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Effects of Na on the electrical and structural properties of $CuInSe_2$

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We found theoretically that Na has three effects on $CuInSe_2$: (1) If available in stoichiometric quantities, Na will replace Cu, forming a more stable $NaInSe_2$ compound having a larger band gap (higher open-circuit voltage) and a $(112)_{\mathrm{tetra}}$ morphology. The ensuing alloy $Na_xCu_{1-x}InSe_2$ has, however, a positive mixing enthalpy, so $NaInSe_2$ will phase separate, forming precipitates. (2) When available in small quantities, Na will form defect on Cu site and In site. Na on Cu site does not create electric levels in the band gap, while Na on In site creates acceptor levels that are shallower than Cu_{In}. The formation energy of $Na_{(In_{Cu})}$ is very exothermic, therefore, the major effect of Na is the elimination of the In_{Cu} defects and the resulting increase of the effective hole densities. The quenching of In_{Cu} as well as V_{Cu} by Na reduces the stability of the $(2V_{Cu}^{-}+In_{Cu}^{2+})$, thus suppressing the formation of the ''Ordered Defect Compounds.'' (3) Na on the surface of $CuInSe_2$ is known to catalyze the dissociation of O_2 into atomic oxygen that substitutes Se vacancy (shallow donors), converting them into O_{Se}. We find, however, that O_{Se} is an (isovalent) *deep* rather than shallow acceptor. We also find that having removed the donors, O atoms in $CuInSe_2$ form Cu_2O and In_2O_3 compounds, and phase separate, forming precipitates at the surfaces and grain boundaries. Our results are compared with previous models and provide new insights into the defect physics of Na in CIS. © *1999 American Institute of Physics.* [S0021-8979(99)07010-3]

I. INTRODUCTION

It has been observed that $CuIn_{1-x}Ga_xSe_2$ (CIGS) solar cells containing small amounts of Na achieve higher efficiencies compared to those without Na.[1–4] The most significant effects are: (a) increased hole density[4–6] and film conductivity[7,8] and (b) suppression of the formation of the ''ordered defect compound'' (ODC).[9,10] Other, more incidental effects were seen as well, e.g., improved film morphology, orientation, and grain sizes,[7,11–13] increased uniformity of photocurrents and short-circuit current,[7] higher open circuit voltage,[2–6,11,12] and higher fill factors.[11,12] Substantial efforts have been invested to model the role of Na in CIGS. For example, Cahen *et al.*,[5] Ruckh *et al.*[6] and Nakada *et al.*[4] suggested that the increase in the open circuit voltage is a consequence of a higher effective acceptor concentration. Three models have been proposed to account for the increase in the hole density:

(i) *The oxygen model:* Cahen *et al.*[5] and Ruckh *et al.*[6] suggested that the increase in the hole density is due to the neutralization of donor-like Se vacancies V_{Se} through an enhanced chemisorption of oxygen atom in the presence of sodium.[5,6] Thus, in their model the Na-induced effects on CIGS are a consequence of oxidation. This assumption was further promoted by Kronik *et al.*[14] who suggest that surface (including grain boundary) formation in CIGS is accompanied by the formation of surface Se vacancies which are electrically active donors. When oxygen substitutes V_{Se} it forms O_{Se} which, in their model is a shallow acceptor at about ~130 meV. Na merely catalyzes O_2 dissociation, thus supplying the needed atomic oxygen.

(ii) *The In_{Cu} model:* Contreras *et al.*[1,15] suggest that the increase of the effective acceptor concentration is due to the elimination of the compensating antisite donor defect In_{Cu}.

(iii) *The Na_{In} model:* Niles *et al.*[16] suggest that the increases in acceptor concentration in the presence of Na could be due to direct creation of acceptors such as antisite defect[16–18] Na_{In}.

Using first-principles total energy and band structure method, we have studied theoretically the Na-induced effects in $CuInSe_2$. We calculated the ground state properties of $NaInSe_2$, $CuInSe_2$, and their alloys and related binary compounds. We also calculated the formation energies and the transition energy levels for a number of point defects: Na_{Cu}, Na_{In}, V_{Se}, and O_{Se} in $CuInSe_2$. We thus clarify models (i)–(iii) on the Na-induced increase in hole density and explain the suppression of ordered defect compounds in the presence of Na.

II. METHOD OF CALCULATION

The method used in this study was described in Ref. 19. Here, we only mention some of its salient features.

Defect calculations are performed by placing the point defect at a center of an artificially large unit cell containing N molecules of $CuInSe_2$. We then impose periodic boundary conditions on this ''supercell'' so that the Schrodinger equation for this system can be solved using standard band structure methods. The unphysical defect–defect interaction between adjacent supercells is reduced by increasing N systematically ($N=8$ is used in the present calculation). The Schrödinger equation solved self-consistently includes interaction between the electrons (Coulomb, exchange, and correlation) as well as interactions between the electrons and the nuclei, and interactions between the nuclei. Atoms are dis-

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placed until the quantum-mechanical forces vanish, thus yielding the equilibrium geometry. At this point, we compute the total energy $E(\alpha,q)$ for a cell containing the relaxed defect α in charge state q. We also compute the total energy $E(\text{CuInSe}_2)$ for the same supercell in the absence of the defect. From these quantities we calculate the ''*defect formation energy*'' $\Delta H_f(\alpha,q)$. It depends on[19] the Fermi energy ϵ_F as well as on the atomic chemical potentials μ_i. The reason that ΔH_f depends on the chemical potentials is that in forming a defect, the atom is transferred to or from a chemical reservoir that has a characteristic energy called the chemical potential μ_i. Similarly, the reason that ΔH_f depends on the Fermi energy is that in forming a charged defect, the electron is transferred to or from a electron reservoir whose energy is ϵ_F. In CuInSe_2:

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

where

$$\Delta E(\alpha,q)=E(\alpha,q)-E(\text{CuInSe}_2)+n_{\text{Cu}}\mu^0_{\text{Cu}}+n_{\text{In}}\mu^0_{\text{In}}+n_{\text{Se}}\mu^0_{\text{Se}}+n_X\mu^0_X+qE_V. \quad (2)$$

Here, $\epsilon_F=\epsilon^a_F-E_V$ (''a'' denotes absolute values) is the Fermi energy of the electrons referenced to the valence band maximum (VBM) of CuInSe_2. $\mu_i=\mu^a_i-\mu^0_i$ is the chemical potential of constituent i relative to its chemical potential μ^0_i in the stable phase (elemental solids for Cu, In, Se, Na, and diatomic molecule for O_2). The n's are the numbers of Cu, In, Se atoms or the impurity ($X=$Na or O) atoms, and q is the the number of electrons, transferred from the supercell to the reservoir in forming the defect cell (e.g., for the Na^{-1}_{In} defect, $n_{\text{Na}}=-1$, $n_{\text{In}}=1$, $q=-1$, and others are null).

The ''*defect transition energy level*'' $\epsilon_\alpha(q/q')$ is the Fermi energy ϵ_F in Eq. (1) at which the formation energy $\Delta H_f(\alpha,q)$ of defect α of charge q is equal to that of another charge q' of the same defect, i.e.,

$$\epsilon_\alpha(q/q')=[\Delta E(\alpha,q)-\Delta E(\alpha,q')]/(q'-q). \quad (3)$$

For example, $\epsilon_\alpha(0/+)$ is a donor level. When ϵ_F is below $\epsilon_\alpha(0/+)$ the defect α is positively charged. When ϵ_F is above $\epsilon_\alpha(0/+)$ the defect α is neutral. Similarly, $\epsilon_\alpha(-/0)$ is an acceptor level. When ϵ_F is below $\epsilon_\alpha(-/0)$ the defect α is neutral, while defect α is negatively charged when ϵ_F is above $\epsilon_\alpha(-/0)$.

There are some thermodynamic limits[19] to μ_i and $\epsilon_F:\epsilon_F$ is bound between the valence band maximum E_v and the conduction band minimum E_c, and μ_i are bound by (i) the values that will cause precipitation of solid elemental Cu, In, and Se, so $\mu_i\leq 0$, (ii) by the values that maintain a stable CuInSe_2 compound, so $\mu_{\text{Cu}}+\mu_{\text{In}}+2\mu_{\text{Se}}=\Delta H_f(\text{CuInSe}_2)$, where $\Delta H_f(\text{CuInSe}_2)$ is the formation energy of solid CuInSe_2 from the elemental solids, and (iii) by the values that will cause formation of binaries (e.g., Cu_2Se and In_2Se_3). Similar consideration applies to the formation of NaInSe_2. Our calculated formation enthalpies are:

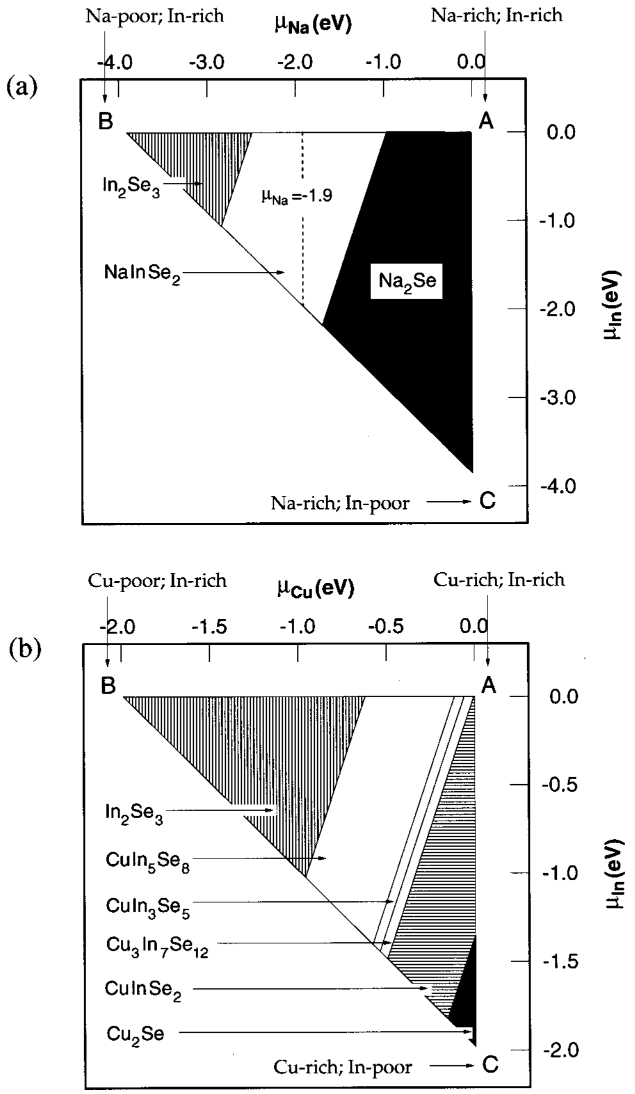

FIG. 1. The calculated stability triangle of (a) the Na–In–Se systems in the $\mu_{\text{Na}},\mu_{\text{In}}$ plane and (b) the Cu–In–Se systems in the $\mu_{\text{Cu}},\mu_{\text{In}}$ plane. The dashed line in (a) gives the boundary $\mu_{\text{Na}}=-1.9$ eV. Under thermal equilibrium between CuInSe_2 and NaInSe_2 $\mu_{\text{Na}}\leq-1.9$ eV [Eq. (6)]. Note the different energy scale in (a) and (b).

$$\Delta H_f(\text{NaInSe}_2)=-3.9\text{ eV};\ (\text{CrNaS}_2\text{ layered structure}),$$

$$\Delta H_f(\text{CuInSe}_2)=-2.0\text{ eV};\ (\text{chalcopyrite structure}),$$

$$\Delta H_f(\text{Na}_2\text{Se})=-3.4\text{ eV};\ (\text{CaF}_2\text{ structure}),$$

$$\Delta H_f(\text{Cu}_2\text{Se})=-0.3\text{ eV};\ (\text{CaF}_2\text{ structure}),$$

$$\Delta H_f(\text{In}_2\text{Se}_3)=-2.1\text{ eV};\ (\text{cubic structure}).^{19} \quad (4)$$

Figure 1 shows our calculated stability triangle for NaInSe_2 and CuInSe_2.

Furthermore, to maintain a stable NaInSe_2 with CuInSe_2, one needs to have

$$\mu_{\text{Na}}+\Delta H_f(\text{CuInSe}_2)=\Delta H_f(\text{NaInSe}_2)+\mu_{\text{Cu}}. \quad (5)$$

So, under equilibrium condition, NaInSe_2 is stable only when μ_{Na} is bound by

$$-3.9\text{ eV}\leq\mu_{\text{Na}}=-1.9\text{ eV}+\mu_{\text{Cu}}\leq-1.9\text{ eV}, \quad (6)$$

since $\mu_{\text{Cu}}\leq 0$ and the calculated formation energy difference

$$\Delta H_f(\text{NaInSe}_2)-\Delta H_f(\text{CuInSe}_2)=-1.9\text{ eV}. \quad (7)$$

Equation (6) indicates that under thermal equilibrium μ_{Na} and μ_{Cu} are related. It is also clear from Fig. 1 and Eq. (6) that at equilibrium, the only Na compound that can coexist with $\mathrm{CuInSe_2}$ is $\mathrm{NaInSe_2}$.

The needed total energies and band structures are calculated using the local density approximation (LDA)[20] as implemented by the general potential linearized augmented plane wave (LAPW) method.[21] The LDA error on the band gap is corrected by adding a constant potential to the conduction states so the band gap of $\mathrm{CuInSe_2}$ matches the experimental value of 1.04 eV. To study the atomic relaxation in anion vacancy V_{Se} and substitutional impurity $\mathrm{O_{Se}}$ we have also used the ''$X\alpha$ method'' [22] to correct the LDA band gap error so that the defect level is inside the band gap, and correct level occupations are achieved. We estimated that the uncertainty in our calculated defect formation energies and defect transition energy levels is about ±0.2 eV.

III. RESULTS AND DISCUSSIONS

Our studies show that Na has three effects on $\mathrm{CuInSe_2}$:

A. Effect 1: Formation of secondary phases at large Na concentration

The calculated enthalpy of the $\mathrm{Na_{Cu}}$ substitution reaction

$$\mathrm{Na_{metal}}+\mathrm{CuInSe_2(chalcopyrite)}\rightleftharpoons\mathrm{NaInSe_2(layered)}+\mathrm{Cu_{metal}},\tag{8}$$

is negative $\Delta H_R=-1.9\,\mathrm{eV}$, so the reaction proceeds forwards. Here we assume that Na and Cu are in the metallic phase, $\mathrm{CuInSe_2}$ is in its stable chalcopyrite structure (space group $I\bar{4}2d$), while the $\mathrm{NaInSe_2}$ is in its stable state $\mathrm{CrNaS_2}$ layered structure (space group $R\bar{3}m$).[23] Details of the predicted structural parameters of $\mathrm{NaInSe_2}$ are given in the Appendix. The formation of this secondary $\mathrm{NaInSe_2}$ phase suggested by our calculated ΔH_R is expected to have the following effects:

(a) Raising the band gap relative to $\mathrm{CuInSe_2}$. For example, if 1/8 of Cu in $\mathrm{CuInSe_2}$ is replaced by Na, the band gap is predicted to increase by 0.11 eV. The increase of the band gap contributes to an enhanced open-circuit voltage.[2–6,11,12]

(b) Being a layered structure with c axis along the [111] direction ($[112]_{\mathrm{tetra}}$ in the tetragonal lattice), the presence of $\mathrm{NaInSe_2}$ in $\mathrm{CuInSe_2}$ also alters the film morphology of $\mathrm{CuInSe_2}$, rendering it a preferred $(112)_{\mathrm{tetra}}$ orientation.[7,11–13,24]

However, we find that $\mathrm{NaInSe_2}$ and $\mathrm{CuInSe_2}$ have but a limited mutual solid solubility since the mixing enthalpy for the reaction

$$x\mathrm{NaInSe_2}+(1-x)\mathrm{CuInSe_2}\rightleftharpoons\mathrm{Na_xCu_{1-x}InSe_2},\tag{9}$$

is *positive* $\Delta H_{\mathrm{mix}}=x(1-x)\Omega$ with $\Omega=0.67\,\mathrm{eV}$. Thus the substitution reaction [Eq. (8)] could lead to phase separation and the precipitation of a secondary phase on surfaces or grain boundaries, as observed by a number of experiments.[15,24–26]

B. Effect 2: Formation of point defects at small Na concentrations

A *small* amount of Na leads to the formation of point defects, rather than to well-developed bulk-like secondary phases as in Eq. (8). We studied two leading Na-related defects:

(a) Na-on-Cu defect $\mathit{Na_{Cu}}$: The formation energy of this substitutional defect is exothermic $\Delta H(\mathrm{Na_{Cu}})=-1.1\,\mathrm{eV}$ at $\mu_{\mathrm{Cu}}=\mu_{\mathrm{Na}}=0$, but becomes endothermic $\Delta H(\mathrm{Na_{Cu}})=+0.8\,\mathrm{eV}$ under equilibrium condition $\mu_{\mathrm{Na}}=\mu_{\mathrm{Cu}}-1.9\,\mathrm{eV}$ [Eq. (6)]. The formation energy of Na occupying a Cu vacancy site is $\Delta H(\mathrm{Na}_{V_{\mathrm{Cu}}})=\Delta H(\mathrm{Na_{Cu}})-\Delta H(V_{\mathrm{Cu}})=0.2\,\mathrm{eV}-\mu_{\mathrm{Cu}}$, where $\Delta H(V_{\mathrm{Cu}})=0.6+\mu_{\mathrm{Cu}}\,\mathrm{eV}$.[19] Thus, under equilibrium condition, only part of the Cu vacancies in $\mathrm{CuInSe_2}$ are quenched by Na. We find that $\mathrm{Na_{Cu}}$ does not introduce gap levels, thus it is electrically inactive.

To assist in experimental identification of $\mathrm{Na_{Cu}}$, we have calculated its core shift. Our calculated core level energies show that $\mathrm{Na_{Cu}}$ has a signature of *reducing* the binding energy of nearest Se core level by 0.34 eV relative to that in pure $\mathrm{CuInSe_2}$.

(b) Na-on-In antisite $\mathit{Na_{In}}$: This defect is expected to exist in lower concentration if In is on the nominally In site, as its calculated formation enthalpy is positive $\Delta H(\mathrm{Na_{In}})=2.5\,\mathrm{eV}$ at $\mu_{\mathrm{In}}=0$ and $\mu_{\mathrm{Na}}=-1.9\,\mathrm{eV}$. We find that $\mathrm{Na_{In}}$ is electrically active, showing single acceptor $E(-/0)=E_v+0.20\,\mathrm{eV}$ as well as double acceptor $E(2-/-)=E_v+0.45$ electrical level transitions. Since the calculated $\mathrm{Na_{In}}$ single acceptor electrical level transition is shallower than the calculated[19] $\mathrm{Cu_{In}}$ acceptors, introduction of $\mathrm{Na_{In}}$ in $\mathrm{CuInSe_2}$ is expected to raise the hole density.[5,6] However, as suggested by Contreras *et al.*,[2,15] if In is at a nominally Cu site, Na can reduce effectively the concentration of $\mathrm{In_{Cu}}$ donors thus enhance significantly the effective hole density.[5,6] This is because the formation energy $\Delta H(\mathrm{Na}_{\mathrm{In}_{\mathrm{Cu}}^{2+}})=-1.0\,\mathrm{eV}$ at $\mu_{\mathrm{In}}=\epsilon_F=0$ and $\mu_{\mathrm{Na}}=-1.9\,\mathrm{eV}$ is strongly exothermic. The latter effect is probably the most important effect of Na in $\mathrm{CuInSe_2}$ since most of the $\mathrm{CuInSe_2}$ solar cells are Cu poor, thus containing significant amount of $\mathrm{In_{Cu}}$ antisite defects bounded to the acceptor V_{Cu}.[19] Indeed, experimentally, it is observed that the *increase* of solar cell efficiency is larger for $\mathrm{CuInSe_2}$ with smaller Cu/In ratios.[3,5]

Again, to assist in the identification of $\mathrm{Na_{In}}$ defect, we calculated its core level energies. We find that the core level binding energy of Se atoms next to $\mathrm{Na_{In}}$ is *reduced* by 0.65 eV relative to that in pure $\mathrm{CuInSe_2}$. Furthermore, the calculated core binding energy of Na on a Cu site is 0.28 eV larger than that of Na on an In site. Thus, the presence of $\mathrm{Na_{In}}$ can be detected by measuring the binding energies.

The ''ordered defect compounds'' are periodic repetitions of $(2V_{\mathrm{Cu}}^{-}+\mathrm{In}_{\mathrm{Cu}}^{2+})$ defect pairs described in Ref. 19. Since Na quenches effectively $\mathrm{In_{Cu}}$ and to some degree also the Cu vacancy V_{Cu}, the formation of the ''building blocks'' $2V_{\mathrm{Cu}}^{-}+\mathrm{In}_{\mathrm{Cu}}^{2+}$ for ODC[19] will be greatly suppressed in the presence of Na. Thus, the ODC region in the phase diagram of CIS [Fig. 1(b)] is predicted to shrink relative to that without Na. This conclusion is supported by many experiment observations,[2,5,9,10,25] but contradicts the observation of

Tanaka *et al.*[27] who find that high Na levels in CIGS lead to a transition from chalcopyrite to ODC.

C. Effect 3: Na-induced oxygen point defects

The presence of Na is known to reduce the work function of the CIGS thin film[28] and to weaken the O–O bond of molecular oxygen,[5,14] forming the chemically active *atomic* oxygen that can penetrate the $\mathrm{CuInSe_2}$ lattice. We find that atomic oxygen can effectively quench Se vacancies (V_{Se}) as the calculated heat of reaction for oxygen substitution of Se vacancy

$$\mathrm{O}+\mathrm{Cu}_n\mathrm{In}_n\mathrm{Se}_{2n-1}V_{\mathrm{Se}}\rightarrow\mathrm{Cu}_n\mathrm{In}_n\mathrm{Se}_{2n-1}\mathrm{O}, \tag{10}$$

is strongly negative $\Delta H_R(\mathrm{O}_{V_{\mathrm{Se}}})=-4.3\,\mathrm{eV}$ when $\mu_{\mathrm{Se}}=\mu_{\mathrm{O}}=0$. To understand the effect of removal of Se vacancy V_{Se}, we first study their properties.

The formation energy $\Delta H(V_{\mathrm{Se}}^0)=3.0$ eV at $\mu_{\mathrm{Se}}=0$. The neutral Se vacancy V_{Se}^0 has a fully occupied *s*-like gap level a_1^2; when ionized, V_{Se}^{2+} has the closed-shell configuration a_1^0. We have calculated the double donor transition energy level $2E(0/2+)=E(V_{\mathrm{Se}}^0)-E(V_{\mathrm{Se}}^{2+})$ as (i) a vertical optical (Frank–Condon) transition (i.e., V_{Se}^{2+} is assumed to have the same structure as V_{Se}^0) and (ii) as a relaxed thermal transition (the structure of V_{Se}^{2+} is relaxed separately from V_{Se}^0). Our atomic relaxation calculations show that relative to pure $\mathrm{CuInSe_2}$ the nearest neighbor (nn) Cu atoms in V_{Se}^0 move *outwards* by about 0.11 Å, while the nn In atoms move *inwards* by about 0.32 Å. In contrast, V_{Se}^{2+} shows large outwards displacements of both the nn Cu and In: relative to V_{Se}^0, the nn Cu atoms move outward by 0.15 Å and the nn In atoms move by 0.70 Å. As a result, the donor $V_{\mathrm{Se}}(0/2+)$ transition is a *deep* level at $E_c-1.0\,\mathrm{eV}$ if one considers (Frank–Cordon) optical excitation in an unrelaxed lattice, whereas the donor level is shallow $E_c-0.1\,\mathrm{eV}$ once one considers thermal excitations in the relaxed lattice. The shallowness of $V_{\mathrm{Se}}(0/2+)$ transition indicates that it is an important native donor in $\mathrm{CuInSe_2}$. Oxygen substitution at the Se vacancy site in $\mathrm{CuInSe_2}$ will destroy these donor levels, thus effectively increasing the hole density.[5,6,14]

We have also tested the assumption of Kronik *et al.*[14] that $\mathrm{O_{Se}}$ creates *shallow isovalent acceptor levels* in $\mathrm{CuInSe_2}$. We find, however, that in the bulk the calculated transition energy levels are rather deep, at $E_v+0.55\,\mathrm{eV}$ and $E_v+0.67\,\mathrm{eV}$ for the $(-/0)$ and $(2-/-)$ transitions, respectively, so oxygen on Se site does not create free holes. Despite the quantitative difference between the calculated and the suggested transition energy level,[14] the fact that $\mathrm{O_{Se}}$ creates a deep level in $\mathrm{CuInSe_2}$ is very interesting since most isovalent impurities (e.g., P_{As} in GaAs) do not generate deep gap levels.[29] Another unusual fact is that the $\mathrm{O_{Se}}$ acceptor has an a_1-like (oxygen $2s$) character, while in a conventional acceptor (e.g., $\mathrm{Cu_{Zn}}$ or $\mathrm{As_{Se}}$ in ZnSe) the acceptor levels are t_2 like with mostly *pd* characters. We find that the creation of the deep $\mathrm{O_{Se}}$ isovalent acceptor level in CIS is mainly due to the large chemical and size differences between O and Se (the O $2s$ atomic energy level is 6.3 eV lower than Se $4s$ atomic energy level). Furthermore, since $\mathrm{O_{Se}}$ has, mostly, an antibonding character, $\mathrm{O_{Se}}$ acceptor levels are expected to be shallower near the CIS surface where covalency is reduced.

Interestingly, once oxygen replaced V_{Se} in CIS, our calculation shows that $\mathrm{CuInSe}_{1-x}\mathrm{O}_x$ is unstable and would decompose exothermically into the constituent oxides $\mathrm{Cu_2O}$ and $\mathrm{In_2O_3}$, since the mixing enthalpy for the following reaction

$$(1-x)\mathrm{CuInSe_2}+\tfrac{1}{2}x(\mathrm{Cu_2O}+\mathrm{In_2O_3})\rightarrow\mathrm{CuIn}(\mathrm{Se}_{1-x}\mathrm{O}_x)_2, \tag{11}$$

is large and positive $\Delta H_R=x(1-x)\Omega$ with $\Omega=2.6\,\mathrm{eV}$. Thus, oxygen removes the donor defect V_{Se} and then precipitates. This observation is important because it suggests that one cannot tell if oxygen is involved in the process of increasing hole density by simply measuring the content of oxygen in bulk $\mathrm{CuInSe_2}$ since a majority of the oxygen, after the removal of the Se vacancy donors, will leave $\mathrm{CuInSe_2}$, forming precipitates either at surfaces or grain boundaries.[16,14,30] Better designed experiments are needed to identify the effects of oxygen.

IV. SUMMARY

Our calculation shows that the main effect of sodium, either via direct substitution $\mathrm{Na_{In_{Cu}}}$ or via the release of oxygen radicals and the subsequent $\mathrm{O}_{V_{\mathrm{Se}}}$ occupation, is to reduce intrinsic donor defects in CIS. We predict that when Na concentration is small, Na will first eliminates $\mathrm{In_{Cu}}$ defects, thus, increase the effective hole densities.[4,5,6,31] This will lower the Fermi energy and remove carrier traps, thus increase the open circuit voltage.[2–6,11,12,31] However, as the Na concentration increases to the level that most of the $\mathrm{In_{Cu}}$ defects have already been eliminated, it will start to remove the acceptor V_{Cu}, therefore, reduce the hole density. Therefore, too much Na in $\mathrm{CuInSe_2}$ is not good for the performance of the solar cells.[32,33] Furthermore, we find that incorporation of Na and O inside CIS and subsequent phase separation of Na and O secondary phases on the surfaces and grain boundaries purify $\mathrm{CuInSe_2}$, so it becomes more stoichiometric.[9,10] The diffusion of Na in $\mathrm{CuInSe_2}$ and the preferred crystal structure of $\mathrm{NaInSe_2}$ also lead to a preferred $(112)_{\mathrm{tetra}}$ orientation for $\mathrm{CuInSe_2}$ crystals.[11,7,12,13,24]

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APPENDIX

In the CuPt-like layered structure, the Se atoms in $\mathrm{NaInSe_2}$ are octahedrally coordinated by three Na and three In nearest neighbor atoms, while the cations form an alternating monolayer superlattice along the [111] direction. The calculated (observed[23]) unit cell lattice parameters are $a=3.987$ (3.972) Å, $c=20.997$ (20.89) Å, and the cellinternal parameter is $u=0.2589$ (0.260) Å. The calculated Na–Se bond length (3.008 Å) is about 8% longer than the In–Se bond length in the layered $CrNaS_2$ structure [in the chalcopyrite structure, the calculated Na–Se bond length (2.856 Å) is about 9% longer than the In–Se bond length]. The calculated formation enthalpy $\Delta H_f = -3.9\,\text{eV}$ of the layered $NaInSe_2$ is 0.20 eV lower (i.e., more stable) than that of $NaInSe_2$ in the chalcopyrite structure. In comparison, due to the strong covalent Cu–Se bonding in $CuInSe_2$, the calculated formation energy of layered $CuInSe_2$ is 0.42 eV higher than that of chalcopyrite $CuInSe_2$.

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