£YHjb'?`Ã'UbX'5'YI'Ni'b[Yf'

7]HUHjcb.'5dd`]YX'D\ngJVg'@YHhYfg'   ž+''f&$$&Ł/Xc].'%$"%$*'#%'%(,&+,'
J]Yk'cb`]bY.'\Hrd.##XI"Xc]'cf[#%$"%$*'#%'%(,&+,'
J]Yk'HUV'Y'cZ7cbHYbhg.'\Hrd.##gWJHUHjcb"U]d"cf[#WcbHYbh#U]d#cifbU`#Ud`#,%#%3jYf1dXZJVcj
Di V`]g\YX'VmhhY'5+D'Di V`]g\]b[

5V!]b]Hjc'ghi XmcZXcbcf!UWWYdhcf'WcXcd]b[' Lcf'b!hmdY'7iC'
>"'5dd`"'D\ng"'   ž%'+$('f&$%'(Ł/%$"%$*'#%'(-$$(-)'

‡XYbHjJWUHjcb'cZb]hfc[Yb!'UbX'\cghfrY'UHYX'XYYd!'Yj'Y'hfUdg']b!b!hmdY'; UB5g'UbX'h\Y]f'Yj'c'i'h]cb'i'dcb'UbbYU]b['
>"'5dd`"'D\ng"'   ž$%'+$)''f&$%'(Ł/%$"%$*'#%'(,,*,)*'

GY'YWhjcb'fi'Y'cZdfYZYffYX'Xcd]b['g]hY'Lcf'b!hmdY'cl]XYg'
5dd`"'D\ng"'@Hh'   ž&*&%$-'f&$%'&Ł/%$"%$*'#%'(+'%+**'

:'Yffca'U[bYHjga'UbX']hg'ghUV]']hm]b!b!hmdY'; X!XcdYX';'UB.':]fghdf]bWd]dYg'WU'Wi'UHjcb'
5dd`"'D\ng"'@Hh'   ž&''&($,'f&$%'&Ł/%$"%$*'#%'(+%+&('

:]fghdf]bWd]dYg'@85'Ž'I'ghiX]Yg'cZh\Y'‡b!XcdYX'NbC'ffUbgdUfYbhVcbXiWHjY'cl]XY'
>"'5dd`"'D\ng"'   ž$*'+$''f&$$,Ł/%$"%$*'#%'&-+,'&('

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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$_2$O, HgO, CuO, PbO, PtO, IrO$_2$, RuO$_2$, PbO$_2$, TiO$_2$, WO$_3$, Bi$_2$O$_3$, Cr$_2$O$_3$, Fe$_2$O$_3$, Sb$_2$O$_3$, Nb$_2$O$_5$, Ta$_2$O$_5$, FeTiO$_3$, and PbTiO$_3$, whose conduction band minimum (CBM) lie below this level (i.e., electron affinity>3.0±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$_2$, and Al$_2$O$_3$, whose CBM lie above this level (i.e., electron affinity<3.0±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.[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$_2$O$_3$. High-electron-affinity oxides, however, will be doped upon H incorporation. Likely examples include Ag$_2$O, HgO, CuO, PbO, PtO, IrO$_2$, RuO$_2$, PbO$_2$, TiO$_2$, WO$_3$, Bi$_2$O$_3$, Cr$_2$O$_3$, Fe$_2$O$_3$, Sb$_2$O$_3$, Nb$_2$O$_5$, Ta$_2$O$_5$, 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

$$\Delta H_f^q(\mu_H, E_F) = E(\text{host}+H^q) - E(\text{host})$$

$$- [\mu_H + \tfrac{1}{2}E(H_2)] + q(E_F + E_{VBM}), \quad (1)$$

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 (+