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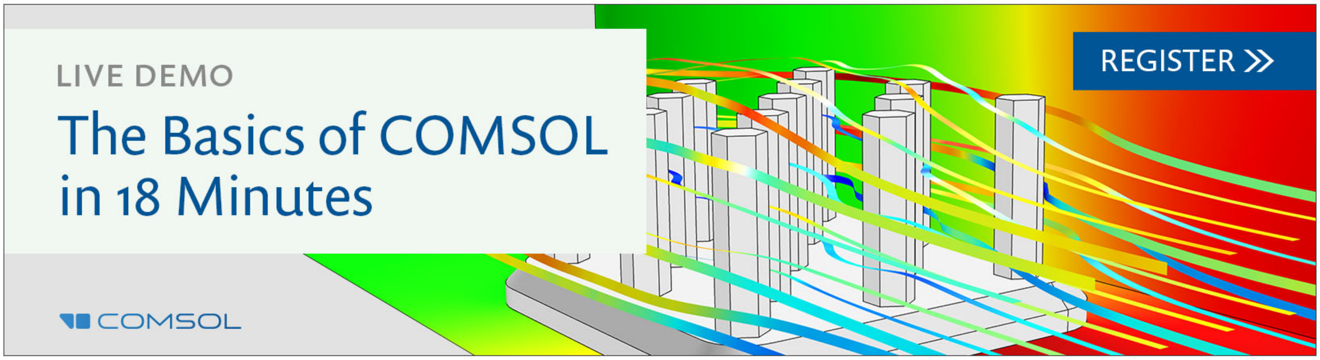

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n-type doping of oxides by hydrogen

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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_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

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

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_1/q_2) is then determined as the value of Fermi energy for which $\Delta H_f^{q_1}=\Delta H_f^{q_2}$, and is independent of μ_H. In Eq. (1), the zero of μ_H is set to the half of the H_2 dissociation energy so that $\mu_H\leqslant0$. The value of E_F is determined by the free-carrier concentration. The total energies $E(\alpha)$ were calculated in the framework of density functional theory within the local density approximation (LDA) using the Ceperley–Alder exchange correlation potential as parameterized by Perdew and Zunger,[4] and utilizing the plane-wave total energy method[5] as implemented in VASP code.[6] In the LDA calculations, the bandgaps of MgO, CdO, and SnO_2 are underestimated[7] as expected from the well known LDA bandgap error.[4] The bandgap error is also present in the defect formation energy through the band structure term of the total energy. We correct this error by an empirical means.[9]

The LDA-corrected formation energies of interstitial H impurity in SnO_2 and MgO are shown for three charge states (H^+, H^0, and H^-) in Fig. 1, as a function of Fermi energy E_F at the hydrogen-rich limit (i.e., $\mu_H=0$). We see that when E_F is at the midgap, H has a low formation energy in SnO_2 (~0 eV), so we expect large solubility. Incorporation of H into MgO, however, requires a high energy, e.g., ~3.5 eV for midgap E_F. The optimized atomic positions are shown in left-hand side panels of Fig. 2: In SnO_2, we found that an asymmetric configuration is the stablest for all charge states H^-, H^0, and H^+. In this configuration, H is bonded to one of the two axial oxygens, with an O–H bond length of 1.02 Å whereas the distance from H to the second oxygen is 1.87 Å. In MgO, on the other hand, only H^+ is bonded to a neighboring oxygen (with bond length of 1.0 Å), whereas H^- and H^0 prefer to stay at the interstitial site without any strong O–H bond, as shown in the left-hand side (bottom) panel of Fig. 2.

The lowest-energy charge state of hydrogen in SnO_2 is H^+ for values of E_F throughout the bandgap (Fig. 1). Being permanently ionized means that H in SnO_2 donates an electron. This clarifies that the observation[2] of the rapid increase of conductivity in H_2 atmosphere is due to the formation of a

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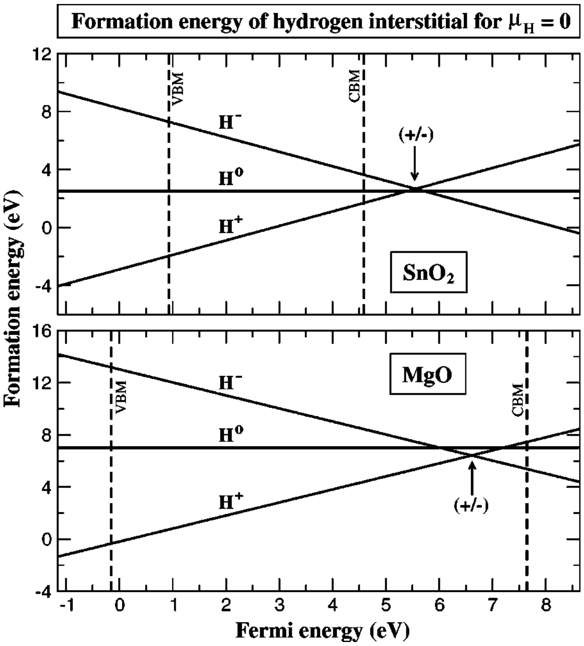

FIG. 1. LDA-corrected formation energy of interstitial hydrogen impurity in SnO_2 and MgO. The band edges of the two materials are aligned according to their band offsets. Arrow points to transition level (+/−).

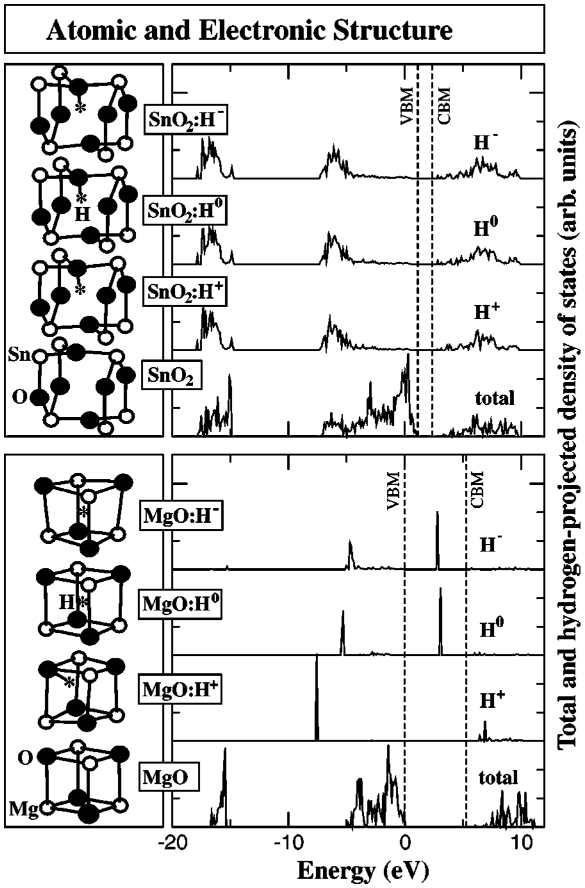

FIG. 2. Atomic structure (left-hand side) and density of states (right-hand side) for H (shown by *) incorporation to SnO_2 (top) and MgO (bottom). Right-hand side panels show also density of states projected on H^-, H^0, and H^+. The projected densities of states are magnified by multiplying by 73 for H in SnO_2, and 65 for H in MgO. The VBM and CBM are shown at their LDA values by vertical dashed lines; the valence band edges are aligned according to their band offset.

hydrogen donor level in SnO_2. Hence, SnO_2 is doped *n* type by hydrogen. We find that CdO is also doped *n* type by hydrogen since the hydrogen donor level is above the conduction band minimum. This confirms the evidence for the existence of a shallow hydrogen donor level in CdO, deduced from a recent muonium implantation experiment.[10] In MgO, however, we find that H forms a deep electronic level inside the bandgap (cf. Fig. 1), so even if H is implanted into MgO, this material is not doped by hydrogen.

The distinction between H as an *n*-type dopant and H as a nondoping impurity is evident in the calculated hydrogen-projected density of states, illustrated in right-hand side panels of Fig. 2 for MgO and SnO_2. We see that the incorporation of H^+ into either MgO or SnO_2 produces delocalized, unoccupied states inside the conduction band. This is due to the hybridization of hydrogen *s* orbital with the cation (Mg and Sn) *s* orbitals. While in SnO_2, even H^0 and H^- produce such conduction-band resonances (thus, delocalized free carriers), in MgO, H^--derived (partially occupied) and H^0-derived (fully occupied) states are shifted down into the band gap, yielding deep, localized states. Thus, electrons donated by hydrogen are trapped by gap states in MgO while they are transferred to the CBM in SnO_2.

The effective Coulomb energy *U* of interstitial hydrogen is the difference between the ionization potential of (+/0) and the electron affinity of (−/0), and is given by

$$U=(\Delta H_f^0-\Delta H_f^+)-(\Delta H_f^- -\Delta H_f^0), \tag{2}$$

in terms of the formation energies of H^-, H^0, and H^+. Generally, hydrogen in a semiconductor forms a *negative-U* system,[1,11] i.e., a system in which the neutral state is not stable at any E_F so that the charge state of H is either *plus* or *minus*. Calculated values of *U* for H in SiO_2 (α-cristobalite), MgO (rocksalt), CdO (rocksalt), and SnO_2 (rutile) are −2.4 (Ref. 8), −1.4, 0., and 0., respectively. Thus, we see that in insulators such as SiO_2 and MgO where H creates gap levels, one has a large *negative U*, but systems where the hydrogen levels are delocalized inside the conduction band (CdO and SnO_2) exhibit almost *zero-U* behavior. In the latter case, the electrons initially occupying electronic levels derived from H^0 and H^- relax to the CBM, yielding $U \simeq 0$.

It is interesting to seek unifying, "universal trends" for the behavior of H in different oxides. For example, comparison of H bonding in various oxides indicates that the distance from H^+ to nearest host O atom in the optimized geometries is not affected much by the cation type and the crystal structure; being 1.02 Å in SnO_2 (rutile), 1.00 Å in CdO (rocksalt), 1.00 Å in MgO (rocksalt), 0.99 Å in ZnO (wurtzite),[3] and 1.02 Å in SiO_2 (α-cristobalite).[8] The near invariance of this distance reflects the localized properties of H^+ attachment to oxygen. Given the latter, one wonders if there are other "universal" electronic manifestations induced by hydrogen incorporation. For example, if the position of H-induced transition level were also insensitive to the host environment, we could imagine that some "pinning rule" would exist, relating the hydrogen transition levels in various oxides. Indeed, it has been previously demonstrated that the energy levels of a given 3*d* impurity aligns in different III–V semiconductors, and separately in II–VI semiconductors, leading to such a pinning rule.[12]

We illustrate this consideration in Fig. 3, showing the

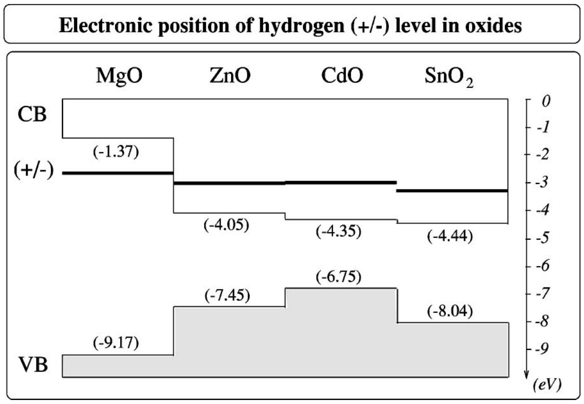

FIG. 3. Position of the hydrogen pinning level (horizontal thick lines) in MgO, ZnO (Ref. 3), CdO, and SnO_2. The CBM and VBM band edge energies are given in parenthesis.

calculated $(+/-)$ transition energy level of hydrogen in MgO, ZnO, CdO, and SnO_2 after aligning the relative band edge energies according to band offsets. The position of $(+/-)$ is the value of the Fermi energy at which the formation energy [cf. Eq. (1)] of H^+ equals that of H^-. The conduction band offsets ΔE_c between these oxides are estimated electrochemically,[13] whereas the valence band offsets ΔE_v are obtained from $\Delta E_v = \Delta E_c - \Delta E_g$ where ΔE_g is the difference between the measured (direct) band gaps.[7] This construct was demonstrated to reproduce oxide flat band potentials within an accuracy of 0.2 eV.[13] Moreover, it yields an electron affinity of 1.37 eV for MgO, in good agreement with measured value of 1.3 eV.[14] Furthermore, comparison with a LDA result, available from literature[15] only between MgO (wurtzite) and ZnO (wurtzite), is satisfactory. Figure 3 shows that the level $(+/-)$ in MgO, ZnO, CdO, and SnO_2 are aligned almost within the error bar of band offsets. The error in this alignment is 0.37 eV for MgO and 0.32 eV for SnO_2 if we assume the position of $(+/-)$ in ZnO and CdO is correct. Note, however, that there is a scatter in the measured band gap values, e.g., $3.5\ \text{eV} \leqslant E_g \leqslant 4.1\ \text{eV}$ for SnO_2.[7]

The results for the transition levels of hydrogen in oxides show that there exists an approximately constant hydrogen pinning level in different oxides at about 3 ± 0.4 eV below vacuum (cf. Fig. 3). If the CBM of a material is well *below* this level, hydrogen incorporation will dope this material, whereas if the CBM is well *above* this level, hydrogen incorporation will not introduce free carriers. Thus, in oxides with small electron affinity (i.e., the CBM close to a vacuum) the hydrogen pinning level will be inside the band gap, and no doping is expected upon hydrogen introduction. Conversely, oxides having high-electron-affinity will have the hydrogen pinning level inside the conduction band, and thus, predicted to be doped *n*-type via hydrogen introduction. Comparing electrochemically determined positions of conduction band edges in various oxides,[13,16] we predict that hydrogen forms a *shallow* donor in Ag_2O, HgO,[17] 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 $PbTiO_3$ *once* H *is implanted via an equilibrium process or otherwise, without reducing the host*. The LDA calculations for H in WO_3 (Ref. 18) and H in $PbTiO_3$ (Ref. 19) confirm our predictions. Thus, the hydrogen pinning rule can provide an easy approximate criterion for deciding if an oxide can be doped by hydrogen.

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