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Su-Huai Wei,[a] S. B. Zhang, and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

Using a first-principles band structure method we have theoretically studied the effects of Ga additions on the electronic and structural properties of CuInSe$_2$. We find that (i) with increasing x_{Ga}, the valence band maximum of CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) decreases slightly, while the conduction band minimum (and the band gap) of CIGS increases significantly, (ii) the acceptor formation energies are similar in both CuInSe$_2$ (CIS) and CuGaSe$_2$ (CGS), but the donor formation energy is larger in CGS than in CIS, (iii) the acceptor transition levels are shallower in CGS than in CIS, but the Ga$_{Cu}$ donor level in CGS is much deeper than the In$_{Cu}$ donor level in CIS, and (iv) the stability domain of the chalcopyrite phase increases with respect to ordered defect compounds. Our results are compared with available experimental observations. © *1998 American Institute of Physics.* [S0003-6951(98)02924-6]

Because CuInSe$_2$ (CIS) has a band gap of only ~1 eV, i.e., lower than the ideal value for photovoltaic solar cells, it has been suggested[1,2] that Ga addition to CuInSe$_2$, forming the CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) alloy, will raise the gap, and thus increase the open circuit voltage. At present, the best CuInSe$_2$ solar cells are made with $x \lesssim 30\%$ CuGaSe$_2$ (CGS).[3,4] However, the effects of Ga additions remain unexplained. Over the years, the following experimental evidence has been accumulated regarding the effects of Ga addition into CuInSe$_2$.

(1) The band gap increases according to[5]

$$E_g(x) = (1-x)E_g(\text{CIS}) + xE_g(\text{CGS}) - bx(1-x)$$

with a measured bowing coefficient that depends on growth. The most reproducible values are[6] $b = 0.15 - 0.24$ eV.

(2) The hole concentration in the stoichiometric 1:1:2 compound (denoting the ratio of I:III:VI) increases significantly.[7]

(3) The stability domain of the 1:1:2 compound in the phase diagram increases, i.e., the chalcopyrite phase becomes more stable, while the 1:3:5 ordered defect compounds (ODC) Cu(In$_{1-x}$Ga$_x$)$_3$Se$_5$ now have a narrower domain of existence in the phase diagram.[8]

(4) As x_{Ga} increases from zero, the open circuit voltage V_{oc} increases, whereas the short circuit current J_{sc} decreases. Initially, the cell efficiency increases.[9] However, when $x > 0.3$, the following happens: the cell efficiency drops off, unless special manipulations are used,[10] and the 1:1:2 phase can no longer be made n type. It has been suggested[10] that the reason for performance deterioration at $x > 0.3$ is related to strain, i.e., that the lattice mismatch between the 1:1:2 and 1:3:5 phases at the interface increases as $x_{Ga} > 0.3$, causing structural defects. We will test this hypothesis below.

(5) The band gap difference $E_g(1:3:5) - E_g(1:1:2)$ is independent[10,11] of x_{Ga}.

In this letter we theoretically study the effects of Ga additions on the electronic and structural properties of CuIn$_{1-x}$Ga$_x$Se$_2$. We use the self-consistent local density approach,[12] as implemented via the linearized augmented plan wave method.[13] Details of the method are described in Ref. 14. We find the following changes.

(1) Change in band gap upon Ga addition. We calculated the bowing parameter by comparing the band gap of CuIn$_{0.5}$Ga$_{0.5}$Se$_2$ alloy (represented by the ''special quasirandom structures'' [6]) to the average of the gaps of CuInSe$_2$ and CuGaSe$_2$. Our calculated value is $b = 0.21$ eV, in good agreement with the measured values $b = 0.15 - 0.24$ eV.[6] The band gap increase upon Ga addition contributes to the increased V_{oc}. It is interesting to note that the bowing coefficient of CuIn$_{1-x}$Ga$_x$Se$_2$ is only about half of that for In$_{1-x}$Ga$_x$As alloy ($b = 0.47$ eV).[15] This is mainly due to the fact that in CuIn$_{1-x}$Ga$_x$Se$_2$, when In is replaced by Ga, only half of the cations are affected, while in In$_{1-x}$Ga$_x$As all cations are affected by the substitution.

(2) Band offset between CuGaSe$_2$/CuInSe$_2$. The offset ΔE_v between the valence band maxima (VBM) of CIS and CGS is calculated using the method described in Ref. 6. We find that the unstrained ΔE_v, i.e., when CIS and CGS each have their own equilibrium lattice constants, is only 0.04 eV. Thus, the conduction band minimum (CBM) of CGS is about 0.6 eV higher than that of CIS. The phenomenological ''doping limit rule'' [16] states that materials whose absolute CBM (VBM) energies, i.e., relative to a fixed reference energy level such as vacuum, higher (lower) than a fixed Fermi pinning levels $E_F^{(n)}$ ($E_F^{(p)}$) will have restricted n-type (p-type) dopability. The calculated ΔE_v suggests that p-type doping in CIS and CGS should be similar, while n-type doping is more difficult in CGS than in CIS.

(3) Change in single defect formation energies upon Ga addition. We model a defect by placing it at the center of an artificially large unit cell containing N units of CIGS and impose periodic boundary conditions on this ''supercell''.[14] All atoms λ ($\lambda = $ Cu, Ga, In, and Se) inside the supercell are relaxed to minimize the total energy. The defect formation energy $\Delta H_f(\alpha, q)$ of defect α, e.g., vacancy or antisite, in charge state q depends on the Fermi energy ϵ_F as well as on

[a]Electronic mail: shw@sst.nrel.gov

TABLE I. Components of the calculated point defect formation energies $\Delta H(\alpha, q)$ [see Eq. (1)] in CuGaSe$_2$ and CuInSe$_2$.

Defect α	$\Delta E(\alpha, q)$ (eV)		n_{Cu}	n_M	q
	CGS (M=Ga)	CIS (M=In)			
V_{Cu}^0	0.66	0.60	+1	0	0
V_{Cu}^-	0.67	0.63	+1	0	−1
V_M^0	2.83	3.04	0	+1	0
V_M^-	3.02	3.21	0	+1	−1
V_M^{2-}	3.40	3.62	0	+1	−2
V_M^{3-}	4.06	4.29	0	+1	−3
Cu_M^0	1.41	1.54	−1	+1	0
Cu_M^-	1.70	1.83	−1	+1	−1
Cu_M^{2-}	2.33	2.41	−1	+1	−2
M_{Cu}^{2+}	2.04	1.85	+1	−1	+2
M_{Cu}^+	3.03	2.55	+1	−1	+1
M_{Cu}^0	4.22	3.34	+1	−1	0
Cu_i^+	1.91	2.04	−1	0	+1
Cu_i^0	3.38	2.88	−1	0	0

TABLE II. Calculated defect transition levels $\epsilon_\alpha(q/q')$ [Eq. (2)] in CuGaSe$_2$ and CuInSe$_2$. The acceptor levels are measured from VBM energy E_V, while the donor levels are measured from CBM energy E_C. Energy is in eV.

Defect α	Defect level	CGS (M=Ga)	CIS (M=In)
V_{Cu}	(−/0)	$E_V + 0.01$	$E_V + 0.03$
V_M	(−/0)	$E_V + 0.19$	$E_V + 0.17$
V_M	(2−/−)	$E_V + 0.38$	$E_V + 0.41$
V_M	(3−/2−)	$E_V + 0.66$	$E_V + 0.67$
Cu_M	(−/0)	$E_V + 0.29$	$E_V + 0.29$
Cu_M	(2−/−)	$E_V + 0.61$	$E_V + 0.58$
M_{Cu}	(0/+)	$E_C − 0.49$	$E_C − 0.25$
M_{Cu}	(+/2+)	$E_C − 0.69$	$E_C − 0.34$
Cu_i	(0/+)	$E_C − 0.21$	$E_C − 0.20$

the *chemical potentials* μ_λ and the number of atom n_λ transferred from the supercell to the chemical reservoir in forming the defect cell. In CIGS, neglecting Se-related defects,

$$\Delta H_f(\alpha, q) = \Delta E(\alpha, q) + n_{Cu}\mu_{Cu} + n_{Ga}\mu_{Ga} + n_{In}\mu_{In} + q\epsilon_F,$$ (1)

where the $\Delta E(\alpha, q)$ for CGS are compared with the results for CIS in Table I. Since the calculation for CuGaSe$_2$ and CuInSe$_2$ are done on the same footing, the energy *difference* between the results for CGS and CIS are more accurate than the absolute values. We see that the calculated defect formation energies $\Delta E(\alpha, q)$ of single *acceptor* defects (V_{Cu}, V_{Ga}, and Cu_{Ga}) in CGS are similar (within experimental and theoretical accuracy) to their counterparts in CIS, so the acceptor density is expected to be similar in both CGS and CIS. However, the calculated formation energies of single donor defects (Ga_{Cu}^0, Cu_i^0) in CGS are larger than their counterparts in CIS at $\mu_\lambda = \mu_\lambda^{solid}$, so the donor density in CGS is expected to be lower in CGS than in CIS under similar growth conditions. The large formation energy of the Ga_{Cu} in CGS relative to In_{Cu} in CIS is mainly due to the larger band gap of CGS compared to CIS and the larger cohesive energy of Ga metal relative to In metal. The differences in the formation energy of the Ga_{Cu} in CGS relative to In_{Cu} in CIS are reduced when the defects are charged.

(4) Change in point-defect energy levels upon Ga addition. The defect transition energy level $\epsilon_\alpha(q/q')$ is the Fermi energy in Eq. (1) at which the formation energy $\Delta E(\alpha, q)$ of defect α of charge q is equal to that of defect α in another charge q', i.e.,

$$\epsilon_\alpha(q/q') = [\Delta E(\alpha, q) - \Delta E(\alpha, q')]/(q' - q).$$ (2)

Table II compares our calculated defect transition energy levels in CuGaSe$_2$ with the corresponding transition energy levels in CuInSe$_2$. We see that the acceptor levels (−/0), (2−/−), and (3−/2−) in CGS are similar to (or slightly shallower than) that in CIS, suggesting slightly more holes in CGS. However, we find that the Ga_{Cu} antisite donor levels are much deeper than those of the In_{Cu} donor levels. Thus, in

so far as III-on-I antisite defects contribute to n typeness, CGS will be less n type than CIS. The reasons for the deeper Ga_{Cu} donor levels are twofold: (1) Ga is a smaller atom than In, so lattice compression pushes its CBM upward more than it pushes the defect level, thus deepening the defect level, and (2) the wave function of Ga_{Cu} and In_{Cu} antisite defects has an s character and is localized on the group III atom. Since the Ga $4s$ atomic orbital energy is about 0.7 eV lower[17] than the In $5s$ orbital energy, the Ga_{Cu} is deeper than the In_{Cu}. Our results above indicate that, since there are more holes (shallower acceptors) and fewer compensating electrons (deep donors) in CGS than in CIS, the hole density in CGS is expected to be higher than in CIS, as has been observed experimentally.[7] Furthermore, because of the difficulty of n-type doping of CGS and its ordered defect compounds, the $p-n$ junction in a CIGS solar cell with high Ga concentration is shifted towards the interface between CIGS and a window material, e.g., CdS.[10] The increased roughness at the CIGS/CdS heterojunction interface (compared to the homojunction interface between CIGS/ODC) can increase minority carrier recombination, thus reduce J_{sc}.

(5) Change in the stability of defect pairs upon Ga addition. We have previously shown[14] that ordered defect compounds in CIS result from the unusual stability of a special defect pair: $In_{Cu} + 2V_{Cu}$ (two Cu vacancies next to an In-on-Cu antisite). A periodic spatial repetition of this pair gives the ordered defect compounds. The formation energy has the following contributions:

(a) Formation of neutral $2V_{Cu}^{-0}$ plus neutral In_{Cu}^0 (or Ga_{Cu}^0), without interaction between the defects. If the elemental solids are used as chemical reservoir,[14] in CIS this step costs 4.5 eV, while in CGS it costs 5.5 eV.

(b) The energy lowering due to the transfer of two electrons from the In_{Cu}^0 (or Ga_{Cu}^0) donor to the $2V_{Cu}^0$ acceptor. In CIS this step gives -1.4 eV, while in CGS it gives -2.2 eV.

(c) The Coulomb attraction between the ensuing charged In_{Cu}^{2+} (or Ga_{Cu}^{2+}) and $2V_{Cu}^-$. In both CIS and CGS this step gives -2.5 eV.
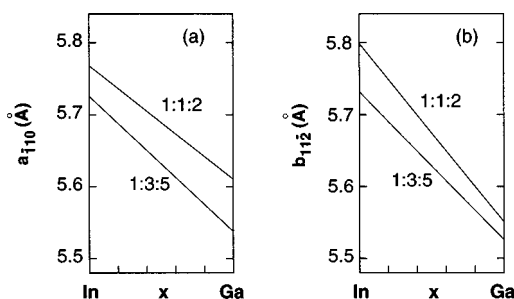
(d) The energy lowering due to atomic relaxation accompa-

FIG. 1. Calculated lattice mismatch between the 1:1:2 and 1:3:5 phases as a function of Ga composition x. The results are projected on (a) the $[\bar{1}10]$ and (b) the $[11\bar{2}]$ directions.

nying the above noted charge transfer. In CIS it is -0.3 eV whereas in CGS it is only -0.1 eV.

The sum of (b)+(c)+(d) is called the ''defect pair interaction energy.'' For $In_{Cu}+2V_{Cu}$ it is -4.2 eV, and for $Ga_{Cu}+2V_{Cu}$ it is -4.8 eV. Adding the formation energy of the neutral defect [step (a)] to the defect pair interaction energy we see that in CIS it costs 0.3 eV to form the charged pair, while in CGS it costs 0.7 eV. We thus see that *Ga addition lowers the relative stability of the defect pairs.*

(6) Defect ordering. The formation energy of the charge defect pairs can be further lowered when they form ordered defect arrays. The ordering energy is about -0.4 eV in CIS and -0.5 eV in CGS. Thus, the formation energy of the ordered defect array is -0.1 eV/pair for CIS and 0.2 eV/pair for CGS when bulk solid elements are used as chemical reservoirs. Because of this unusually low formation energy of the ordered defect array, ordered defect compounds are predicted to form spontaneously under proper thermodynamic growth conditions.[14] Furthermore, since our calculated formation energy of 1:1:2 CGS (2.1 eV) is larger than 1:1:2 CIS (2.0 eV), while CGS ODC is less stable than CIS ODC, the stability domain of the 1:1:2 CIGS increases with Ga addition.

(7) Effect of Ga addition on lattice mismatch between 1:1:2 and 1:3:5 phases. The equilibrium lattice constants of a given phase are calculated by minimizing the total energy with respect to the lattice constants. The calculated lattice constants for CIS and CGS are projected on the $[\bar{1}10]$ and $[11\bar{2}]$ directions which are orthogonal to the (111) interface between the 1:1:2 and 1:3:5 phases.[18] Figure 1 shows how the addition of Ga changes the lattice mismatch between the 1:1:2 and 1:3:5 phases, assuming that the lattice mismatch changes linearly as a function of x. We see that the lattice mismatch between the 1:1:2 and 1:3:5 phases is increased along the $[\bar{1}10]$ direction, but is decreased along the $[11\bar{2}]$ direction. In either case, the *change* of the lattice mismatch due to Ga addition is small, thus is unlikely to be the main reason for device deterioration at $x>0.3$.

(8) Effect of Ga addition on band gap difference be-

tween 1:1:2 and ODC phases. The calculated band gap differences $E_g(1{:}3{:}5)-E_g(1{:}1{:}2)$ are 0.24 eV for CIS and only 0.07 eV for CGS. The smaller band gap increase in CGS than in CIS is due to the significant lowering of the 1:3:5 CGS conduction band minimum (for the same reason that the Ga_{Cu} donor states are deep relative to CBM in CGS). However, experimental measurements[10,11] show that the difference is ~ 0.2 eV and is nearly independent of the Ga concentration in CIGS. It is not clear whether this difference with respect to theory reflects a structural change in Ga-rich ODCs.[11] Further investigations are needed to solve this discrepancy.

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[18] We use here the notations for the cubic (zinc-blende) structure. If one uses the notations for the tetragonal chalcopyrite structure, a factor of 2 should be multiplied on the z component of the cubic notation. For example, [111] in the cubic notation is [112] in the tetragonal notation.