

***n*-type doping and passivation of CuInSe₂ and CuGaSe₂ 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 amphoteric center; yet hydrogen does dope *n*-type some oxides such as SnO₂ and ZnO. We studied theoretically whether or not H could dope chalcopyrite I-III-VI₂

where E_S

$$E_{\text{H}^- - / 0} = E_{\text{H}^- - / 0}^{\text{lda}} + \frac{1}{2}(1 - C_{- / 0}) \frac{E_g^{\text{exp}} - E_g^{\text{lda}}}{\epsilon}, \quad (5)$$

$$E_{\text{H}^- + / -} = E_{\text{H}^- + / -}^{\text{lda}} + \frac{1}{2}(1 - C_{- / 0} + C_{- + / -}) \frac{E_g^{\text{exp}} - E_g^{\text{lda}}}{\epsilon},$$

$$E_{\text{H}^- + / 0} = E_{\text{H}^- + / 0}^{\text{lda}} + C_{- + / 0} \frac{E_g^{\text{exp}} - E_g^{\text{lda}}}{\epsilon},$$

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 ($\text{V}_{\text{Cu}} + \text{H}$), 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! ($Dx = 0.79-1.27$) and GaN ($Dx = 1.23$), 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 difficulty³⁸ 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 hy-*

drogen 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

$$DE_D^{(m,n)} = E_{D+mH_n}^{(0)} - E_D^{(0)} - mn\mu_H + m\mu_H^0, \quad -6!$$

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 $DE_D^{(m,n)}$ 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

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)Se₂] for practical applications.

D. Hydrogen in nonstoichiometric *p*-Cu(In,Ga)Se₂

As we mentioned in Sec. II B, the effect of hydrogen in nonstoichiometric chalcopyrite -i.e., containing V_{Cu} and/or $\text{III}_{\text{Cu}} + 2V_{\text{Cu}}$) 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)Se₂, 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 $(V_{\text{Cu}} + \text{H}_i)^0$. 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)Se₂, hydrogen will then be incorporated into the $(V_{\text{Cu}} + \text{H}_i)^0$ defect complex. Since neutral $(V_{\text{Cu}} + \text{H}_i)^0$ is electrically inactive, hydrogen will thus passivate *p*-type Cu(In,Ga)Se₂. Table IV also shows that pairing of H^+ with $(\text{III}_{\text{Cu}} + 2V_{\text{Cu}})^0$ to form donorlike $(\text{III}_{\text{Cu}} + 2V_{\text{Cu}} + \text{H})^+$ is *exothermic*, whereas that of H^- to form acceptorlike $(\text{III}_{\text{Cu}} + 2V_{\text{Cu}} + \text{H})^-$ is *endothermic*. Thus, similar to the case with V_{Cu}^- , hydrogen prefers to be incorporated next to $(\text{III}_{\text{Cu}} + 2V_{\text{Cu}})^0$. Hence, the incorporation of hydrogen into nonstoichiometric Cu(In,Ga)Se₂ and the effect of H on electrical conduction are controlled by the amounts of preexisting intrinsic defects V_{Cu}^- and $(\text{III}_{\text{Cu}} + 2V_{\text{Cu}})^0$.

$$G_{1da} \sim q_1/q_2! = G \sim q_1/q_2! + C \sim q$$

- Campos, A. Weidinger, M.V. Yakushev, and S.F.J. Cox, *Physica B* **326**, 181 -2003!.
- ³²C. Herring, N.M. Johnson, and C.G. Van de Walle, *Phys. Rev. B* **64**, 125209 -2001!.
- ³³C. Wang and Q.-M. Zhang, *Phys. Rev. B* **59**, 4864 -1999!.
- ³⁴J. Neugebauer and C.G. Van de Walle, *Phys. Rev. Lett.* **75**, 4452 -1995!.
- ³⁵Ç. Kılıç, L.-G. Wang, and A. Zunger -unpublished!.
- ³⁶K. Otte, T. Chasse, G. Lippold, B. Rauschenbach, and R. Szargan, *J. Appl. Phys.* **91**, 1624 -2002!.
- ³⁷S.B. Zhang, S.-H. Wei, and A. Zunger, *J. Appl. Phys.* **83**, 3192 -1998!.
- ³⁸A. Weidinger, J. Krauser, Th. Riedle, R. Klenk, M.Ch. Lux-Steiner, and M.V. Yakushev, in *Hydrogen in Semiconductors and Metals*, edited by N. H. Nickel, W. B. Jackson, and R. C. Bowman, MRS Symposia Proceedings No. 513 -Materials Research Society, Pittsburgh, 1997!, p. 177.
- ³⁹S.B. Zhang, S.-H. Wei, and A. Zunger, *Phys. Rev. Lett.* **84**, 1232 -2000!.
- ⁴⁰C. Stampfl, C.G. Van de Walle, D. Vogel, P. Krüger, and J. Pollmann, *Phys. Rev. B* **61**, R7846 -2000!.