n-type doping of CuInSe$_2$ and CuGaSe$_2$

Clas Persson,* Yu-Jun Zhao, Stephan Lany, and Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401, USA

Received 5 January 2005; published 14 July 2005

The efficiency of CuInSe$_2$ based solar cell devices could improve significantly if CuGaSe$_2$, a wider band gap chalcopyrite semiconductor, could be added to the CuInSe$_2$ absorber layer. This is, however, limited by the

tween the host material and some atomic and electronic reservoirs.[7] Thus, the formation energy for a defect comprising of atoms α in the charge state q can be computed using the expression[8,9]

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

In the first term, $E_{D,q}$ and E_H are the total energies of a solid with and without defect D, respectively. The second term of Eq. (1) represents the energy change due to exchange of atoms with the chemical reservoirs. μ_α is the absolute value of the chemical potential of atom α, and n_α is the number of such defect atoms; $n_\alpha = -1$ if an atom is added, while $n_\alpha = 1$ if an atom is removed. For example, the energy $\Delta H_{D,q}\left(E_F, \mu\right)$ to introduce a $D = V_{Cu}$ (Cu vacancy) is higher the greater is the Cu chemical potential μ_{Cu}, since the Cu atom ejected from the solid upon forming V_{Cu} must join the Cu reservoir whose energy is μ_{Cu}. The third term in Eq. (1) represents the energy change due to exchange of electrons and holes with the carrier reservoirs. E_v represents the energy at the VBM of the defect free system, i.e., the energy to remove an electron from the VBM to Fermi reservoir, or to insert an electron

sible in the gap. This requires Cu-poor and In-rich (Se-poor) conditions.

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 an extended range of chemical potentials, Rules 1 – 5 impose intrinsically conflicting requirements, e.g., 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. We therefore must establish next the thermodynamic limit on $\Delta\mu_{Cu}$, $\Delta\mu_{In/Ga}$, and $\Delta\mu_{Se}$, and examine then if Rules 1 – 5 of Fig. 1 can be accommodated with no conflicts within the limited, *allowed* range of $\Delta\mu$.

B. Restrictions posed by equilibrium chemical potentials

The chemical potentials μ_α are bound by the values that maintain a stable host compound, and avoid formation of all other competing phase (including their elemental solids). We will formulate these conditions in four steps. The procedure is based on equilibrium conditions for the crystal growth. When a nonequilibrium process is proposed, some constrains should be re-evaluated.

(i) The atomic chemical potential should be smaller than that of the corresponding elemental solid to avoid precipitation of the latter. That is:

$$\Delta\mu_{Cu} \leqslant 0; \quad \Delta\mu_{In,Ga} \leqslant 0; \quad \Delta\mu_{Se} \leqslant 0; \qquad (3)$$

or

$$\mu_{Cu} \leqslant \mu_{Cu}^{solid}; \quad \mu_{In,Ga} \leqslant \mu_{In,Ga}^{solid}; \quad \mu_{Se} \leqslant \mu_{Se}^{solid}. \qquad (4)$$

The point $\mu_\alpha = \mu_\alpha^{solid}$, corresponds to a "maximum α-rich condition," i.e., the chemical potential of α is equilibrium with elemental α solids.

(ii) To maintain a stable compound the sum of chemical potentials of its constituent atoms must equal the heat of formation of the compound. That is

$$\Delta\mu_{Cu} + \Delta\mu_{In,Ga} + 2\Delta\mu_{Se} = \Delta H (Cu(In,Ga)Se_2); \qquad (5)$$

or

$$\mu_{Cu} + \mu_{In,Ga} + 2\mu_{Se} = \Delta H (Cu(In,Ga)Se_2) + \mu_{Cu}^{solid}$$
$$+ \mu_{In,Ga}^{solid} + 2\mu_{Se}^{solid}. \qquad (6)$$

(iii) The chemical potentials are further restricted by requiring that, other possible competing phases with Cu, (In,Ga), and Se do not form. For example, if Cu and Se forms Cu_mSe_n naturally, the following condition is applied:

$$m\Delta\mu_{Cu} + n\Delta\mu_{Se} \leqslant \Delta H (Cu_mSe_n). \qquad (7)$$

The higher the number of conditions one adds to avoid competing phases, the more realistic is the region of the atomic potentials. For CIS we consider as competing phases InSe (having mP8 structure in Pearson's symbol), Cu_3Se_2 (the tP10 structure), and $CuIn_5Se_8$ (type D in Ref. 10), while for CGS we consider GaSe (the hP8 structure), Cu_3Se_2, and $CuGa_5Se_8$ (same structure as $CuIn_5Se_8$). All of these

10 . Thus $\Delta\mu_{Cd}$ is limited by formation of CdSe for Cu-rich

D. Selecting optimal growth conditions for Cl, Br, I in CIS and CGS

In the case of anion-site doping, some of the conflicting requirements noted in Fig. 1 do remain, even if we consider the restricted chemical potential range. Figure 3 b shows the contour plot for ΔH Cl_{Se} , where $\Delta\mu_{Se}$ is maximized as far as allowed by Eqs. 8 and 9 . Comparing Figs. 3 b –3 d , we see that minimal ΔH Cl_{Se} required by Rule 1 is obtained at "point P," but maximal ΔH V_{Cu} and minimal ΔH In_{Cu} , as required by Rules 3 and 4 , are both fulfilled only at point N. We thus decided to use two different growth conditions. Under the first strategy "point P" we will maximize the concentration of halogen, thus following Rule 1 . This is consistent with Rules 2 and 3 , but conflicts with Rule 4 . We will refer to this as "*halogen favored conditions*," and "Cl_{Se} favored conditions" when the halogen dopant is Cl. This gives values collected in Table I. "Point P" corresponds to "Se, In intermediate, Cu-rich."

Under the second strategy "point N" we minimize ΔH In_{Cu} according to Rule 4 , which is referred as "In_{Cu} *favored*(1)-39.8(wh2-80.we)-280.1b11Tf9009985.3CF4inimize*

energy difference between the neutral host and the host with a VBM electron removed. We found that the energy difference converges to the eigenvalue of VBM, ε_{VBM}, in the limit of dilute hole concentration. Therefore, ε_{VBM} could be used as the value of VBM for the diluted defects along with a potential alignment between two supercell calculations. This is described in Sec. 1 in the Appendix.

    ii *LDA energy gap correction*

In_{Cu} is a double donor and, accordingly contributes $2c_{In_{Cu}}$ to Δc. On account of the charge neutrality condition, the self-consistent equilibrium Fermi energy E_F^{eq} is pinned around $E_F^{n,comp}$ in case of Cl doping Fig. 4 . For n-type doping, E_F^{eq} generally needs to be high in the gap.

In order to compare our results with measured electron concentrations for Cl and Cd doping in CIS, we perform an additional self-consistent calculation for room temperature $T=300$ K . It is assumed that due to kinetic barriers, the

where the concentrations of the ionized defect alone yield

should be as high as possible in the gap. At this point the intrinsic donors tend to compensate the intrinsic acceptors. Figure 4 shows the energy needed to form Ga_{Cu} in CGS and In_{Cu} in CIS. We see that $\Delta H\ Ga_{Cu} > \Delta H\ In_{Cu}$. This reflects the larger band gap of CGS. Note from Fig. 4 that the self-consistently calculated E_F^{eq} is therefore higher in the gap for CIS than for CGS. Since, in the present case, the concentration of the ionized defects V_{Cu}^-, In_{Cu}^{++} are much higher than the carrier concentration, E_F is pinned to the vicinity of the point

TABLE V. Transition energies $\varepsilon(D,q/q')$ of substitutional neutral and charged group-II donors and acceptors in CIS and CGS relative to the CBM, E_c, for the donors and to the VBM, E_v, for the acceptors. Values within bracket are the transition energies without the Makov-Payne correction.

	q/q'	$\varepsilon(D,q/q')$ eV	
		$CuInSe_2$	$CuGaSe_2$
Mg_{Cu}	$+/0$	$E_c-0.14$ -0.06	$E_c-0.11$ -0.02
Zn_{Cu}	$+/0$	$E_c-0.14$ -0.06	$E_c-0.20$ -0.11
Cd_{Cu}	$+/0$	$E_c-0.10$ -0.00	$E_c-0.18$ -0.06
Mg_{III}	$0/-$	$E_v+0.13$ $+0.05$	$E_v+0.15$ $+0.06$
Zn_{III}	$0/-$	$E_v+0.05$ -0.02	$E_v+0.17$ $+0.07$
Cd_{III}	$0/-$	$E_v+0.07$ $+0.00$	$E_v+0.16$ $+0.07$

occurs between E_v and E_v-5 eV and has two peaks: the deeper one is bonding Cu, d-Se, p and the upper one is antibonding Cu, d-Se, p. The conduction band is made of Ga, s-Se,p orbitals. Deeper in the valence band we find the Ga, s-Se, p bonding states E_v-6 eV ; the Se s-band E_v-14 eV , and the Ga $3d$ band E_v-16 eV .

The projected density of states PDOS of the Cd_{Cu}^0 and Cd_{Ga}^0 show strong similarities, with Cd,d-like resonance state at $E_v-9.0$ eV. This is consistent with the atomic Cd, $4d$-states which are 7 eV below the Cu,$3d$-states and 5 eV above the Ga,$3d$-states. The Cd,d-Se,p interaction yield pronounced Cd,d-like peaks also at $E_v-13.5$ eV and $E_v-3.0$ eV. The PDOS of the Cd_{Cu}^0 donor electron states at $E_v+2.5$ eV is well above the experimental band-gap energy of 1.68 eV. This indicates a shallow character of the Cd_{Cu} donor. The acceptor Cd_{Ga}^0, has its acceptor hole states at the VBM the s-like states at $E_v+2.5$ eV are unoccupied . The PDOS of Cd_{Ga} show stronger PDOS at the VBM, than of that of the Cd_{Cu} donor.

V. TRANSITION ENERGIES

Table V shows the calculated transition energies according to Eq. 11 . They are depicted graphically in Fig. 7. In Fig. 7, we do not include the Makov-Payne correction since the defect levels calculated here are rather shallow, and thus the truncated multipole expansion[18] is no good for the image charge correction.

In Fig. 7, we show schematically the transition energies of divalent doping of donors $\varepsilon(II_{Cu},0/+)$ and acceptors $\varepsilon(II_{III},-/0)$. The trend is that CGS has somewhat deeper group-II donors than CIS, and this trend is more pronounced for the group-II acceptors. However, the calculated transition energies indicates that the group-II donors could be thermally ionized both in CIS and in CGS. The multipole correction gives 0.1 eV deeper donor and acceptor level since the correction increase the formation energy for charged states. The multipole correction is probably somewhat overestimated for shallow defect, and one would expect that the transition energies lies between the values with and without this correction.
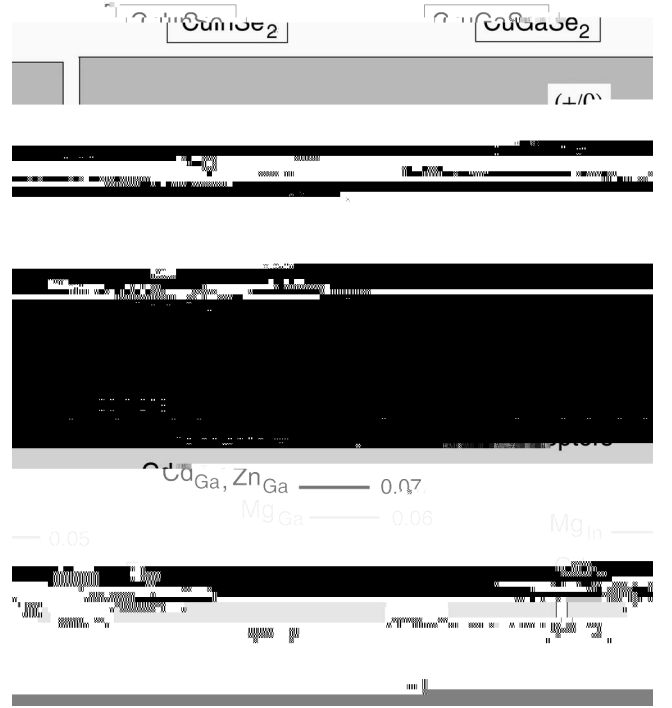

FIG. 7. Schematic picture of the transition energies in units of eV

VI. DEFECT AND CARRIER CONCENTRATIONS: CAN CGS BE DOPED n-TYPE?

Having calculated the optimal chemical potential growth conditions Secs. II C and II D , the formation energy Sec. III A and transition energy Sec. III B , we can now calculate self-consistently the defect concentration and carrier concentration. They are shown for divalent doping in CIS and CGS in Fig. 8 and for halogen doping in Fig. 9. In case of Cd-doping of CIS under Se-poor "point N" conditions, and using a Cd chemical potential corresponding to equilibrium with CdSe maximal $\Delta\mu_{Cd}$, we find undesirably high Cd incorporation. Therefore, we used a slightly lower $\Delta\mu_{Cd}$ by 0.2 eV .

Using $T=800$ K,[19] the calculated concentrations for the "halogen favored" and the "In$_{Cu}$ favored" conditions are shown as a bar chart in Figs. 9 a and 9 b , respectively. Here, the doping balance, e.g., $\Delta c = c_{Cl_{Se}} + 2c_{In_{Cu}} - c_{V_{Cu}}$ for Cl-doping, indicates whether net donor doping $\Delta c > 0$ or net acceptor doping $\Delta c < 0$ is obtained under the respective conditions. We see that under "halogen favored" conditions Fig. 9 a , the halogen donors have concentrations of about 10^{19} cm^{-3}, but are overcompensated by Cu vacancies. The sample ends up being p-type with net acceptor concentrations in the 10^{17} cm^{-3} range cf. Fig. 9 a .

Under the "In$_{Cu}$ favored" conditions, we find that the concentrations of the intrinsic defects In$_{Cu}$ and V$_{Cu}$ are practically independent on the type of the halogen dopant, being present in only low concentration, halogen $c_{halogen} \leqslant 10^{17}$ cm^{-3} Fig. 9 b . In fact, $c_{In_{Cu}} = 2 \times 10^{20}$ cm^{-3} and $c_{V_{Cu}} = 3 \times 10^{20}$ 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 $\Delta c = 10^{18}$ cm^{-3} Fig. 9 a . In order to determine the resulting free electron concentration at room temperature,[22] we perform another self-consistent calculation, now for $T = 300$ K, but maintaining the total concentrations of In$_{Cu}$ and V$_{Cu}$ obtained for 800 K. The calculated carrier concentration is c_e 2×10^{14} 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 con-

centration of donors. The calculated carrier concentration is somewhat below the range of experimentally observed electron concentrations[23] $5 \times 10^{15} - 1.5 \times 10^{17}$ cm^{-3}, probably because of a slight overestimation of the ionization energies within the LDA supercell approach.

We find that the calculated electron concentrations at room temperature are much lower than the net donor concentrations, i.e., c_e 2×10^{14} cm^{-3} in the case of Cl and intrinsic doping, and c_e 2×10^{15} cm^{-3} in the case of Cd doping of CIS. These numbers are below the maximal electron concentrations observed after Cl and intrinsic n-type doping, and after Cd doping, being about 10^{17} cm^{-3} and 10^{18} cm^{-3}, respectively. We attribute this discrepancy mostly to a slight overestimated of the donor ionization energies within the LDA supercell approach. Nevertheless, these results qualitatively explain why the limit c_e 10^{17} cm^{-3}

already at a low value of $E_F=0.7$ eV , it is not possible to shift E_F to higher values under equilibrium conditions. Thus, future attempts should focus on nonequilibrium conditions, in which the atomic Cu reservoir is decoupled.

APPENDIX : TECHNICAL DETAILS ON HOW TO CALCULATE DEFECTS ENERGIES IN THE LDA SUPERCELL APPROACH

Determining the valence-band maximum

In this section, we show how the energy of the VBM, E_v, in Eq. 2 is determined from the total energy of the charged pure host crystal: The formation energy of charged defects depends on the Fermi energy. In a nondegenerate system, the Fermi energy lies in the band-gap energy region. It is, therefore, convenient to determine the energy of the VBM, E_v, and regard the Fermi energy E_F as a free parameter $0 \leqslant E_F \leqslant E_g$.

We define the energy of the VBM, E_v, as the energy difference between the pure host crystal with and without a hole at the VBM, i.e.,

$$\Delta E_H \, q \;=\; E_H \, 0 \;-\; E_H \, q \;\; /q, \qquad\qquad A1$$

where q is the number of electro1Tf13hlremov.1 a 0.8787 332.f-665.4 D c.9 he 336.9 ner 17.9 gy 39 Tj/F41Tf2.8-35A3between 255 f 43352

$\eta_{j\mathbf{k}}$ is the electron occupation number at level j, reciprocal point $\mathbf{k}$. For example: $z_e D, q = 1$ for shallow neutral divalent donors e.g., Zn_{Cu}^0, while $z_e D, q = 0$ for shallow charged divalent donors e.g., Zn_{Cu}^+, and $z_e D, q = 2$ for shallow neutral double donors e.g., Ga_{Cu}^0, and $z_e D, q = 1$ for shallow partially charged $q = +$ double donors e.g., Ga_{Cu}^+, and $z_e D, q = 0$ for shallow charged $q = ++$ double donors e.g., Ga_{Cu}^{++}. Analogously, $z_h D$ is the number of acceptor holes occupying the acceptor states near or below the host VBM.

If the VBM is shifted downward by ΔE_v, one also has to shift the reference energy E_v in Eqs. 2 and 11 by

$$E_v = E_v^{\text{LDA}} - \Delta E_v, \qquad \text{A4}$$

and this correction will affect the formation energy of charged defects due to the term $q E_v + E_F$ in Eq. 2 .

Band filling correction

The formation and transition energies of dopants are normally referenced to a doping concentration in the dilute limit i.e., $\ll 10^{18}$ cm^{-3}. However, for a single defect in a finite supercell calculation, the defect concentration is much higher, e.g., 10^{21}–10^{22} cm^{-3} in a 64-atom supercell. The

energy of a periodically repeated electrically charged system diverges, and thus a jellium background is adopted to neutralize the charge in general. Makov and Payne[18] argued that the charge density in a crystalline solid with a point defect can be the sum of two contributions—the periodic charge density of the underlying crystalline solid and the charge density of the aperiodic defect, which is the charge difference between with and without the defect. The multipole correction ΔE_{mp} of the total energy of a practical finite supercell with respect to the total energy of an ideal infinite cell of a charged aperiodic system is[18]

$$\Delta E_{mp}\ D,q\ = +\frac{q^2 \alpha_M}{2\varepsilon_0 V_c^{1/3}} + \frac{2\pi q Q}{3\varepsilon_0 V_c} + O\ V_c^{-5/3}\ . \qquad A7$$

Here, α_M is the lattice-dependent Madelung constant and V_c is the volume of the cubic supercell. ε_0 and Q are properties of the periodic density and the aperiodic density; ε_0 is the static dielectric constant and Q is the second radial moment only of that part of the aperiodic density. The first and second correction terms in Eq. A7 are the monopole and quadrupole corrections, respectively. Typically, the quadrupole correction is 30% of the monopole correction with opposite sign. In principal, also higher order of the multipole correction should be included.

We notice that Eq. A7 is based on the assumption that defect charge is rather localized. However, the defect charge of very shallow levels might be rather delocalized, and the restriction to monopole and quadrupole corrections in Eq. A7 may not be sufficient, i.e., higher order terms may be needed. In the limit of completely delocalized charges, the multipole correction should be zero since an uniform electron gas does not have a net charge moment. One can therefore argue that the Makov-Payne correction is the upper limit of correction for shallow defects. We therefore present the formation and transition energies both with and without the multipole correction.

As in the case of the correction for the band-filling see above , the multipole correction should be zero or at least smaller if one intentionally calculates total energies of heavily doped semiconductors. For those highly doped systems, the choice of assuming periodic instead of, for instance, randomly distributed donors may however have an effect on the impurity-impurity interaction.

With the corrections above, the total energy of the crystal with a defect is

$$E\ D,q\ = E_{FSC}^{LDA}\ D,q\ + \Delta E_{bf}\ D,q\ + \Delta E_{mp}\ D,q\ + \Delta E_{pa}\ D,q$$
$$+ \Delta E_g\ D,q\ , \qquad\qquad A8$$

where $E_{FSC}^{LDA}\ D,q$ is the LDA total energy of the finite supercell with the defect see Fig. 11 .

[1] D. Lillington, H. Cotal, J. Ermer, D. Friedman, T. Moriarty, and A. Duda, *35341.e41.5(D.)-341.5(Friedman,)-341.5(T)3.0.)weden*

[5] T. Nakada, K. Furumi, K. Sonoda, and A. Kumioka, *2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion*, Hofbur, Kongresszentrum, Wien, Austria, July, 1998.

[6] K. Ramanathan, F. S. Hasoon, S. Smith, A. Mascarenhas, H. Al-Thani, J. Alleman, H. S. Ullal, J. Keane, P. K. Johnson, and J. R. Sites, *Twenty-Ninth IEEE Photovoltaic Specialists Conference 2002*, May 2002, New Orleans, LA, USA, p. 523.

[7] S. B. Zhang and S.-H. Wei, Appl. Phys. Lett. **80**, 1376 2002 .

[8] S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 1991 .

[9]