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## Halogen $n$ -type doping of chalcopyrite semiconductors

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We theoretically identify the chemical thermodynamic boundary conditions that will produce  $n$ -type CuInSe<sub>2</sub> via halogen doping. Remarkably, we find that due to the low formation energies of the intrinsic defects,  $V_{\text{Cu}}$  and  $\text{In}_{\text{Cu}}$  in CuInSe<sub>2</sub>, the growth conditions that maximize the halogen donor incorporation do not yield  $n$ -type conductivity, whereas the conditions that maximize the concentration of the intrinsic donor  $\text{In}_{\text{Cu}}$  do yield  $n$ -type conductivity. Under the latter conditions, however, the contribution of the halogen donors to the net donor concentration stays significantly below that of  $\text{In}_{\text{Cu}}$ . © 2005 American Institute of Physics. [DOI: 10.1063/1.1854218]

Solar cells based on CuInSe<sub>2</sub> (CIS) chalcopyrite semiconductors require that a region of the  $p$ -type material becomes  $n$ -type (“type inversion”).<sup>1</sup> In CIS,<sup>2,3</sup> electron concentrations in the  $10^{17}$  cm<sup>-3</sup> range can be obtained by adjusting the growth conditions. Cation-site substitution by divalent doping (Zn, Cd) resulted in electron concentrations around  $10^{18}$  cm<sup>-3</sup> in CIS.<sup>3</sup> Here, we study anion-site substitution by using halogen donors.<sup>4,5</sup>

Whether a semiconductor becomes  $p$ - or  $n$ -type is crucially determined by the chemical thermodynamic boundary conditions during the growth and the doping process, i.e., by the chemical potentials  $\mu_{\alpha}$  of all relevant types  $\alpha$  of atoms. Being a potential for mass transport, the chemical potentials determine the equilibrium dopant concentration by the requirement that the  $\mu_{\alpha}$  be inside the semiconductor crystal equal to their value in the chemical reservoir. In elemental semiconductors, the optimum choice for the chemical potentials for a desired conductivity type is straightforward: “maximize  $\mu$  of the dopant.” In binary and ternary systems, however, the situation is more complex and the conditions suitable for doping of the desired polarity can be estimated using “doping rules”.<sup>6</sup> In the following, we will first outline the general  $n$ -type doping rules in CIS that emerge from such thermodynamic boundary conditions. Next, we will use first-principles total-energy calculations to deduce quantitative information about the relevant formation energies. Finally, using these energies we calculate the equilibrium defect concentrations for different chemical potential (growth) conditions. This identifies the trends of doping efficiency at different growth conditions.

The formation energy  $\Delta H_{D,q}$  of a defect  $D$  is defined as

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

where  $E_{D,q}$  is the total energy of the semiconductor with the defect  $D$  in charge state  $q$ , and  $E_H$  is the energy of the pure host. The second term represents the energy of the chemical reservoir, while the third is the energy of the carrier reservoir.  $E_F$  is the Fermi energy relative to the valence band maximum,  $E_V$ . What is important in the context of the following discussion is that  $\Delta H_{D,q}$  depends on the chemical potentials  $\mu_{\alpha} = \mu_{\alpha}^{\text{elem}} + \Delta\mu_{\alpha}$  of atoms  $\alpha$  added to (dopant,  $n_{\alpha} = -1$ ) or

removed from (host atom,  $n_{\alpha} = +1$ ) the lattice when the defect is formed. Here,  $\Delta\mu_{\alpha}$  is the deviation from the chemical potential  $\mu_{\alpha}^{\text{elem}}$  of the elemental phase (solid phase, or diatomic molecule in case of halogen, e.g. Cl<sub>2</sub>). There are four, often mutually conflicting, factors that control  $n$ -type doping, illustrated here for anion-site doping in CIS:

(1) *Enhancing the solubility of donor dopants.* Maximizing the solubility of the donor species means minimizing its formation energy. According to Eq. (1), this can be achieved by maximizing the chemical potential of the dopant atom, while minimizing simultaneously the host anion chemical potential. At the same time, the chemical potentials of the host atoms must be consistent with the stability of the host with respect to decomposition: first, the stability condition of the host  $\Delta\mu_{\text{Cu}} + \Delta\mu_{\text{In}} + 2\Delta\mu_{\text{Se}} = \Delta H_f(\text{CuInSe}_2)$  has to be fulfilled, and second, the  $\Delta\mu$  must assume values that are consistent with boundary conditions imposed by other phases that may form out of the elements Cu, In, and Se [e.g.,  $\Delta\mu_{\text{In}} + \Delta\mu_{\text{Se}} \leq \Delta H_f(\text{InSe})$ ]. Figure 1 shows our calculated stability diagram of CIS where the stability region of CIS is bounded by the phases In<sub>2</sub>Se<sub>3</sub>, InSe, CuIn<sub>5</sub>Se<sub>8</sub>, and Cu<sub>3</sub>Se<sub>2</sub>. The compounds formation energies  $\Delta H_f$ , as well as the defect formation energies  $\Delta H_{D,q}$ , were obtained from total-energy calculations in the local density approximation (LDA).

(2) *Constraints imposed by formation of competing compounds with dopant atoms.* For anion-site doping, compounds between the host cation and the anion dopant (here, CuCl and InCl) can form, giving rise to additional constraints on the chemical potentials, e.g.,  $\Delta\mu_{\text{Cu}} + \Delta\mu_{\text{Cl}} \leq \Delta H_f(\text{CuCl})$  or  $\Delta\mu_{\text{In}} + \Delta\mu_{\text{Cl}} \leq \Delta H_f(\text{InCl})$ . This means that

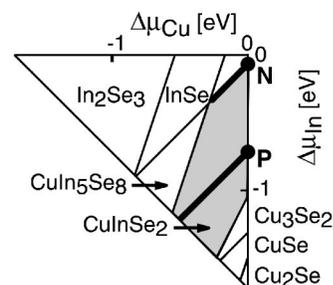


FIG. 1. Phase diagram of CIS indicating the stability region of CIS (gray) and the competing phases. The bold lines ending at points  $P$  and  $N$  give the chemical potentials for which the formation energies of  $\text{Cl}_{\text{Se}}$  and  $\text{In}_{\text{Cu}}$ , respectively, are constant and minimal. The points  $P$  and  $N$  define the “halogen favored” ( $P$ ) and “ $\text{In}_{\text{Cu}}$  favored” ( $N$ ) conditions.

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for the allowed range of  $\Delta\mu_{\text{Cu}}$  and  $\Delta\mu_{\text{In}}$  (cf. Fig. 1), the maximal halogen chemical potential required by rule (1) is obtained in equilibrium with Cu- and In-halides ( $\Delta\mu_{\text{halogen}} < 0$ ) rather than with molecular halogen ( $\Delta\mu_{\text{halogen}} = 0$ ).

(3) *Suppressing electron-killer defects.* The most prominent intrinsic electron killer (acceptor) in chalcopyrite semiconductors is the cation site vacancy  $V_{\text{Cu}}$ , having a particular low formation energy,<sup>7</sup> even at Cu-rich conditions ( $\Delta\mu_{\text{Cu}} = 0$ ). Being negatively charged, the formation energy is further lowered at high Fermi energies, which are expected to be present under  $n$ -type doping conditions. In order to obtain  $n$ -type conductivity it is thus needed to maintain maximum Cu-rich conditions ( $\Delta\mu_{\text{Cu}} = 0$ ) to minimize formation of  $V_{\text{Cu}}$ .

(4) *Assisting  $n$ -type doping by formation of intrinsic donors.* In CIS, there are mainly two donor-like intrinsic defects, i.e., the  $\text{In}_{\text{Cu}}$  antisite and the anion vacancy  $V_{\text{anion}}$ .<sup>2,8</sup> While the anion vacancy has recently been ruled out as a source of  $n$ -type conductivity, because of its deep ionization energy,<sup>9</sup> the formation of the intrinsic double donor  $\text{In}_{\text{Cu}}$  could support  $n$ -type doping. Thus, one would aim to minimize  $\Delta H(\text{In}_{\text{Cu}})$  by maximizing  $\Delta\mu_{\text{In}} - \Delta\mu_{\text{Cu}}$ .

To quantify rules (1)–(4) above, we determine from first-principles supercell calculations the formation energies [Eq. (1)] of the relevant defects, as well as the formation energies of the compounds that can be present as competing phases. Here, total energies are calculated in the pseudopotential-momentum space formalism<sup>10</sup> using the projector augmented wave potentials<sup>11</sup> and the local density approximation. The point defects are modeled within a fully relaxed 64 atoms supercell. The underestimation of the CIS band gap in the LDA has been remedied by adjusting both the energy of the valence band maximum,  $E_V$ , and that of the conduction band minimum,  $E_C$ . Here,  $E_V$  is shifted down by using the LDA +U method<sup>12</sup> which corrects for the LDA underbinding of the Cu- $d$  electrons with respect to experimental photoemission data, whereas  $E_C$  is shifted up by the *remaining* band gap error. The correction for  $E_V$  ( $E_C$ ) was also applied to shallow acceptor (donor) states which are assumed to follow the band edges. We also corrected for band-filling errors that occur due to the very high defect concentrations implied by the use of a finite supercell. Since the defect levels calculated here are rather shallow, having extended wave functions, we do not use the truncated multipole expansion of Ref. 13 for image charge correction. A complete account of the procedure of total-energy calculation will be presented elsewhere.<sup>14</sup> The equilibrium defect concentration is calculated according to  $c_{D,q}(E_F, \mu, T) = N \exp[-\Delta H_{D,q}(E_F, \mu)/kT]$ , where  $N$  is the concentration of atomic sites that are substituted by the defect. 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. Thus, we determine, for given temperature and chemical potentials the self-consistent solution that comprises  $c_{D,q}$ ,  $E_F$ , and the carrier concentrations  $n$  and  $p$ .<sup>15</sup> We calculated the defect formation energies  $\Delta H_{D,q}(E_F, \mu)$  according to Eq. (1) for the intrinsic  $V_{\text{Cu}}$  and  $\text{In}_{\text{Cu}}$  defects, as well as for the halogen donors, as a function of  $E_F$  and of the chemical potentials  $\Delta\mu_{\text{Cu}}$ ,  $\Delta\mu_{\text{In}}$ ,  $\Delta\mu_{\text{Se}}$ , and  $\Delta\mu_{\text{halogen}}$  that describe the chemical boundary conditions. In the following, we discuss two specific choices of these conditions, where the corresponding  $\Delta\mu$  values are given in Table I.

TABLE I. Chemical potentials ( $\Delta\mu$  in eV) for the CIS host atoms and for the halogen atoms for “halogen favored” conditions (point  $P$  in Fig. 1) and for “ $\text{In}_{\text{Cu}}$  favored” conditions (point  $N$ ).  $P$ : Cu-rich, In- and Se-intermediate, and halogen rich.  $N$ : Cu-rich, In-rich, and maximally Se-poor.

	$\Delta\mu_{\text{Cu}}$	$\Delta\mu_{\text{In}}$	$\Delta\mu_{\text{Se}}$	$\Delta\mu_{\text{Cl}}$	$\Delta\mu_{\text{Br}}$	$\Delta\mu_{\text{I}}$
$\text{Cl}_{\text{Se}}$ favored ( $P$ )	0	-0.70	-0.51	-1.11	...	...
$\text{Br}_{\text{Se}}$ favored ( $P$ )	0	-0.70	-0.51	...	-0.90	...
$\text{I}_{\text{Se}}$ favored ( $P$ )	0	-0.63	-0.55	...	...	-0.77
$\text{In}_{\text{Cu}}$ favored ( $N$ )	0	-0.07	-0.83	-1.74	-1.53	-1.27

(i) *Halogen favored conditions.* The conditions that maximize the incorporation of halogen donors are denoted “halogen favored” conditions. These conditions are given by the set of  $\Delta\mu_{\text{halogen}}$ ,  $\Delta\mu_{\text{Cu}}$ ,  $\Delta\mu_{\text{In}}$ , and  $\Delta\mu_{\text{Se}}$  that minimize the halogen donor formation energy [Eq. (1)] and, at the same time, fulfill the stability condition of CIS [see (1)] and the constraints imposed by the precipitation of Cu- and In-halides [see (2)]. This still does not define a unique set of the  $\Delta\mu$ , but leaves one degree of freedom, i.e., all points in the phase diagram in Fig. 1 that lie on the bold line ending in point  $P$  fulfill the requirement of minimal  $\Delta H_{\text{halogen}}$ . In order to reduce the impact of the electron-killer  $V_{\text{Cu}}$  as far as possible we further choose  $\Delta\mu_{\text{Cu}} = 0$  [see (3)]. The resulting chemical potentials correspond to point  $P$  in Fig. 1 and are listed in Table I. They correspond to “Cu-rich, In, Se intermediate, and halogen rich.” The respective defect formation energies as a function of  $E_F$  are depicted in Fig. 2(a).

(ii)  *$\text{In}_{\text{Cu}}$  favored conditions.* As a second choice of growth conditions, we consider those that maximize the concentration of the intrinsic donor  $\text{In}_{\text{Cu}}$ , denoted as “ $\text{In}_{\text{Cu}}$  favored” conditions. According to argument (1) and Eq. (1) these conditions are given when the difference ( $\Delta\mu_{\text{Cu}} - \Delta\mu_{\text{In}}$ ) is minimal. This requirement is met under In-rich conditions which are obtained by establishing equilibrium with InSe (Fig. 1). Also here, one degree of freedom is left, corresponding to the bold line ending in point  $N$  in Fig. 1. Again, we choose  $\Delta\mu_{\text{Cu}} = 0$  to minimize the  $V_{\text{Cu}}$  concentration according to argument (3). This yields “Cu- and In-rich and Se-poor” (see Table I). In order to increase the halogen concentration as far as possible under these conditions,  $\Delta\mu_{\text{halogen}}$  is now maximized by establishing equilibrium with the In-halides imposing a stronger restriction (upper bound) to the halogen potential than the Cu-halides. Thus, the Cl potential, for example, becomes  $\Delta\mu_{\text{Cl}} = \Delta H_f(\text{InCl}) - \Delta\mu_{\text{In}}$ . The chemical potentials for the “ $\text{In}_{\text{Cu}}$  favored” conditions (point  $N$ ) are listed in Table I, and the respective defect formation energies are plotted in Fig. 2(b).

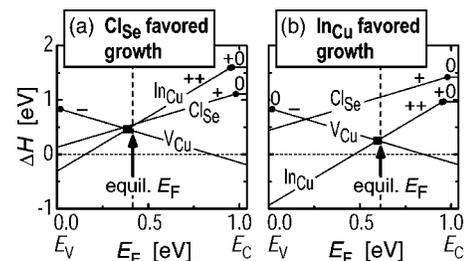


FIG. 2. Defect formation energies as a function of Fermi level  $E_F$  for (a) “ $\text{Cl}_{\text{Se}}$  favored” (point  $P$  in Fig. 1) and (b) “ $\text{In}_{\text{Cu}}$  favored” (point  $N$ ) chemical potential conditions. The vertical arrow marks the equilibrium Fermi energy (equil.  $E_F$ ), calculated self-consistently for  $T = 800$  K.

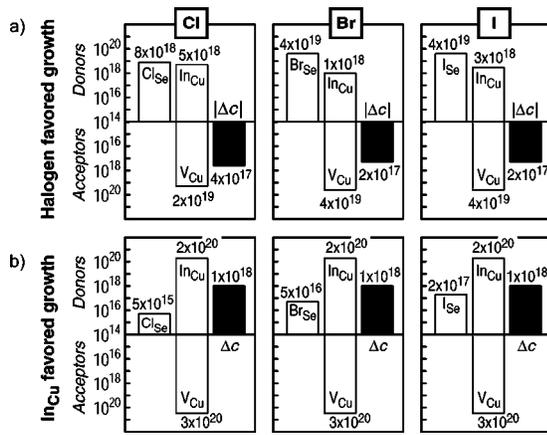


FIG. 3. Calculated defect concentrations in  $\text{cm}^{-3}$  at  $T=800$  K for (a) “halogen favored” (point  $P$  in Fig. 1) and (b) “InCu favored” (point  $N$ ) conditions. The black bars showing the doping balance  $\Delta c$  (see the text) indicate a net acceptor doping in (a), and a net donor doping in (b).

**Defect formation energies (Fig. 2).** For Fermi energies in the upper part of the band gap and halogen favored conditions [Fig. 2(a)], we see that the formation energies of the halogen donors are lower than that of the  $\text{In}_{\text{Cu}}$  donor, but higher than that of the compensating acceptor  $V_{\text{Cu}}$ . Under the  $\text{In}_{\text{Cu}}$  favored conditions [Fig. 2(b)], the formation energies of the halogen donors are always higher than that of  $\text{In}_{\text{Cu}}$ , and higher than  $\Delta H$  of  $V_{\text{Cu}}$  for most Fermi energies. The high formation energies of the halogen donors are a result of these In-rich conditions, under which, e.g.,  $\mu_{\text{Cl}}$  is reduced according to constraint (2) by almost 1.74 eV with respect to  $\text{Cl}_2$  (Table I). Importantly for the possibility to obtain  $n$ -type conditions,  $\Delta H$  of  $\text{In}_{\text{Cu}}$  is lower than  $\Delta H$  of the acceptor  $V_{\text{Cu}}$  for some Fermi levels above midgap, i.e., for  $E_F \leq 0.6$  eV [Fig. 2(b)]. Similar results are obtained for Br and I doping.

**Defect transition energies (Fig. 2).** The solid dots in Fig. 2 give the values of the Fermi energy at which the formation energies of the different charge states are equal. [These “transition energies”  $\varepsilon(q/q')$  are independent of the chemical potentials and hence the same for Figs. 2(a) and 2(b).] We find  $\varepsilon(0/+)=E_C-0.06$  eV,  $E_C-0.08$  eV, and  $E_C-0.05$  eV for the halogen donors Cl, Br, and I, respectively. For the intrinsic  $\text{In}_{\text{Cu}}$  double donor, we find  $\varepsilon(0/+)=E_C-0.08$  eV and  $\varepsilon(+/+)=E_C-0.09$  eV, for the intrinsic  $V_{\text{Cu}}$  acceptor, we calculated  $\varepsilon(0/-)=E_V+0.02$  eV. Thus, within the LDA supercell approach, we find for all defects considered here shallow levels that can be thermally ionized.

**Defect concentrations (Fig. 3).** Using  $T=800$  K,<sup>16</sup> the calculated concentrations for the “halogen favored” and the “InCu favored” conditions are shown as a bar chart in Figs. 3(a) and 3(b), respectively. Here, the doping balance, e.g.,  $\Delta c=c_{\text{Cl}_{\text{Se}}}+2c_{\text{In}_{\text{Cu}}}-c_{V_{\text{Cu}}}$  for Cl-doping, indicates whether net donor doping ( $\Delta c > 0$ ) or net acceptor doping ( $\Delta c < 0$ ) is obtained under the respective conditions ( $\text{In}_{\text{Cu}}$  is a double donor and, accordingly contributes  $2c_{\text{In}_{\text{Cu}}}$  to  $\Delta c$ ). We see that under “halogen favored” conditions [Fig. 3(a)], the halogen donors have concentrations of about  $10^{19}$   $\text{cm}^{-3}$ , but are overcompensated by Cu vacancies. The sample ends up being  $p$ -type with net acceptor concentrations in the  $10^{17}$   $\text{cm}^{-3}$  range [cf. Fig. 3(a)].

Under the “InCu favored” conditions, we find that the concentrations of the intrinsic defects  $\text{In}_{\text{Cu}}$  and  $V_{\text{Cu}}$  are practically independent on the type of the halogen dopant, being

present in only low concentration,  $c_{\text{halogen}} \leq 2 \times 10^{17}$   $\text{cm}^{-3}$  [Fig. 3(b)]. In fact,  $c_{\text{In}_{\text{Cu}}}=2 \times 10^{20}$   $\text{cm}^{-3}$  and  $c_{V_{\text{Cu}}}=3 \times 10^{20}$   $\text{cm}^{-3}$  are practically equal to the concentrations obtained under Se-poor conditions without additional halogen doping, and show a high compensation ratio. The sample ends up being  $n$ -type with a net donor concentration of  $\Delta c = 10^{18}$   $\text{cm}^{-3}$  [Fig. 3(b)]. In order to determine the resulting free electron concentration at room temperature, we perform another self-consistent calculation, now for  $T=300$  K, but maintaining the total concentrations of  $\text{In}_{\text{Cu}}$  and  $V_{\text{Cu}}$  obtained for 800 K. The calculated carrier concentration is  $n \approx 2 \times 10^{14}$   $\text{cm}^{-3}$ , meaning that only a relatively small fraction of electrons are thermally activated into the conduction band. This is a consequence of the high compensation ratio and the ensuing very high total (neutral+ionized) concentration of donors. The calculated carrier concentration is somewhat below the range of experimentally observed electron concentrations  $5 \times 10^{15}$ – $1.5 \times 10^{17}$   $\text{cm}^{-3}$ ,<sup>2</sup> probably because of a slight overestimation of the ionization energies within the LDA supercell approach.

We conclude that (i) the halogen incorporation is limited by chemical potential bounds imposed by precipitation of Cu- and In-halides and, hence, halogen incorporation is overwhelmed by the doping effect of the abundant intrinsic defects  $\text{In}_{\text{Cu}}$  and  $V_{\text{Cu}}$ . (ii) The formation of the intrinsic  $\text{In}_{\text{Cu}}$  double donor under Se-poor growth conditions results in net  $n$ -type doping. (iii) Due to the low formation energy of the compensating acceptor  $V_{\text{Cu}}$ , even at Cu-rich conditions ( $\Delta\mu_{\text{Cu}}=0$ ), a high degree of compensation will always be present for  $n$ -type doping in CIS. (iv) Under Se-poor conditions, which simultaneously imply Cu- and In-rich conditions, the Cu-site defect concentrations ( $V_{\text{Cu}}, \text{In}_{\text{Cu}}$ ) are in the  $10^{20}$   $\text{cm}^{-3}$  range [Fig. 3(b)], meaning that several percent of the Cu sites are not occupied by Cu. Thus, CIS is highly non-stoichiometric Cu-poor even at this “Cu-rich” ( $\Delta\mu_{\text{Cu}}=0$ ) growth condition.

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<sup>15</sup>Instead of using the simplification  $n \cdot p = \exp(-E_g/kT)$ , as used in most textbook examples, the Fermi-Dirac distribution function is integrated numerically to obtain  $n$  and  $p$ . Accordingly, there is no assumption necessary that  $E_F$  is separated from the band edges by  $\Delta E \gg kT$ .

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