Effects of Na on the electrical and structural properties of CuInSe 2

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Effects of Na on the electrical and structural properties of CuInSe$_2$

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National Renewable Energy Laboratory, Golden, Colorado 80401

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 $(112)_{tetra}$ morphology. The ensuing alloy Na$_x$Cu$_{1-x}$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 $(2V_{Cu}^2 1 In_{Cu}^{21})$, 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$_2$O and In$_2$O$_3$ 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$_x$Se$_2$ (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-

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$_2$:

$$\Delta H_f(\alpha,q) 5 \Delta E(\alpha,q)$$

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 CuInSe$_2$ is 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 CuInSe$_2$ matches the experimental value of 1.04 eV. To study the atomic relaxation in anion vacancy V_{Se} and substitutional impurity 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 $\ominus$0.2 eV.

III. RESULTS AND DISCUSSIONS

Our studies show that Na has three effects on CuInSe$_2$:

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

The calculated enthalpy of the Na_{Cu} substitution reaction

$$Na_{metal} 1 CuInSe_2(chalcopyrite) \rightleftharpoons NaInSe_2(layered) 1 Cu_{metal},$$
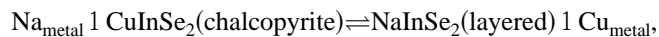
Tanaka *et al.*[27] who find that high Na levels in CIGS lead to a transition from chalcopyrite to ODC.

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 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

$$O + Cu_n In_n Se_{2n-1} V_{Se} \rightarrow Cu_n In_n Se_{2n-1} O, \qquad (10)$$
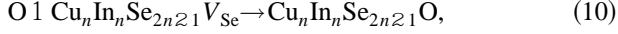
is strongly negative $\Delta H_R(O_{V_{Se}}) = -4.3$ eV when $\mu_{Se} = \mu_O = 0$. To understand the effect of removal of Se vacancy V_{Se}, we first study their properties.

The formation energy $\Delta H(V_{Se}^0) = 3.0$ eV at $\mu_{Se} = 0$. 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 $2E(0/2+) = E(V_{Se}^0) - E(V_{Se}^{2+})$ 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 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 $V_{Se}(0/2+)$ transition is a *deep* level at $E_c - 1.0$ eV if one considers (Frank–Cordon) optical excitation in an unrelaxed lattice, whereas the donor level is shallow $E_c - 0.1$ eV once one considers thermal excitations in the relaxed lattice. The shallowness of $V_{Se}(0/2+)$ transition indicates that it is an important native donor in CuInSe$_2$. Oxygen substitution at the Se vacancy site in 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 O_{Se} creates *shallow isovalent acceptor levels* in CuInSe$_2$. We find, however, that in the bulk the calculated transition energy levels are rather deep, at $E_v + 0.55$ eV and $E_v + 0.67$ 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 O_{Se} creates a deep level in 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 O_{Se} acceptor has an a_1-like (oxygen 2*s*) character, while in a conventional acceptor (e.g., Cu_{Zn} or As_{Se} in ZnSe) the acceptor levels are t_2 like with mostly *pd* characters. We find that the creation of the deep O_{Se} isovalent acceptor level in CIS is mainly due to the large chemical and size differences between O and Se (the O 2*s* atomic energy level is 6.3 eV lower than Se 4*s* atomic energy level). Furthermore, since O_{Se} has, mostly, an antibonding character, 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 CuInSe$_{12-x}O_x$ is unstable and would decompose exothermically into the constituent oxides Cu$_2$O and In$_2$O$_3$, since the mixing enthalpy for the following reaction

(

internal 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 $\Delta H_f = -3.9\,\mathrm{eV}$ 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 $CuInSe_2$.

[1] J. E. Granata, Ph.D. thesis, Colorado State University (unpublished); J. E. Granata and J. R. Sites, in *Proceedings of the Second World Conference on Photovoltaic Energy Conversion* (IEEE, New York, 1998).

[2] B. M. Basol, V. K. Kapur, C. R. Leidholm, A. Minnick, and A. Halani, in *Proceedings of the First World Conference on Photovoltaic Energy Conversion* (IEEE, New York, 1994), p. 148.

[3] D. F. Dawson-Elli, C. B. Moore, R. R. Gay, and C. L. Jensen, in *Proceedings of the First World Conference on Photovoltaic Energy Conversion* (IEEE, New York, 1994), p. 152.

[4] T. Nakada, H. Ohbo, M. Fukuda, and Kunioka, *Technical Digest: The Ninth International Photovoltaic Science and Engineering Conference*, Miyazaki (1996), p. 139.

[5] D. Cahen, E. Moons, L. Chernyak, I. Lyubomirski, M. Bruening, A. Shanzer, and J. Libman, Proceedings of the 5th International Symposium for Uses of Se and Te, Brussels, 1994, p. 207.

[6] M. Ruckh, D. Schmid, M. Kaiser, R. Schaffler, T. Walter, and H. W. Schock, in *Proceedings of the First World Conference on Photovoltaic Energy Conversion* (IEEE, New York, 1994), p. 156.

[7] V. Probst, J. Rimmasch, W. Riedl, W. Stetter, J. Holz, H. Harms, F. Karg, and H. W. Schock, in *Proceedings of the First World Conference on Photovoltaic Energy Conversion* (IEEE, New York, 1994), p. 144.

[8] J. Holz, F. Karg, and H. von Philipsborn, in *Proceedings of the 12th European Photovoltaic Solar Energy Conference*, edited by R. Hill, W. Palz, and P. Helm (H. S. Stephens, Bedford, 1994), p. 1592.

[9] R. Herberholz, H. W. Schock, U. Rau, J. H. Werner, T. Haalboom, T. Gadecke, F. Ernst, C. Beilharz, K. W. Benz, and D. Cahen, in *The Conference Record of the 26th IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1997), p. 323.

[10] B. J. Stanbery, E. S. Lambers, and T. J. Anderson, in *The Conference Record of the 26th IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1997), p. 499.

[11] J. Hedstrom, H. J. Olsen, M. Bodegard, A. Kylner, L. Stolt, D. Hariskos, M. Ruckh, and H. W. Schock, in *The Conference Record of the 23rd IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1993), p. 364; M. Bodegard, L. Stolt, and J. Hedstrom, in *Proceedings of the 12th European Photovoltaic Solar Energy Conference*, edited by R. Hill, W. Palz, and P. Helm (H. S. Stephens, Bedford, 1994), p. 1743.

[12] V. Probst, J. Rimmasch, W. Stetter, H. Harms, W. Riedl, J. Holz, and F. Karg, in *Proceedings of the 13th European Photovoltaic Solar Energy Conference*, edited by W. Freiesleben (H. S. Stephens, Bedford, 1995), p. 2123.

[13] M. Bodegard, J. Hedstrom, K. Granath, A. Rockett, and L. Stolt, in *Proceedings of the 13th European Photovoltaic Solar Energy Conference, International Conference*, edited by W. Freiesleben (H. S. Stephens, Bedford, 1995), p. 2080.

[14] L. Kronik, D. Cahen, and H. W. Schock, Adv. Mater. **10**, 31 (1998); L. Kronik, D. Cahen, U. Rau, R. Herberholz, and H. W. Schock, in *Proceedings of the Second World Conference on Photovoltaic Energy Conversion* (IEEE, New York, 1998).

[15] M. A. Contreras, B. Egaas, P. Dippo, J. Webb, J. Granata, K. Ramanathan, S. Asher, A. Swartzlander, and R. Noufi, in *The Conference Record of the 26th IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1997), p. 359.

[16] D. W. Niles, K. Ramanathan, F. Hasoon, R. Noufi, B. J. Tielsch, and J. E. Fulghum, J. Vac. Sci. Technol. A **15**, 3044 (1997).

[17] D. W. Niles, M. Al-Jassim, and K. Ramanathan, J. Vac. Sci. Technol. A **17**, 291 (1999).

[18] A. Klein, T. Loher, C. Pettenkofer, and W. Jaegermann, J. Appl. Phys. **80**, 5039 (1996).

[19] S. B. Zhang, S.-H. Wei, A. Zunger, and H. Katayama-Yoshida, Phys. Rev. B **57**, 9642 (1998).

[20] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[21] S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985); D. J. Singh, *Planewaves, Pseudopotentials, and the LAPW Method* (Kluwer, Boston, 1994).

[22] J. C. Slater, Phys. Rev. **81**, 385 (1951); **82**, 538 (1951).

[23] P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (ASM International, Materials Park, OH, 1991), p. 4019, and references therein.

[24] A. Rockett, M. Bodegard, K. Granath, and L. Stolt, in *The Conference Record of the 25th IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1996), p. 985.

[25] B. J. Stanbery, A. Davydov, C. H. Chang, and T. J. Anderson, in *Proceedings of the 14th NREL/SNL Photovoltaics Program Review Meeting*, edited by C. E. Witt, M. Al-Jassim, and J. M. Gee (AIP, New York, 1996), p. 579.

[26] S. Zweigart, G. Bilger, and H. W. Schock, in *Proceedings of the Thirteenth European Photovoltaic Solar Energy Conference*, edited by W. Freiesleben (H. S. Stephens, Bedford, 1995), p. 1991.

[27] T. Tanaka, N. Tanahashi, Y. Yamamoto, T. Yamaguchi, and A. Yoshida, *Technical Digest: The Ninth International Photovoltaic Science and Engineering Conference*, Miyazaki (1996), p. 383.

[28] C. Heske, R. Fink, D. Jacob, and E. Umbach, in *Proceedings of the 13th European Photovoltaic Solar Energy Conference*, edited by W. Freiesle-