

# First-principles calculations of the phase diagrams and band gaps in $\text{CuInSe}_2$ - $\text{CuGaSe}_2$ and $\text{CuInSe}_2$ - $\text{CuAlSe}_2$ pseudobinary systems

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The phase diagrams and band gaps in  $\text{CuInSe}_2$ - $\text{CuGaSe}_2$  (CIS-CGS) and  $\text{CuInSe}_2$ - $\text{CuAlSe}_2$  (CIS-CAS) pseudobinary systems are determined using a combination of first-principles calculations based on a hybrid Hartree-Fock density functional approach, cluster expansion, and Monte Carlo simulations. The CIS-CGS and CIS-CAS systems show phase-separation critical temperatures of 420 and 460 K, respectively. For both  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS) and  $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$  (CIAS) alloys, the dependence of the band gaps on the temperature before quench is suggested to be small through the analysis of atomic configurational effects. The band gaps are generally close to those at the ideal disorder state and exhibit nearly quadratic composition dependences, i.e., band bowing. Composition-dependent bowing behavior is identified for CIAS, with a stronger bowing in a higher CAS composition range.

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The pseudobinary alloys of  $\text{CuInSe}_2$  (CIS) and  $\text{CuGaSe}_2$  (CGS) with the chalcopyrite structure,  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS), are utilized as light absorbers in CIGS thin-film solar cells.<sup>1,2</sup> The formation of the CIGS alloys enables us to tune the band gap for increasing the cell efficiency.  $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$  (CIAS), in which the band gap is controlled via alloying of CIS with  $\text{CuAlSe}_2$  (CAS), has been studied as an alternative absorber material.<sup>3-6</sup> A great impact of the characteristics of the CIGS and CIAS alloys on the cell efficiency has stimulated the investigation of phase-transition and phase-separation behavior,<sup>7-9</sup> alloy inhomogeneity,<sup>10,11</sup> and the composition dependence and spatial fluctuation of the band gap.<sup>3-7,11,12</sup> Tinoco *et al.* constructed a phase diagram of the CIS-CGS system at temperature above 1073 K and found no phase separation of CIS and CGS in the entire composition range.<sup>7</sup> Alloy inhomogeneity associated with the spatial fluctuation in In and Ga concentrations has been observed in CIGS thin films alongside the fluctuation in stoichiometry.<sup>10</sup> Such inhomogeneity leads to the fluctuation in band gap, as observed in a spatially resolved photoluminescence study.<sup>11</sup>

Theoretical approaches to the alloy structure and phase diagram have also been reported, but they are limited to the examination of the spatial distribution of In and Ga in CIGS (Ref. 8) and a phase-diagram calculation for the CIS-CGS system using the coherent-potential approximation (CPA) for the enthalpy of mixing and the ideal solution model for configurational entropy.<sup>9</sup> In addition, the prediction of the band gaps of CIGS and CIAS alloys has been made via first-principles calculations for special quasirandom structures (SQSs).<sup>12</sup> However, an explicit treatment of the atomic-configuration effects has not been reported in the evaluation of the band gaps of CIGS and CIAS alloys as well as the calculation of their phase diagrams.

In general, theoretical determination of the phase diagrams and the atomic-configuration dependences of the band gaps of alloys requires total energies and band gaps for an astronomical

number of atomic configurations. Therefore, an approach solely using first-principles calculations is unfeasible. The cluster expansion (CE) method<sup>13-15</sup> enables us to predict such configurational properties by performing first-principles calculations for selected configurations. In this study, the temperature-composition phase diagrams and band gaps in the CIS-CGS and CIS-CAS pseudobinary systems are determined using a combination of first-principles calculations, CE, and Monte Carlo (MC) simulations.

The CIS-CGS and CIS-CAS pseudobinary systems are treated by considering the configurations of In and Ga atoms and those of In and Al atoms, respectively, in the chalcopyrite structure (Fig. 1). For respective systems, the total energies and band gaps of 43 ordered structures are obtained using first-principles calculations. All structures are described using 64-atom supercells, which are constructed by the  $2 \times 2 \times 1$  expansion of the unit cell of the chalcopyrite structure. The cell volume and atomic positions are fully relaxed. The calculations are performed using the projector augmented-wave method<sup>16</sup> with the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional<sup>17</sup> as implemented in the VASP code.<sup>18-21</sup> A plane-wave cutoff energy of 400 eV and  $2 \times 2 \times 2$   $k$ -point mesh are employed. The amount of Hartree-Fock exchange mixing in the HSE06 functional is increased from the standard value of  $a = 0.25$  to 0.3 so as to better reproduce the band gaps of CIS, CGS, and CAS.<sup>22-24</sup> As listed in Table I, the calculated band gaps of CIS, CGS, and CAS are 1.04, 1.62, and 2.56 eV, using the HSE06 ( $a = 0.3$ ) functional, respectively, and 0.78, 1.34, and 2.27 eV, using the standard HSE06 ( $a = 0.25$ ) functional, whereas the experimental values are 1.05 (Ref. 25), 1.68 (Ref. 26), and 2.7 eV.<sup>27</sup> Note that standard approximations to density functional theory, i.e., the local density approximation (LDA) and the generalized gradient approximation (GGA), significantly underestimate the band gaps of CIS, CGS, and CAS: for instance, the band gap does not appear in the case of CIS.

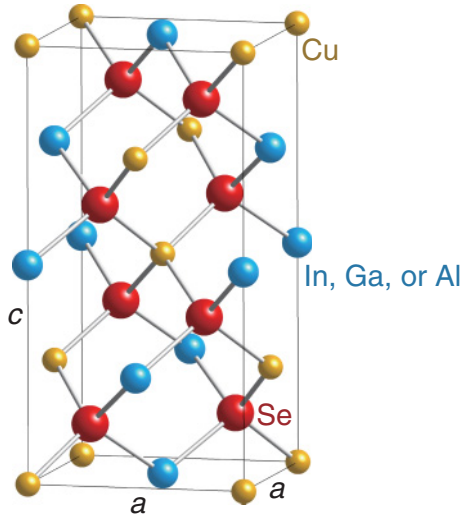


FIG. 1. (Color online) Unit cell of CIS, CGS, and CAS with the chalcopyrite structure.

Within the formalism of the CE, the configurational property  $A$ , such as the total energy and band gap, of a binary or pseudobinary system is expressed using the pseudospin configurational variable  $\sigma_i$  for lattice site  $i$  and effective cluster interactions (ECIs)  $V$  as

$$A = V_0 + \sum_i V_i \sigma_i + \sum_{i,j} V_{ij} \sigma_i \sigma_j + \sum_{i,j,k} V_{ijk} \sigma_i \sigma_j \sigma_k + \dots$$

$$= \sum_{\alpha} V_{\alpha} \cdot \varphi_{\alpha}, \quad (1)$$

where  $\varphi_{\alpha}$  is called the correlation function of cluster  $\alpha$ . In order to estimate the ECIs that reconstruct the first-principles total energies and band gaps, we optimize the combination of clusters on the basis of the minimization of the cross validation (CV) score, which is generally used for evaluating the prediction error of the CE.<sup>28,29</sup> The optimization is performed by using the genetic algorithm.<sup>30,31</sup> The ECIs for the optimized combination of clusters are estimated using the least-squares fitting. The CV scores for the total energy are less than 0.1 meV/cation for both CIGS and CIAS, respectively. Those for the band gap are 1.0 and 3.6 meV. Thermodynamic averages of atomic configurations and band gaps are obtained by performing semigrand-canonical MC simulations using the ECIs. Supercells for MC simulations are constructed by the  $10 \times 10 \times 5$  expansion of the

TABLE I. Band gaps of CIS, CGS, and CAS calculated using the HSE06 ( $a = 0.25$ ) and HSE06 ( $a = 0.3$ ) hybrid functionals. Reported experimental values are also shown. Values are in eV.

|                      | CIS               | CGS               | CAS              |
|----------------------|-------------------|-------------------|------------------|
| HSE06 ( $a = 0.25$ ) | 0.78              | 1.34              | 2.27             |
| HSE06 ( $a = 0.3$ )  | 1.04              | 1.62              | 2.56             |
| Experiment           | 1.05 <sup>a</sup> | 1.68 <sup>b</sup> | 2.7 <sup>c</sup> |

<sup>a</sup>Reference 25.

<sup>b</sup>Reference 26.

<sup>c</sup>Reference 27.

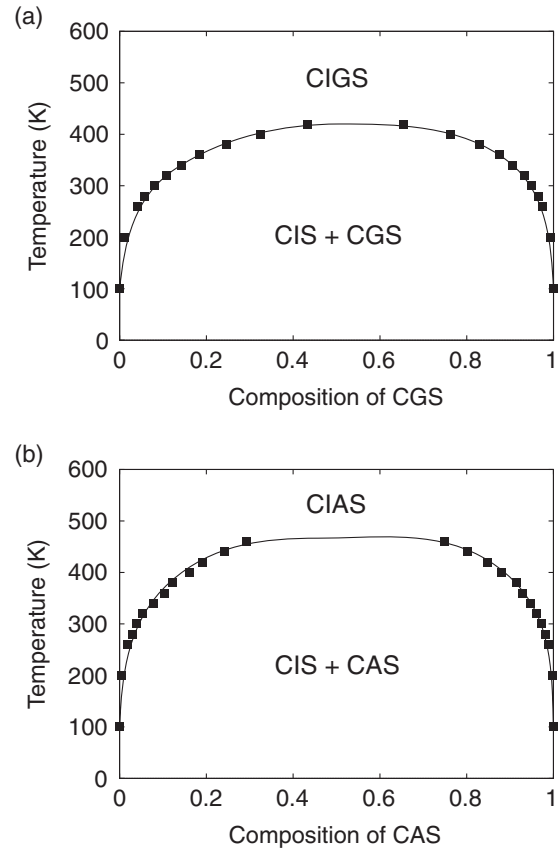


FIG. 2. Phase diagrams of (a) the CIS-CGS and (b) the CIS-CAS pseudobinary systems.

chalcopyrite unit cell, which includes 2000 trivalent cation sites. The thermodynamic averages are evaluated over 5000 steps/site after 5000 steps/site for equilibration. Phase boundaries are determined from the semigrand potentials estimated by the thermodynamic integration. The CE and MC simulations are performed using the CLUPAN code.<sup>32,33</sup>

Figure 2 shows the calculated phase diagrams of the CIS-CGS and CIS-CAS pseudobinary systems. Both systems exhibit the phase separation at low temperature. The binodal curves give the phase-separation critical temperatures of 420 and 460 K for CIS-CGS and CIS-CAS, respectively. The result for CIS-CGS is consistent with the experimental phase diagram constructed for temperature above 1073 K, showing no phase separation of CIS and CGS.<sup>7</sup> Ludwig *et al.* suggested using a combination of first-principles calculations within the GGA, CE, and canonical MC simulations that the phase boundary is located between 290 and 406 K for  $\text{CuIn}_{0.25}\text{Ga}_{0.75}\text{Se}_2$  and  $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$ ,<sup>8</sup> which is similar to our result. In contrast, a critical temperature of  $\sim 15\,000$  K for CIS-CGS has been obtained by Tani *et al.*,<sup>9</sup> who used first-principles calculations based on the CPA and pseudo-self-interaction correction approach for the evaluation of the enthalpy of mixing and the ideal solution model for the configurational entropy. The rather high critical temperature may be attributed to the exclusion of atomic relaxation effects and the resultant overestimation of the enthalpy in their study. Our values of the critical temperature, 420 K for CIS-CGS and 460 K for CIS-CAS, are supported by the fact that these

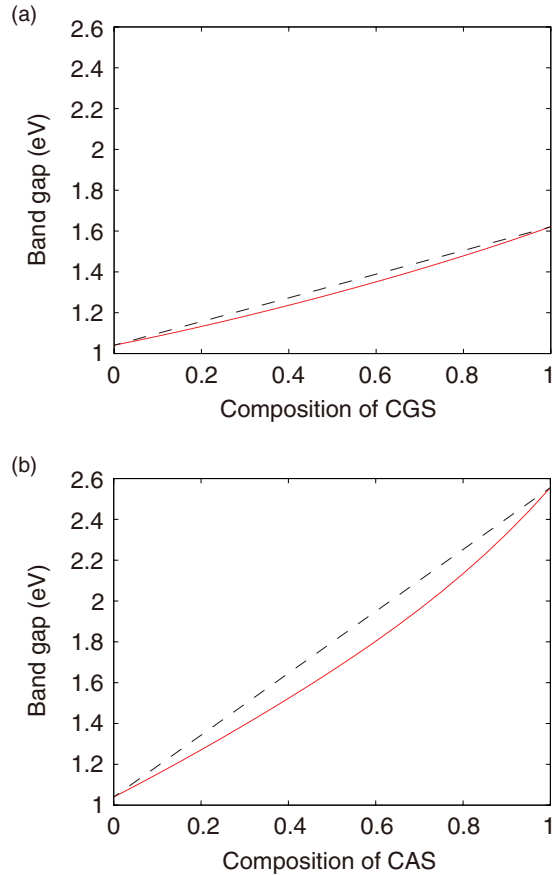


FIG. 3. (Color online) Band gap at the ideal disorder state for (a) CIGS and (b) CIAS. The dashed line corresponds to the linear combination of the band gaps of CIS and CGS or CAS.

alloys are readily quenched down to room temperature for the whole range of composition;<sup>4,5,7</sup> however, the tendency to phase separation can cause alloy inhomogeneity to some extent, as suggested for CIGS by Ludwig *et al.*<sup>8</sup> and Tani *et al.*<sup>9</sup>

Using the ECIs for the band gap and the correlation functions at the ideal disorder state, which are analytically calculated from the composition, the band gap at the ideal disorder state is predicted. The results are shown in Fig. 3. In the whole range of the composition, the band gaps of CIGS and CIAS are smaller than the linear combination of the band gaps of CIS and CGS or CAS and show nearly quadratic composition dependences. Such behavior is referred to as band bowing and often observed for multicomponent semiconductors. The band gap of an A–B binary or pseudobinary alloy  $A_{1-x}B_x$ ,  $E_g(x)$ , can be expressed by

$$E_g(x) = (1-x)E_g^A + xE_g^B - bx(1-x), \quad (2)$$

where  $b$  denotes the bowing parameter, and  $E_g^A$  and  $E_g^B$  are the band gaps of alloy components A and B, respectively. By fitting the calculated band gaps to Eq. (2) in the entire composition range, we obtain the bowing parameters of 0.16 and 0.57 eV for CIGS and CIAS, respectively. It has been reported that the bowing behavior of InGaN alloys cannot be well described by a single bowing parameter but is composition dependent, in which a strong bowing occurs for low In

content.<sup>34</sup> In our results, the bowing of CIAS exhibits such a composition dependence, with a stronger bowing for a higher CAS composition range: the bowing parameter estimated for limited composition ranges of  $x = 0 - 1/3$ ,  $1/3 - 2/3$ , and  $2/3 - 1$  are 0.15, 0.16, and 0.16 eV for CIGS, respectively, whereas those for CIAS are 0.46, 0.56, and 0.72 eV.

Previously, the bowing parameters of CIGS and CIAS have been estimated to be 0.21 and 0.59 eV, respectively, by Wei and Zunger via first-principles calculations for SQSs within the LDA.<sup>12</sup> Our results based on the explicit treatment of atomic configurations are close to their values when the entire composition range is considered in the fitting. As summarized in Ref. 12, a number of experimental values are available for the bowing parameter of CIGS. Most of them are situated between 0.15 and 0.17 eV, and our value is within this range. For CIAS, the experimentally estimated bowing parameter is 0.51 (Ref. 4), 0.57 (Ref. 6), and 0.62 eV (Ref. 3), whereas a larger value of  $\sim 1$  eV has also been reported.<sup>5</sup> Our result is close to the former.

The atomic configurational contributions to the temperature dependence of the band gap, excluding other contributions such as phonons, can be evaluated using the average atomic configuration obtained from the MC simulations at temperature  $T$ . This enables us to estimate the band gaps of the alloys quenched from temperature  $T$ . In Fig. 4, the results are shown

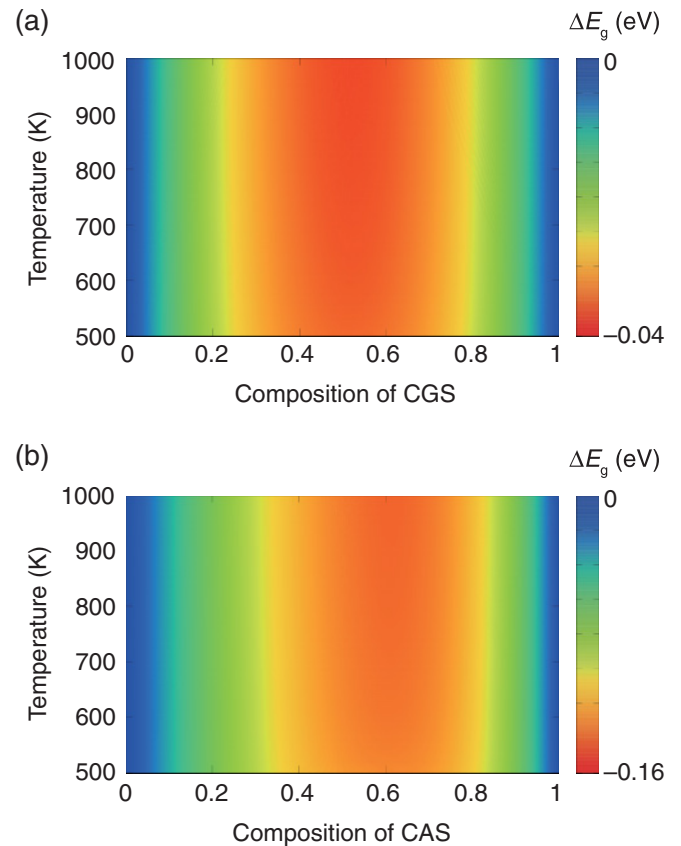


FIG. 4. (Color online) Band gap as a function of the composition and the temperature before quench in (a) CIGS and (b) CIAS. Actually shown is a difference from the linear combination of the band gaps of CIS and CGS or CAS, which is defined as  $\Delta E_g(x) = E_g(x) - [(1-x)E_g^{\text{CIS}} + xE_g^{\text{B}}]$  ( $B = \text{CGS or CAS}$ ).

as a difference from the linear combination of the band gaps of CIS and CGS or CAS. For both CIGS and CIAS, the band gaps are not significantly dependent on the temperature before quench in the entire composition range. Even at temperatures just above the binodal curves, the band gaps are close to those at the high-temperature limit, corresponding to the ideal disorder state considered in Fig. 3. Thus, the atomic configurational contributions to the temperature dependences of the band gaps are small for both CIGS and CIAS.

In summary, we have determined the phase diagrams and band gaps in the CIS-CGS and CIS-CAS pseudobinary systems using a combination of first-principles calculations, CE, and MC simulations. The phase-separation critical temperatures are estimated to be 420 and 460 K for the

CIS-CGS and CIS-CAS systems, respectively. For both CIGS and CIAS alloys, the atomic configurational contributions to the temperature dependence of the band gaps, which lead to the dependence on the temperature before quench, are not significant. The band gaps are generally close to those at the ideal disorder state and show bowing against the composition. For CIAS, composition-dependent bowing behavior is identified, with a stronger bowing in a higher CAS composition range.

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