n-type doping and passivation of $CuInSe_2$ and $CuGaSe_2$ by hydrogen

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An impurity in a semiconductor can have either amphoteric behavior ~no net production of electron or holes!, or be an energetically deep center ~carriers produced only at high temperature!, or a shallow center ~carriers produced even at low temperature!. In most semiconductors ~e.g., Si, GaAs, GaP, InP, and ZnSe! hydrogen impurities do not produce free carriers, being instead an amphoretic center; yet hydrogen does dope *n*-type some oxides such as SnO_2 and ZnO. We studied theoretically whether or not H could dope chalcopyrite I-III-VI_2

where E_S

$$E_{\mathrm{H}^{\sim}}(-/0) = E_{\mathrm{H}}^{lda}{}_{\sim}(-/0) + \left(1 - C_{\sim}(-/0)\right)\left(E_g^{exp} - E_g^{lda}\right), \quad \sim 5$$

$$E_{\mathrm{H}^{\sim}}(+/-) = E_{\mathrm{H}}^{lda}{}_{\sim}(+/-) + \frac{1}{2}\left(1 - C_{\sim}(-/0) + C_{\sim}(+/-)\right)\left(E_g^{exp} - E_g^{lda}\right),$$

$$E_{\mathrm{H}^{\sim}}(+/0) = E_{\mathrm{H}}^{lda}{}_{\sim}(+/0) + C_{\sim}(+/0)\left(E_g^{exp} - E_g^{lda}\right),$$

where $C(-/0) = 0.78$ and $C(+/0) = 0.67$ are derived in the Appendix.

III. RESULTS

We carried out first-principles calculations for the following H-involving defects: nonsubstitutionally incorporated hydrogen H_i, substitutional hydrogen on Cu site (H_{Cu}), hydrogen incorporated next to the copper vacancy ($V_{Cu}+H$), and hydrogen incorporated next to the complex formed by an indium or gallium antisite plus two copper vacancies (III_{Cu} +

more electronegative compounds Mg~S,Se,Te! (Δx = 0.79–1.27) and GaN (Δx = 1.23), H^0 takes up the tetra-

of H next to (III

ing place spontaneously, whereas incorporation from H_2 is *endothermic*. This explains the experimental difficulty[38] with H incorporation from H_2 gas, and verifies that the use of atomic hydrogen is crucial.[38] We find in the latter case that the implanted hydrogen atoms can decorate copper vacancies inside $Cu(In,Ga)Se_2$, causing formation of an *internal hydrogen reservoir*. To explain this point, we first consider the decoration of a defect D by a number m of H atoms or H_2 molecules. The resulting defect complex is denoted as $D+mH_n$, where $n=1$ and 2 for atomic and molecular hydrogen, respectively. The change in energy upon incorporation of m H_n species into $S=Cu(In,Ga)Se_2$ next to defect D is *termed* as the *hydrogen incorporation energy*, given by

$$\Delta E_D^{(m,n)} = E_{D+mH_n}^{(0)} - E_D^{(0)} - mn[\mu_H + \mu_H^0], \qquad (6)$$

where the zero of hydrogen chemical potential is set to the energy of H atom, i.e., $\mu_H^0 = E(H)$. We first note that $D+mH_n$ forms spontaneously if $\Delta E_D^{(m,n)}$ is *negative*. We next consider incorporation of hydrogen into the host system S from some external hydrogen source. The top panel of Fig. 4 shows this situation schematically. The external hydrogen source (with chemical potential μ_H^e) pumps H into the system S if $\mu_H < \mu_H^e$ (otherwise hydrogen would lea00 0 9.9780 0 9.9780 0 9

increasing the value of m_{HH}

tral H-involving defects: H_i, $(V_{Cu}+H)$, $(V_{Cu}$ $+2H_2)$, and $(V_{Cu}+4H_2)$. The incorporation ener external reservoir of H_2 is shown in the bottom pa comparison. It is seen that $\mathsf{D}E_D^{m,n}$ can be positive or ne depending on the value of m_{H}. Hence, the range of into two regions, as indicated by shading in $D+mH_n$: ~i! $m_{\mathrm{H}}^*(D+mH_n)<m_{\mathrm{H}}$ and ~ $mH_n)$, where $m_{\mathrm{H}}^*(D+mH_n)$ denotes the $\mathsf{D}E_D^{m,n}=0$. For external reser st then D ecies takes place sp If m_{H} has a value within region ~ii!, then $D+mH_n$ acts an internal reservoir since $\mathsf{D}E_D^{(m,n)}>0$. Thus, the internal hydrogen reservoir forms in two stages characterized by the value of m_{H}: The first stage involves spontaneous decoration of D by m H_n species (i.e., m_{H} adjusted to some value within region ~i! as in, e.g., implantation experiments[9,10,36,38]# so that a significant amount of hydrogens is incorporated. In the second stage, the subsequent relaxation of the system following the implantation make m_{H} decrease to some value within region ~ii!, so that $D+mH_n$ acts as a reservoir. In this process,

conditions so that chalcopyrites may be utilized for hydrogen storage. The atomic weight percent of hydrogen, however, seems to be rather low [; 0.2–0.3 % for 10% Cu deficient $Cu(In,Ga)Se_2$] for practical applications.

D. Hydrogen in nonstoichiometric *p*-$Cu(In,Ga)Se_2$

As we mentioned in Sec. II B, 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 IV. We see that pairing of V_{Cu}^{-} and H_i^{+} to form H_{Cu}^{0} is *endothermic*, whereas it is *exothermic* for forming $(V_{Cu}+H_i)^0$. Thus, hydrogen prefers to reside *next* to copper vacancy, as opposed to substitute the vacant Cu site. In systems where the negatively charged copper vacancies preexist, e.g., in chemically pure *p*-type $Cu(In,Ga)Se_2$, hydrogen will then be incorporated into the $(V_{Cu}+H_i)^0$ defect complex. Since neutral $(V_{Cu}+H_i)^0$ is electrically inactive, hydrogen will thus passivate *p*-type $Cu(In,Ga)Se_2$. Table IV also shows that pairing of H^+ with $(III_{Cu}+2V_{Cu})^0$ to form donorlike $(III_{Cu}+2V_{Cu}+H)^+$ is *exothermic*, whereas that of H^- to form acceptorlike $(III_{Cu}+2V_{Cu}+H)^-$ is *endothermic*. Thus, similar to the case with V_{Cu}^{-}, hydrogen prefers to be incorporated next to $(III_{Cu}+2V_{Cu})^0$. 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 preexisting intrinsic defects V_{Cu}^{-} and $(III_{Cu}+2V_{Cu})^0$.

IV. 2V0.Ourl)Tjrst-p253cipleslstudyls0 0 6 mai5 0 0 2131 TD [(amductio.2.8(are)-548.ef)F4 9.8(contrf 0ed)-548f 0edTJ 6.985

$$\mathsf{G}_{lda}\tilde{}q_1/q_2! = G\tilde{}q_1/q_2! + C\tilde{}q$$

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