. The "point N" conditions are defined by $\Delta\mu_{Cu}=0$, $\Delta\mu_{In}=-0.07$ eV, and $\Delta\mu_{Se}=-0.83$ eV in CIS, and by $\Delta\mu_{Cu}=0$, $\Delta\mu_{Ga}=-0.21$ eV, and $\Delta\mu_{Se}=-0.86$ eV. The maximal Cd chemical potentials under these conditions are $\Delta\mu_{Cd}=-0.21$ eV in CIS, and $\Delta\mu_{Cd}=-0.18$ 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 ΔH of In$_{Cu}$ according to rule (4). Under these conditions, the maximal Cl chemical potentials are limited by InCl and GaCl$_3$ formation ($\Delta\mu_{Cl}=-1.74$ eV in CIS, and $\Delta\mu_{Cl}=-1.47$ eV in CGS, given with respect to the diatomic Cl molecule; that is, $\mu_{Cl}^{elem}=\frac{1}{2}\mu_{Cl_2}$). 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.

ΔH_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,[14] projector augmented wave potentials[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,[16] which corrects for the underbinding of the Cu-d electrons by fitting U to place the Cu-d band at the photoemission value $E_V-2.5$ 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.[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 $c_{D,q}(E_F,\mu_\alpha,T)=N\times\exp[-\Delta H_{D,q}(E_F,\mu_\alpha)/kT]$, where N is the concentration of atomic sites that are substituted by the defect, the chemical potentials μ_α correspond to the growth conditions described earlier ("point N"), and $T=800$ K is a temperature used in the growth of solar cell devices.[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 $c_{D,q}$, E_F, and the carrier concentration. Using the self-consistently calculated defect concentrations, we define the "net doping balance" $\Delta c=c_{Cl_{Se}}+2c_{In_{Cu}}-c_{V_{Cu}}$ in case of Cl doping, and $\Delta c=c_{Cd_{Cu}}+2c_{In_{Cu}}-c_{Cd_{In}}-c_{V_{Cu}}$ in case of Cd doping. The doping balance Δc 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, $E_F^{n,comp}$ and $E_F^{n,pin}$ 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); $\Delta c=1\times10^{18}$ cm^{-3}. In contrast, in CGS, the positions of $E_F^{n,comp}$ and $E_F^{n,pin}$ are closer to the VBM. This results in a net *acceptor* doping [Fig. 2(b); $\Delta c=-5$

$\times10^{18}$ cm^{-3}]. Note that the contribution of Cl$_{Se}$ to the net Δc is rather small. Figure 3(a) shows ΔH_D 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 $\Delta c=-1\times10^{18}$ cm^{-3}, indicating a net *acceptor* excess and the failure of n-type doping. In CIS, Cd doping yields a higher net donor concentration [$\Delta c=5\times10^{18}$ 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 Δc 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, Δc increases from 1×10^{18} to 7×10^{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 2×10^{14} to 5×10^{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$_{Cu}$.

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