Supplementary Information

A first-principles study of copper-deficient layer and its effect in chalcopyrite-based solar cells: carrier dynamics characteristics

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The calculation processes for defect formation energy and defect charge transition level, defect and carrier concentration, defect non-radiative recombination:

The calculation of defect formation energy and defect charge transition level

The following equation (a) was applied for the calculation of formation energy of defect α with charge state q[1]:

$$\Delta E_{\mathrm{f}}(\alpha, \mathrm{q}) = E(\alpha, \mathrm{q}) - E(\mathrm{bulk}) - \sum_i n_{\mathrm{i}} (E_{\mathrm{i}} + \mu_{\mathrm{i}}) + q(E_{\mathrm{F}} + E_{\mathrm{VBM}}) + E_{\mathrm{corr}} \qquad \text{(a)}$$

Among them, $E(\alpha, \mathrm{q})$ and $E(\mathrm{bulk})$ are the total energies of the supercells with and without defect, μ_{i} is the elemental chemical potential referenced to the total energy of pure elementary phase, E_{F} is the Fermi level referenced to the eigenvalue of valence band maximum (VBM) level of the bulk defect-free supercell of OVC. E_{corr} is the correction for charged defects to account for the finite-size effect, with FNV (Freysoldt–Neugebauer–Van de Walle) method[2]. The defect charge transition level is the Fermi level position that formation energies in two charge states equal to each other.

The calculation of defect and carrier concentration

The following equation (b) was applied for the calculation of the concentration of the defect α with charge state q under thermodynamic equilibrium:

$$\mathrm{n}(\alpha, \mathrm{q}) = \mathrm{N}_{\mathrm{sites}} \mathrm{g}_{\mathrm{q}} \mathrm{e}^{(-\Delta \mathrm{E_f}/\mathrm{k_B T})} \qquad \text{(b)}$$

Among them, N_{sites} is the concentration of the possible defect sites, g_q is the charge-dependent degeneracy factor, and ΔE_f is the defect formation energy, which can be determined by the given Fermi energy and elemental chemical potentials, as seen in Figure S1 and 2. Furthermore, the equilibrium-state Fermi energy can be calculated by solving for the charge neutrality using the following equation (c):

$$n_0 + \sum_{a;q<0}[(-q) \cdot n(a, q)] = p_0 + \sum_{a;q>0}[q \cdot n(a, q)] \qquad \text{(c)}$$

Where, the $\sum_{a;q>0}[q \cdot n(\alpha, q)]$ represents summed charge from electron carriers, and the $\sum_{a;q<0}[(-q) \cdot n(\alpha, q)]$ stands for the summed charge from hole carriers. n_0 and p_0 are free carrier concentrations, which can be defined using equations (d) and (e):

$$n_0 = \int_{\varepsilon CBM}^{+\infty} g_C(E) f(e) dE \qquad \text{(d)}$$

$$p_0 = \int_{-\infty}^{\varepsilon VBM} g_V(E)(1 - f(e)) dE \qquad \text{(e)}$$

where $g_C(E)$ and $g_V(E)$ are the density of states for the conduction and valence bands, respectively, and $f(e)$ is the Fermi–Dirac occupation function[3-6].

The calculation of defect non-radiative recombination

The non-radiative recombination characteristic of deep-level defect with high concentration was studied with the phonon spectrum and electron-phonon coupling characteristics as the following equation (f)[7]:

$$C_{\mathrm{p}} = \frac{2\pi V}{\hbar} W_{\mathrm{if}}^2 \sum_m \omega_m \sum_n \left\langle \chi_{im} | \Delta Q | \chi_{fn} \right\rangle^2 \delta\left(\Delta E + E_{im} - E_{fn}\right) \quad \text{(f)}$$

Among these parameters in the above equation, W_{if} is the electron-phonon coupling matrix element and was determined using VASP via bulk/single-particle wave functions under related approximations, methods and theories in the published references[7, 8]. ω_m is the thermal occupation of the initial vibrational state m, χ_{im} and χ_{fn} are the vibrational wave functions and E_{im} and E_{fn} are the related eigenvalues, ΔQ is the difference in the equilibrium geometries of the initial and final state along the configuration coordinate. The carrier transition energy was denoted by ΔE, which is exactly the same as the transition level for the calculated defect.

Formation energy of intrinsic defects in $CuIn_5Se_8$ as a function of the Fermi energy:

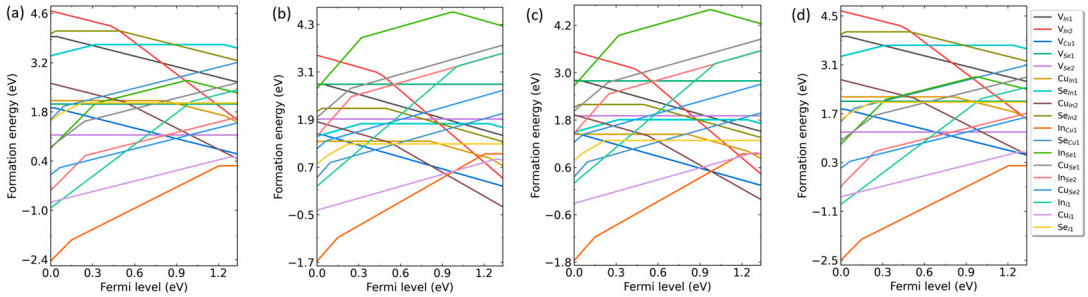


Figure S1. The formation energy of intrinsic defects in $CuIn_5Se_8$ as a function of the Fermi energy, as displayed in the sequence of p1-p4-p2-p3 that corresponds to Figure (a)-(b)-(c)-(d).

Formation energy of doping defects in Cd doped $CuIn_5Se_8$ as a function of the Fermi energy:

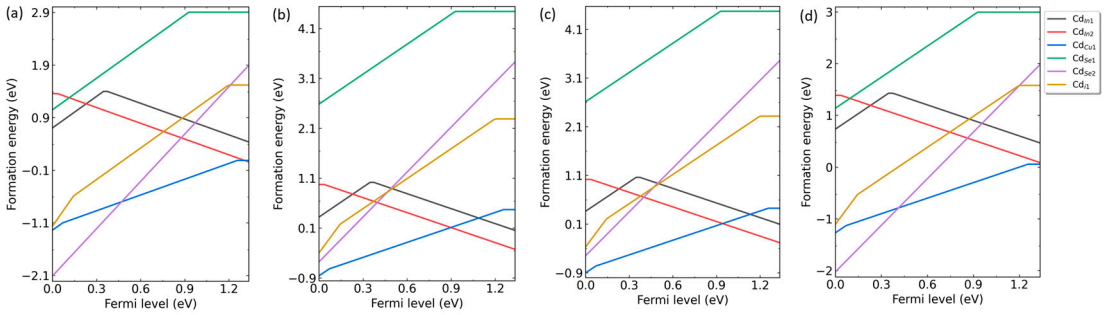


Figure S2. The formation energy of doping defects in Cd doped $CuIn_5Se_8$ as a function of the Fermi energy, as displayed in the sequence of p1-p4-p2-p3 that corresponds to Figure (a)-(b)-(c)-(d).

Non-radiative characteristic of deep-level defect Cd_{Cu} in Cd doped $CuIn_5Se_8$:

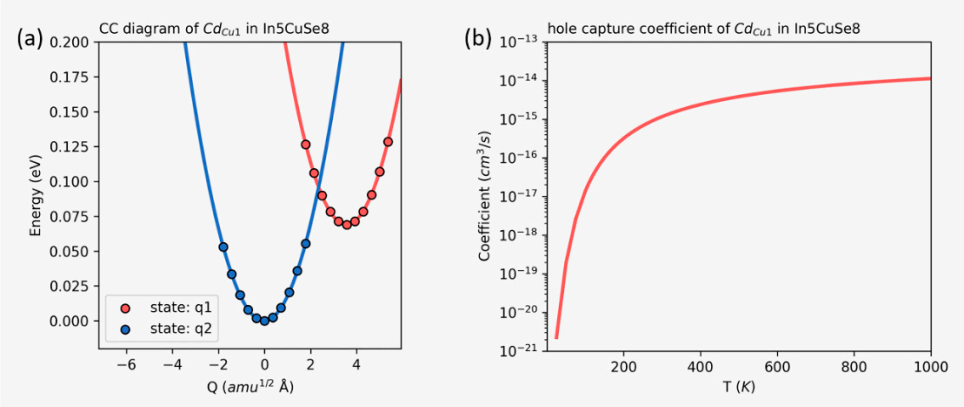


Figure S3. (a) The Configuration Coordinate (CC) diagram for non-radiative calculation and (b) corresponding temperature-dependent hole capture coefficient of Cd_{Cu} from q1 to q2 in Cd doped $CuIn_5Se_8$.

Table S1. Parameters used in solar cell device simulation for $CuInSe_2$ absorber layer, $CuIn_5Se_8$ layer, Cd doped $CuIn_5Se_8$ layer and Cadmium Sulfide layer (CdS).

Parameters	CdS	Cd doped $CuIn_5Se_8$	$CuIn_5Se_8$	$CuInSe_2$
Thickness (nm)	50	10	30	500
Bandgap E_g (eV)	2.45	1.33	1.33	1.02
electron affinity (eV)	4.20	4.52	4.52	4.30
dielectric permittivity (relative)	10.00	13.6	13.6	13.6
N_C (cm^{-3})	2.200E+18	2.200E+18	2.200E+18	2.200E+18
N_V (cm^{-3})	1.800E+19	1.800E+19	1.800E+19	1.800E+19
electron thermal velocity (cm/s)	1.000E+7	1.000E+7	1.000E+7	1.000E+7
hole thermal velocity (cm/s)	1.000E+7	1.000E+7	1.000E+7	1.000E+7
electron mobility ($cm^2/V{\cdot}s$)	1.000E+2	1.000E+2	1.000E+2	1.000E+2
hole mobility ($cm^2/V{\cdot}s$)	2.500E+1	2.500E+1	2.500E+1	5.000E+1
N_D (cm^{-3})	1.000E+17	3.180E+14	1.540E+14	1.295E+2
N_A (cm^{-3})	1.000E+0	5.300E+1	1.097E+2	9.827E+17
Defect type	Neutral	Donor (Cd_{Cu} (2+/1+) and acceptor (Cd_{In} 0/-1)	Donor (In_{Cu} +2/+4) and acceptor (Cu_{In} -1/-2)	Donor
N_t (cm^{-3})	1.00E+17	1.515E+21 and 1.843E+19	1.440E+19 and 2.000E+19	1.119E+16
E_{defect} (eV)	E_g	0.07 eV and 0.37 eV	0.15 eV and 0.53 eV	0.601 eV
σ_e/σ_h (cm^2)	(1.000E-12)/(1.000E-12)	Donor (8.896E-25)/(1.165E-15) Acceptor (8.896E-25)/(1.165E-15)	Donor (8.896E-25)/(1.165E-15) Acceptor (8.896E-25)/(8.896E-25)	(1.000E-15)/(1.000E-15)

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