



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 CuInSe₂

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(Received 4 January 1998; accepted for publication 16 February 1999)

We found theoretically that Na has three effects on CuInSe₂: (1) If available in stoichiometric quantities, Na will replace Cu, forming a more stable NaInSe₂ compound having a larger band gap (higher open-circuit voltage) and a (112)_{tetra} morphology. The ensuing alloy Na_xCu_{1-2x}InSe₂ has, however, a positive mixing enthalpy, so NaInSe₂ 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_(InCu) 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}¹), thus suppressing the formation of the "Ordered Defect Compounds." (3) Na on the surface of CuInSe₂ is known to catalyze the dissociation of O₂ 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 CuInSe₂ form Cu₂O and In₂O₃ 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_{1-2x}Ga_xSe₂ (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 density⁴⁻⁶ 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 O₂ 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 defect¹⁶⁻¹⁸ Na_{In}.

Using first-principles total energy and band structure method, we have studied theoretically the Na-induced effects in CuInSe₂. We calculated the ground state properties of NaInSe₂, CuInSe₂, 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 CuInSe₂. 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 CuInSe₂. We then impose periodic boundary conditions on this "supercell" so that the Schrödinger 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 on¹⁹ 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 an electron reservoir whose energy is ϵ_F . In CuInSe_2 :

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

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 .

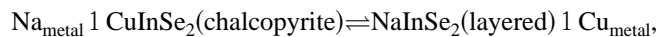
The needed total energies and band structures are calculated using the local density approximation (LDA)²⁰ as implemented by the general potential linearized augmented plane wave (LAPW) method.²¹ The LDA error on the band gap is corrected by adding a constant potential to the conduction states so the 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 ± 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

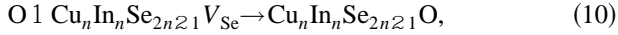
The calculated enthalpy of the Na_{Cu} substitution reaction



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 film²⁸ and to weaken the O–O bond of molecular oxygen,^{5,14} forming the chemically active *atomic* oxygen that can penetrate the CuInSe₂ 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



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

The formation energy $\Delta H(V_{\text{Se}}^0) \approx 3.0$ eV at $\mu_{\text{Se}} \approx 0$. 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 $2E(0/2) \approx E(V_{\text{Se}}^0) - 2E(V_{\text{Se}}^{2+})$ 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 CuInSe₂ 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 $V_{\text{Se}}(0/2)$ transition is a *deep* level at $E_c \approx 1.0$ eV if one considers (Frank–Cordon) optical excitation in an unrelaxed lattice, whereas the donor level is shallow $E_c \approx 0.1$ eV once one considers thermal excitations in the relaxed lattice. The shallowness of $V_{\text{Se}}(0/2)$ transition indicates that it is an important native donor in CuInSe₂. Oxygen substitution at the Se vacancy site in CuInSe₂ 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 CuInSe₂. We find, however, that in the bulk the calculated transition energy levels are rather deep, at $E_v \approx 0.55$ eV and $E_v \approx 0.67$ eV for the $(2/0)$ and $(22/2)$ 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 CuInSe₂ 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 *2s*) 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 *2s* atomic energy level is 6.3 eV lower than Se *4s* 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 $\text{CuInSe}_{1.2x}\text{O}_x$ is unstable and would decompose exothermically into the constituent oxides Cu_2O and In_2O_3 , since the mixing enthalpy for the following reaction

(

internal parameter is $u \approx 0.2589$ (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 CrNaS₂ 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 $\Delta H_f \approx 23.9$ eV of the layered NaInSe₂ is 0.20 eV lower (i.e., more stable) than that of NaInSe₂ in the chalcopyrite structure. In comparison, due to the strong covalent Cu–Se bonding in CuInSe₂, the calculated formation energy of layered CuInSe₂ is 0.42 eV higher than that of chalcopyrite CuInSe₂.

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