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Citation: Applied Physics Letters **83**, 2007 (2003); doi: 10.1063/1.1608494
View online: http://dx.doi.org/10.1063/1.1608494
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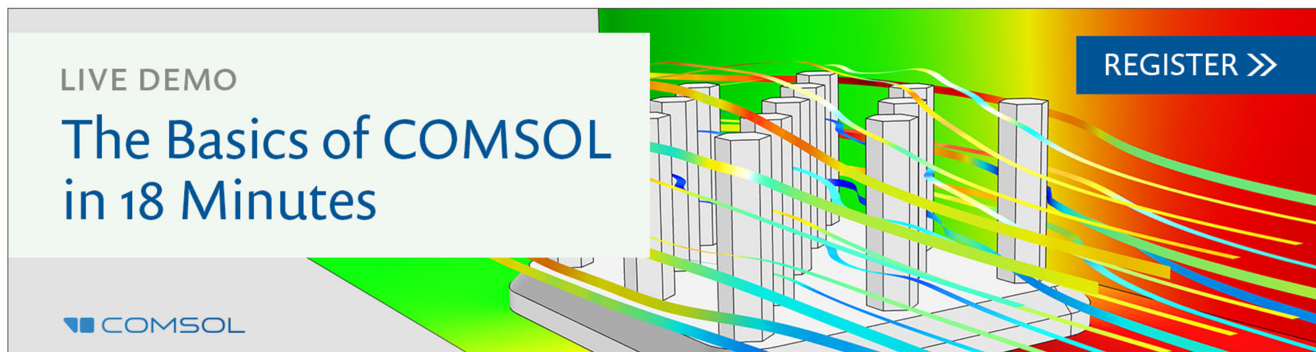

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APPLIED PHYSICS LETTERS VOLUME 83, NUMBER 10 8 SEPTEMBER 2003

Doping of chalcopyrites by hydrogen

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(Received 18 April 2003; accepted 9 July 2003)

First-principles total-energy calculations for hydrogen impurities in $CuInSe_2$ (CIS) and $CuGaSe_2$ (CGS) show that H^+ takes up the Cu–Se bond center position, whereas H^0 and H^- take up tetrahedral interstitial site next to In (in CIS) or Ga (in CGS). Hydrogen creates a negative-U center (i.e., H^0 is never stable), with a $(+/-)$ transition level at $E_c-0.39$ eV in CIS, and $E_c-0.57$ eV in CGS. However, once combined with the $2V_{Cu}^-+III_{Cu}^{2+}$ complex, hydrogen forms shallower centers with transition levels at $E_c-0.15$ eV in CIS, and $E_c-0.39$ eV in CGS. We conclude that hydrogen could convert CIS to n type, but not CGS. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1608494]

The doping of chalcopyrite semiconductors $CuInSe_2$ and $CuGaSe_2$ used in solar cells is usually done via stoichiometry control:[1] p-type samples are made from Cu-deficient material (since V_{Cu} is an acceptor), whereas n-type samples are attempted via Se-deficient material (since V_{Se} is a donor). Such doping via stoichiometry control during growth has weaknesses: it forces growth conditions that are less than ideal for sample morphology; it often creates insufficient doping (especially n type), and the nonstoichiometric samples are strongly compensated.[2] In this letter, we enquire if $CuInSe_2$ and $CuGaSe_2$ could be doped n type by hydrogen. This is unusual since H is an *amphoteric* center in Si (Ref. 3), GaAs (Ref. 4), GaP (Ref. 5), InP (Ref. 6), and ZnSe (Ref. 7). However, it has recently been demonstrated[8,9] that hydrogen implantation cause p-to-n conductivity-type conversion in $CuInSe_2$. Based on first-principles calculations, we find that hydrogen forms a deep donor in $CuGaSe_2$, but a relatively shallow donor in $CuInSe_2$. The interaction of hydrogen with the abundant defect complex $(2V_{Cu}+In_{Cu})^0$ yields an even shallower donor, making $CuInSe_2$ n type. In addition, our results show that hydrogen passivates the acceptor-like copper vacancies in both $CuInSe_2$ and $CuGaSe_2$, thus reducing p typeness. These findings, in conjunction with typical conditions under which $CuInSe_2$ and $CuGaSe_2$ are grown indicate that $CuInSe_2$ could be doped n type via hydrogen incorporation, whereas $CuGaSe_2$ could not. Experimental testing of such predictions is called for.

We calculate the excess energy for incorporating H in charge state q:

$$\Delta H_D^{(q)}=[E_D^{(q)}-E_S]+\sum_\alpha n_\alpha(\mu_\alpha+\mu_\alpha^0)-n_{\rm H}(\mu_{\rm H}+\mu_{\rm H}^0)+q(E_{\rm F}+E_v), \quad (1)$$

where $E_D^{(q)}$ denotes the total energy for defect D in charge state q embedded in the host system $S=CuInSe_2$ or $CuGaSe_2$, and E_S is the total energy of the pure host crystal S. Here, the first term denotes the change in total energy due to breaking host bonds and forming defect bonds; the second and third terms denote the change in chemical potential due to exchange of atoms between the host system and the atomic reservoirs of the elemental solids $\alpha=$Cu, In or Ga, and Se, and due to incorporation of hydrogen, respectively. n_α is then the number of atoms transferred to the atomic reservoir α, and $n_{\rm H}$ is the number of hydrogens incorporated; μ_α and $\mu_{\rm H}$ denote the respective atomic chemical potentials with μ_α^0 being the zero of μ_α. The last term denotes the energy change owing to exchange of carriers between the defect and the Fermi reservoir E_F. E_v denotes the valence band maximum, which we set as the zero of E_F.

The chemical potentials $\{\mu_\alpha\}$ need to satisfy a set of conditions set out to avoid unwanted competing reactions such as precipitation of elemental solids Cu, In, Ga, Se, or Cu_2Se, In_2Se_3, or Ga_2Se_3. This is assured by calculating formation enthalpies of all of these hypothetical products, and setting up a set of chemical-potential inequalities that assures no precipication. We find that $\mu_{Cu}=0$ implies maximally Cu-rich conditions, whereas $\mu_{Cu}=\Delta H(CuIIISe_2)$ imples maximally Cu-poor conditions, etc. The formation enthalpies as well as the total energies used in Eq. (1) were calculated in the framework of the density functional theory within the local density approximation (LDA) employing the Ceperley–Alder exchange correlation potential[10] as parameterized by Perdew and Zunger.[11] We utilized the plane-wave total energy method as implemented in VASP code,[12] and used approximately cubic supercells with fully relaxed atomic positions including 16 molecular units of $Cu(In,Ga)Se_2$. We sampled the supercell Brillouin zones by a $2\times2\times2$ **k**-point mesh generated according to Monkhorst–Pack scheme.[13] The hydrogen (s^1), copper ($d^{10}p^1$), indium (s^2p^1), gallium (s^2p^1), and selenium (s^2p^4) atoms were modeled using ultrasoft pseudopotentials.[14] The plane wave basis sets were determined by imposing a kinetic energy cutoff of 234 eV. The atomic positions were relaxed until the error in the total energy (of $\geqslant$64 atoms) become smaller than 1 meV. Neutralizing jellium background was added to charged supercells, and the total energy was corrected to $O(L^{-5})$ where L is the supercell size.[15] Convergence tests were conducted with respect to the basis set size and number of **k** points to assure that an accurate description of $CuInSe_2$ and $CuGaSe_2$ crystals, compared to experimental

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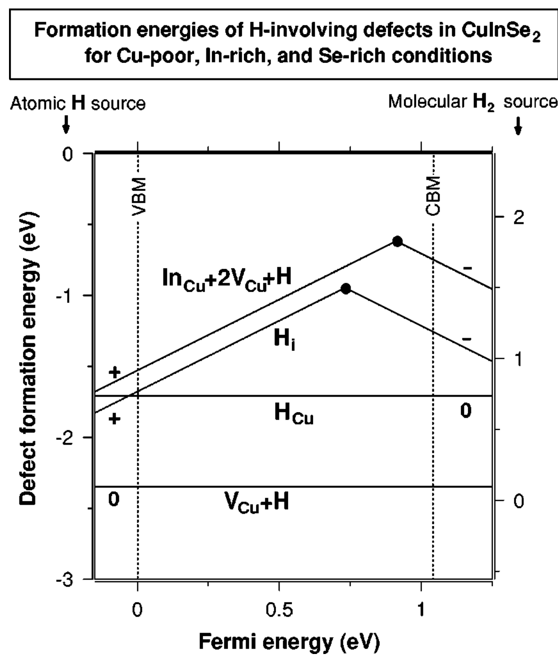

FIG. 1. The LDA-corrected formation energies of H_i, H_{Cu}, $(V_{Cu}+H)$, $(In_{Cu}+2V_{Cu}+H)$ in $CuInSe_2$ as a function of the Fermi energy E_F for Cu-poor, In-rich, and Se-rich conditions. Two different hydrogen sources are considered: atomic H (left scale) or molecular H_2 (right scale). The zero of E_F is set to the valence band maximum. +, 0, and − denote the charge states. The transition energies are marked by filled circles.

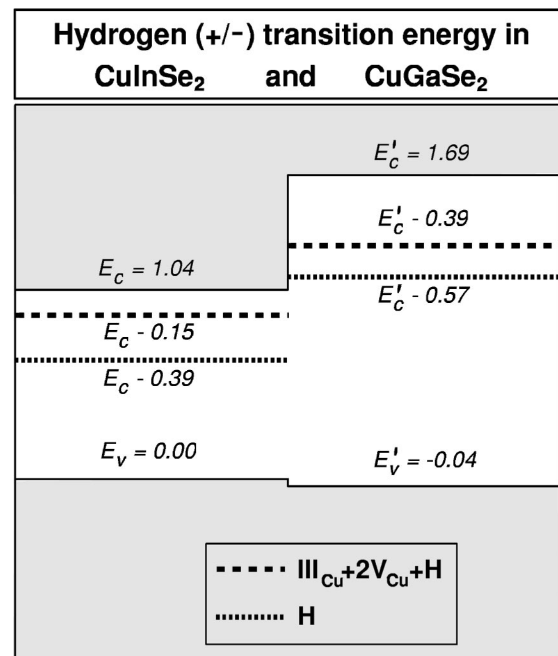

FIG. 2. The electrical hydrogen level in $CuInSe_2$ and $CuGaSe_2$. LDA-calculated valence band offset (see Ref. 22) is used to put valence-band maximums of $CuInSe_2$ and $CuGaSe_2$ on the same energy scale in electron volts.

structures,[16] is obtained. The supercell size was twice as big as in earlier LDA calculations[17] for intrinsic defects in $CuInSe_2$.

The defect transition energies, e.g., acceptor $E_H(0/-)$ is calculated as the value of Fermi energy in Eq. (1) where the energy to form the neutral defect equals that of the negatively charged defect. This energy does not depend on the chemical potentials. The effect of the "LDA band gap error" $\Delta = E_g^{exp} - E_g^{lda}$ on the transition energy is corrected via $E_H(0/-) = E_H^{lda}(0/-) + C(0/-)\Delta$, where the coefficient $C(0/-) = 0.22$ was determined empirically via a regression of $E_H^{lda}(0/-)$ vs E_g^{lda} for H in different semiconductors.[18,19]

Minimizing the total energy with respect to the H lattice positions for different charge states reveals that H^+ resides at the center of the Cu–Se bond, whereas both H^0 and H^- reside at the tetrahedral site next to column III element. Figure 1 shows the formation energy for H in $CuInSe_2$ using chemical potentials correspoding to $\mu_{Cu} = -0.42$ eV, $\mu_{In} = -1.30$ eV, and $\mu_{Se} = 0$, i.e., Cu-poor, In-rich, Se-rich conditions, similar to what is used in hydrogenation experiments.[8,9] The formation energies are depicted both for a source of atomic H (left-hand-side scale), and molecular H_2 (right-hand-side scale). We see that:

(i) If there are no intrinsic defects, one can have H in non-substitutional ("H_i") or in substitutional (H_{Cu}) positions. We find that H_i^+ (at the Cu–Se bond center site) is stable in p-type material, and it transforms directly into H_i^- (at the tetrahedral interstitial site next to In), without ever becoming H_i^0, at the transition energy $E_H(+/-) = E_c - 0.39$ eV.

(ii) H substituting Cu exists throughout the band gap as a neutral, electrically inactive center. H is positively charged when it resides next to a negatively charged Cu vacancy, so $(V_{Cu}+H)$ is also charge neutral. The formation energies of these centers are low under the Cu-poor conditions considered in Fig. 1. This implies that H will neutralize the negative V_{Cu}^- (a source of p typeness in Cu-poor $CuInSe_2$), thus reduce p typeness.

(iii) H can attach to the $In_{Cu}+2V_{Cu}$ complex, giving a transition $E_H(+/-) = E_c - 0.15$ eV, i.e., a rather shallow donor. This explains the observed[8,20] fact that hydrogenation of $CuInSe_2$ pins the Fermi level at $E_c - 0.1(\pm 0.1)$ eV, converting the material to n type.

(iv) According to Fig. 1, hydrogen incorporation from atomic H source into $Cu(In,Ga)Se_2$ is *exothermic*, taking place spontaneously, whereas incorporation from H_2 is *endothermic*. This shows that the use of atomic hydrogen is rather crucial, and explains the experimental difficulty with H incorporation from H_2 gas.[21]

Figure 2 summarizes the calculated electrical levels, i.e., the hydrogen transition energies, in $CuInSe_2$ and $CuGaSe_2$. It is seen that hydrogen electrical levels in $CuGaSe_2$ are ~0.2 eV deeper relative to $CuInSe_2$. Thus, n-type doping by hydrogen will be much *less* effective in $CuGaSe_2$ compared to $CuInSe_2$. The fact that the conduction-band minimum (CBM) of $CuGaSe_2$ is ~0.6 eV above that of $CuInSe_2$ (Ref. 22) explains why hydrogen forms a deeper donor level in the former and a relatively shallow level in the latter.

We find that the effect of hydrogen in nonstoichiometric chalcopyrite (i.e., containing V_{Cu} and/or $III_{Cu}+2V_{Cu}$) depends on the interplay between passivation and n-type doping. This can be explained in terms of reaction enthalpies for pairing of the defects in $Cu(In,Ga)Se_2$, listed in Table I. We see that pairing of V_{Cu}^- and H_i^+ to form H-on-Cu site H_{Cu}^0 is *endothermic* whereas this pairing is *exothermic* for forming $(V_{Cu}+H)^0$. Thus, hydrogen prefers to reside *next* to copper vacancy, as opposed to substitute the vacant Cu site. In sys-

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TABLE I. The enthalpies (in electron volts) of defect-pairing reactions in $CuInSe_2$ and $CuGaSe_2$. There is no dependence on the atomic chemical potentials or the Fermi energy since the pairing reactions are atom and charge balanced.

Reaction	$CuInSe_2$	$CuGaSe_2$
$V_{Cu}^- + H_i^+ \rightarrow H_{Cu}^0$	0.32	0.29
$V_{Cu}^- + H_i^+ \rightarrow (V_{Cu}+H)^0$	−0.33	−0.35
$(III_{Cu}+2V_{Cu})^0 + H_i^+ \rightarrow (III_{Cu}+2V_{Cu}+H)^+$	0.00	−0.35
$(III_{Cu}+2V_{Cu})^0 + H_i^- \rightarrow (III_{Cu}+2V_{Cu}+H)^-$	0.36	0.14

tems where the (negatively charged) copper vacancies preexist, e.g., in Cu-poor, p-type $Cu(In,Ga)Se_2$, hydrogen will be incorporated next to copper vacancy, forming the $(V_{Cu}+H)^0$ defect complex. Since neutral $(V_{Cu}+H)^0$ is the stable charge state (Fig. 1), and is electrically inactive, hydrogen will passivate p-type $Cu(In,Ga)Se_2$. Table I also shows that pairing of H^+ with $(III_{Cu}+2V_{Cu})^0$ to form *donor*-like $(III_{Cu}+2V_{Cu}+H)^+$ is *exothermic* whereas that of H^- to form *acceptor*-like $(III_{Cu}+2V_{Cu}+H)^-$ is *endothermic*. Thus, hydrogen prefers to be incorporated *next* to $(III_{Cu}+2V_{Cu})^0$, forming a donor. Hence, the incorporation of hydrogen into nonstoichiometric $Cu(In,Ga)Se_2$ and the effect of H on electrical conduction are controlled by the amounts of pre-existing intrinsic defects V_{Cu}^- and $(III_{Cu}+2V_{Cu})^0$.

Our first-principles study shows that the main electrical effect of hydrogen incorporation on chalcopyrites can be summarized as an interplay between n-type doping and passivation. The former is determined by the location of the chalcopyrite CBM while the latter is controlled by the interaction with the intrinsic defects, i.e., nonstoichiometry. In this respect, H incorporation leads to n-type doping and passivation of acceptor-like defects in $CuInSe_2$ while only passivation of acceptor-like defects in $CuGaSe_2$. This is explained by noting that the CBM of $CuGaSe_2$ is considerably higher than that of $CuInSe_2$.

The authors like to thank to L. G. Wang for useful discussions. This work was supported by U.S. DOE–EERE under Contract No. DE-AC36-99GO10337.

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