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Su-Huai Wei, S. B. Zhang, and Alex Zunger

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Effects of Ga addition to $CuInSe_2$ on its electronic, structural, and defect properties

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

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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 $CuIn_{1\,2\,x}Ga_xSe_2$ ~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.
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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 $CuIn_{1\,2\,x}Ga_xSe_2$ ~CIGS! alloy, will raise the gap, and thus increase the open circuit voltage. At present, the best $CuInSe_2$ solar cells are made with $x<30\%$ $CuGaSe_2$ ~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]

$$E_g\text{~}x\text{! 5 ~}1\;2\;x\text{!}E_g\text{~CIS! 1 }xE_g\text{~CGS! 2 }bx\text{~}1\;2\;x\text{!}$$

with a measured bowing coefficient that depends on growth. The most reproducible values are[6] b 5 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! $Cu(In_{1\,2\,x}Ga_x)_3Se_5$ 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 $E_g(1{:}3{:}5)\,2\,E_g(1{:}1{:}2)$ 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 $CuIn_{1\,2\,x}Ga_xSe_2$. 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 5 0.21 eV, in good agreement with the measured values b 5 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 $CuIn_{1\,2\,x}Ga_xSe_2$ is only about half of that for $In_{1\,2\,x}Ga_xAs$ alloy (b 5 0.47 eV).[15] This is mainly due to the fact that in $CuIn_{1\,2\,x}Ga_xSe_2$, when In is replaced by Ga, only half of the cations are affected, while in In the *chemical potentials* μ_1 and the number of atom n_1 transferred from the supercell to the chemical reservoir in forming the defect cell. In CIGS, neglecting Se-related defects,

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

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^0_{Cu}, Cu^0_i) in CGS are larger than their counterparts in CIS at $\mu_1 = \mu_1^{solid}$, 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 $\epsilon_a(q/q')$ 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.,

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

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: (i) nying the above noted charge transfer. In CIS it is 2 0.3 eV whereas in CGS it is only 2 0.1 eV.

The sum of ~b! 1 ~c! 1 ~d! is called the ''defect pair interaction energy.'' For In_{Cu} 1 2V_{Cu} it is 2 4.2 eV, and for Ga_{Cu} 1 2V_{Cu} it is 2 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