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Doping of chalcopyrites by hydrogen

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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.*

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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

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'' tems where the negatively charged) copper vacancies pre-exist, 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 $(V_{Cu}+H)^0$