n-type doping of oxides by hydrogen

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First-principles total-energy calculations suggest that interstitial hydrogen impurity forms a *shallow* donor in SnO_2, CdO, and ZnO, but a deep donor in MgO. We generalize this result to other oxides by recognizing that there exist a ''hydrogen pinning level'' at about 3.0 ± 0.4 eV below vacuum. Materials such as Ag_2O, HgO, CuO, PbO, PtO, IrO_2, RuO_2, PbO_2, TiO_2, WO_3, Bi_2O_3, Cr_2O_3, Fe_2O_3, Sb_2O_3, Nb_2O_5, Ta_2O_5, $FeTiO_3$, and $PbTiO_3$, whose conduction band minimum ~CBM! lie below this level ~i.e., electron affinity$>3.0\pm0.4$ eV! will become conductive once hydrogen is incorporated into the lattice, without reducing the host. Conversely, materials such as BaO, NiO, SrO, HfO_2, and Al_2O_3, whose CBM lie above this level ~i.e., electron affinity$<3.0\pm0.4$ eV! will remain nonconductive since hydrogen forms a deep impurity. © *2002 American Institute of Physics.* @DOI: 10.1063/1.1482783#

Hydrogen is a ubiquitous impurity in most semiconductors, including elemental ~e.g., Si!, compound ~e.g., GaAs! and wide gap ~e.g., III–V nitrides and II–VI's! semiconductors.[1] In these systems, hydrogen is known to be *amphoteric*, forming an acceptor level in *n*-type and a donor level in *p*-type materials. In contrast, hydrogen can lead to electron conduction in some wide gap oxides such as SnO_2 ~Ref. 2! and ZnO ~Ref. 3!. These observations raise the question of what is the basic systematic at work here: if H can be incorporated into some materials, which one will be doped by H ~i.e., become conductive! and which will not? Our first-principles study presented here show that SnO_2 and CdO can be doped *n*-type by hydrogen incorporation, whereas H in MgO yield a deep level inside the band gap, so MgO is not doped by hydrogen. Our results indicate that the distinction between H as an *n*-type dopant and as a nondoping impurity depends on whether the ''hydrogen pinning level,'' estimated to be located approximately at 3.0 ± 0.4 eV below the vacuum level, is above the conduction band minimum ~CBM! of the material ~in which case H dopes it! or below the CBM of materials ~in which case H is nondoping!. Generally, low-electron-affinity oxides ~whose CBM is close to a vacuum! will not be doped upon H incorporation. Likely examples include BaO, NiO, SrO, HfO_2, and Al_2O_3. High-electron-affinity oxides, however, will be doped upon H incorporation. Likely examples include Ag_2O, HgO, CuO, PbO, PtO, IrO_2, RuO_2, PbO_2, TiO_2, WO_3, Bi_2O_3, Cr_2O_3, Fe_2O_3, Sb_2O_3, Nb_2O_5, Ta_2O_5, $FeTiO_3$ and $PbTiO_3$.

We calculate formation energies as well as ~donor, acceptor! defect transition energies. The formation energy of interstitial H impurity in charge state q is given by

$$\Delta H_f^q(\sim \mu_H, E_F!) = E(\sim host) + H^q(!) - E(\sim host!) - (\mu_H + \tfrac{1}{2}E(\sim H_2!) + q(\sim E_F + E_{VBM}!), \quad (1)$$

where $E(\alpha)$ denotes the total energy of the system α, μ_H is the hydrogen chemical potential, and E_F is the Fermi energy measured from the valence band maximum ~VBM! E_{VBM}. The defect transition level (q

calculated ~+