



£Yhjb? `Ä`UbX`5`YI `Ni b[Yf`

7]hUjcb. `5dd`jYX`D\ng]Mj`@YHfYfg` ž+' f&\$\$&L/Xc].`%\$"%\$\*' #6%(, &+, '  
J]Yk `cb`]bY. `hhd.##xl "Xc]cf[ #6"%\$\*' #6%(, &+, '  
J]Yk `HUV`Y`cZ7`cbYbfg. `hhd.##gV]hUjcb"U]d"cf[ #6bYbhU]d#ci fbU`#Ud`#`%#3] Yf1dXZVtj  
Di V]g\YX`VmiH`Y`5`D`Di V]g\]b[

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5V! ]b]hc`gh`XmcZXcbcf!UWV]drcf`VtXcd]b[ `Zcf`b!hmdY`7`i`C`  
>"5dd""D\ng"" ž\$%`+\$( f&\$(L/%\$"%\$\*' #6%(-,\$\$(-)`

≠Ybh]Z]W]h]cb`cZb]fc[ Yb!`UbX`cgHfY`UH`YX`XYd!`Yj`Y`hfUdg]b`b!hmdY;`UB`5g`UbX`h`Y]f`Yj`c`i`h]cb`i`dcb`UbbYU]b[`  
>"5dd""D\ng"" ž\$%`+\$( f&\$(L/%\$"%\$\*' #6%(, , \*, )`\*

GY`YV]cb`fi`Y`cZdfYZffYX`Xcd]b[ `g]Y`Zcf`b!hmdY`cl`]XYg`  
5dd""D\ng""@YHf` ž&`&%\$- f&\$(L/%\$"%\$\*' #6%(+'%+\*\*`

:`Yffca`U[`bY]ga`'UbX`]hg`ghUV]]m]b`b!hmdY;`X!XcdYX;`UB.;`]fghdf]bV]d`Yg`WU`W`U]h]cb`  
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:`]fghdf]bV]d`Yg`@85`Ž`l`'gh`X]Yg`cZH`Y`b!XcdYX`NbC`hfUbgdUfYbhVtXi`W]j`Y`cl`]XY`  
>"5dd""D\ng"" ž\$\*`+\$( f&\$\$, L/%\$"%\$\*' #6%&- +, ' &(`

# ***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<sub>2</sub>, 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  $3.0 \pm 0.4$  eV below vacuum. Materials such as Ag<sub>2</sub>O, HgO, CuO, PbO, PtO, IrO<sub>2</sub>, RuO<sub>2</sub>, PbO<sub>2</sub>, TiO<sub>2</sub>, WO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, FeTiO<sub>3</sub>, and PbTiO<sub>3</sub>, whose conduction band minimum (CBM) lie below this level (i.e., electron affinity  $> 3.0 \pm 0.4$  eV) will become conductive once hydrogen is incorporated into the lattice, without reducing the host. Conversely, materials such as BaO, NiO, SrO, HfO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, whose CBM lie above this level (i.e., electron affinity  $< 3.0 \pm 0.4$  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.<sup>1</sup> 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<sub>2</sub> (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<sub>2</sub> 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  $3.0 \pm 0.4$  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<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>. High-electron-affinity oxides, however, will be doped upon H incorporation. Likely examples include Ag<sub>2</sub>O, HgO, CuO, PbO, PtO, IrO<sub>2</sub>, RuO<sub>2</sub>, PbO<sub>2</sub>, TiO<sub>2</sub>, WO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, FeTiO<sub>3</sub> and PbTiO<sub>3</sub>.

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

$$\Delta H_f^q(\mu_H, E_F) = E(\text{host} + H^q) - E(\text{host}) - [\mu_H + \frac{1}{2}E(\text{H}_2)] + q(E_F + E_{\text{VBM}}), \quad (1)$$

where  $E(\alpha)$  denotes the total energy of the system  $\alpha$ ,  $\mu_H$  is the hydrogen chemical potential, and  $E_F$  is the Fermi energy

measured from the valence band maximum (VBM)  $E_{\text{VBM}}$ . The defect transition level ( $q$



calculated (+