Supplementary Material for

Theoretical Perspective of Performance-limiting Parameters in $Cu(In_{1-x}Ga_x)Se_2$-based Photocathodes

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Table S1. Material parameters used in electrical simulations of CdS/Cu($In_{1-x}Ga_x$)Se_2-based photocathodes.

Parameters	CdS	Cu($In_{1-x}Ga_x$)Se_2
Thickness	$70\ nm$ {ref. [1]}	$1800\ nm$ {ref. [1]}
Effective density of states for conduction and valence band	$10^{19}\ cm^{-3}$ {ref. [2]}	$10^{19} cm^{-3}$ {ref. [2]}
Mole fraction x	-	0-1
Dielectric constant	10 {ref. [1,2]}	13.6 {ref. [1]}
Doping density	$10^{16}\ cm^{-3}$ (Donor) {ref. [1]}	$10^{16}\ cm^{-3}$ (Acceptor) {ref. [1]}
Electron affinity	3.8 eV	3.5 (x=0) to 4.2 (x=1) eV[1]
Energy band gap	2.4 eV {ref. [1]}	0.98 (x=0) to 1.5 (x=1)[1]
Electron mobility	$100\ cm^2/(Vs)$ {ref. [2]}	$100\ cm^2/(Vs)$ {ref. [2]}
Hole mobility	$25\ cm^2/(Vs)$ {ref. [2]}	$25\ cm^2/(Vs)$ {ref. [2]}
Bulk defect density/carrier lifetime	-	10^{13},$10^{14}\ cm^{-3}$/1,0.1 μs

Parameterization of Optical Constants:

The Forouhi–Bloomer (FB) dispersion relation is generally used to obtain optical constants like the refractive index *n(E)* and extinction coefficient *k(E)* of crystalline semiconductors[3,4] and is given as

$$k(E) = \left[\sum_{i=1}^{m} \frac{A_i}{E^2 - B_i E + C_i}\right](E - E_g)^2, \qquad (1)$$

$$n(E) = n_\infty + \sum_{i=1}^{m} \frac{B_i^{'} E + C_i^{'}}{E^2 - B_i E + C_i}. \qquad (2)$$

Here, E_g is the onset energy of optical absorption, n_∞ is the refractive index in the high frequency range, and the independent parameters A_i, B_i, and C_i characterize distinct interband transitions. Every summation term in eq. 1 and 2 is the contribution from either a peak or shoulder in the spectra of extinction coefficient *k* and refractive index *n*. The upper limit *m* is the number of different curvatures observed in optical constant *k*. The dependent parameters $B_i^{'}$ and $C_i^{'}$ in eq. 2 are calculated using following expressions:

$$B_i^{'} = \frac{A_i}{Q_i}\left[-\frac{B_i^2}{2} + E_g B_i - E_g^2 + C_i\right],$$

$$C_i^{'} = \frac{A_i}{Q_i}\left[\frac{B_i\left(E_g^2 + C_i\right)}{2} - 2E_g C_i\right],$$

$$Q_i = \frac{1}{2}\sqrt{4C_i - B_i^2}.$$

Each independent parameter, i.e., E_g, n_∞, A_i, B_i, and C_i is approximated by a second-order polynomial of mole fraction x; i.e., $q_2x^2 + q_1x + q_0$, where, q_0, q_1, and q_2 are fitting coefficients. Numerical values of fitting coefficients for respective independent parameters are provided in Table S2.

Table S2: Numerical values of coefficients of the second-order polynomial (q_2x^2+ q_1x +q_0) used to obtain different parameters for parameterization of optical constants such as refractive index *n(E)* and extinction coefficient *k(E)* using the Forouhi–Bloomer dispersion relation.[4]

Parameter	q_2	q_1	q_0
A_1	0.032	-0.128	0.117
B_1(eV)	0.82	0.68	2.39
C_1(eV^2)	1.778	0.343	1.738
A_2	0.091	0.063	0.066
B_2(eV)	-0.54	0.69	5.90
C_2(eV^2)	-1.33	2.60	9.16
E_g(eV)	0.26	0.46	0.53
n_∞	0.054	-0.046	2.450

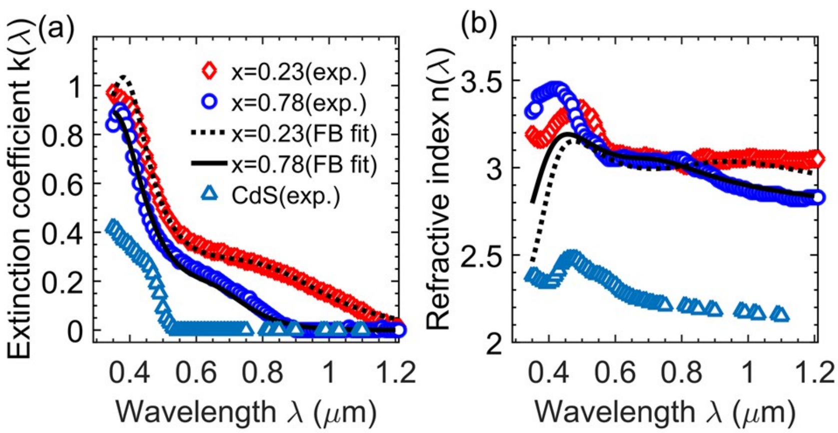

Figure S1. Parametrization of optical constants using the Forouhi-Bloomer (FB) dispersion relation for CdS/CIGS photocathodes with different mole fraction x. Variation of optical constants such as (a) extinction coefficient $k(\lambda)$ and (b) refractive index $n(\lambda)$ with wavelength λ for the CIGS layer (x=0.23 and 0.78) and CdS front window layer. Symbols indicate the extracted experimental data from the literature,[4] while the black solid (for x=0.23) and dotted (for x=0.78) lines correspond to the FB fit.

The FB fit enables us to calculate optical constants for different x. For instance, in Fig. S1a, the calculated extinction coefficient *k* matches closely with the experimental data over the wavelength range for different x (=0.23 and 0.78). Furthermore, Fig. S1b shows that the estimated refractive index *n* is in close agreement with actual data at long wavelength, but it deviates at short wavelength (<400 nm). To analyze the effect of the mismatch of *n*, we performed optical simulations by incorporating optical constants *n* and *k* obtained from experiments and the FB fit for x=0.23.

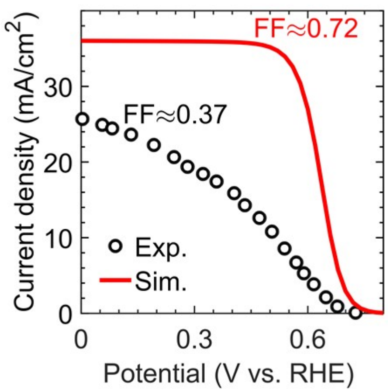

Figure S2. Current potential characteristics (symbols-baseline experimental data; line- simulation) of CdS/CIGS based photocathode with mole fraction x=0.5. For simulation data, the interface defect density $N_I = 2.5 \times 10^8\ cm^{-2}$ and bulk defect density $N_B = 10^{14} cm^{-3}$.

Table S3. Parameters extracted from the comparison of simulation and experimental data of current potential characteristics of CdS/Cu($In_{1-x}Ga_x$)Se_2 photocathodes with different mole fraction x.

Mole fraction x	Resistance R_s ($\Omega\ cm^2$)	Shunt Resistance R_{sh} ($\Omega\ cm^2$)	Interface defect density N_I	Bulk life time in CIGS τ (μs)	Attenuation constant Ac (%)
0	8.5	25	-	1	73.43
0.5	12	55	$3 \times 10^8\ cm^{-2}$	1	86.27
0.7	15	168	$12 \times 10^8\ cm^{-2}$	0.1	61.06
1	25	500	$4 \times 10^8\ cm^{-2}$	0.1	25

References:

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