Hydrogen interactions with acceptor impurities in SnO$_2$: First-principles calculations

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Using first-principles calculations, we investigate the role of hydrogen in the passivation of Al, Ga, and In acceptors in SnO$_2$. We find that interstitial hydrogen bonds to oxygen atoms next to the acceptor impurities and effectively neutralizes their electrical activities. Based on calculated binding energies and migration barriers we discuss conditions under which hydrogen can be removed and acceptor activation can take place. We also calculate the stretch-mode vibrational frequencies associated with the hydrogen-impurity complexes, providing a signature for their experimental identifications.

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I. INTRODUCTION

SnO$_2$ is a wideband-gap material with great potential for electronic and optoelectronic device applications.[1–4] However the development of semiconducting SnO$_2$ has been hindered by the lack of control over its conductivity. SnO$_2$ typically exhibits unintentional *n*-type conductivity, the cause of which has been widely debated.[4–8] Recent first-principles studies have shown that this *n*-type behavior likely arises not from intrinsic point defects,[8] but from the unintentional incorporation of impurities into the host lattice with hydrogen being a prime candidate as a shallow donor.[7–9] Interestingly, SnO$_2$ has been proposed to offer good prospects for ambipolar doping: group III-A elements (Al, Ga, and In) have been calculated to produce shallow acceptors with appreciable solubilities and a low degree of self-compensation.[8]

An important question to be addressed is how hydrogen interacts with these acceptors. Many growth techniques such as metal-organic chemical vapor deposition contain an abundance of hydrogen in the growth environment. Since interstitial hydrogen in SnO$_2$ is a highly mobile shallow donor,[7–9] it is expected to strongly interact with negatively ionized acceptors. Understanding the effect of hydrogen on the desired *p*-type conductivity is therefore crucial. Here we present first-principles investigations of hydrogen interacting with Al, Ga, and In acceptors in SnO$_2$. We compute atomic configurations and binding energies, as well as activation energies for dissociation of the hydrogen-acceptor complexes. We find that the incorporation of hydrogen lowers the formation energy of acceptors, thus enhancing their solubilities. To aid in experimental identification we also report vibrational frequencies for H-related stretching modes.

II. COMPUTATIONAL APPROACH

Our calculations are based on density functional theory using a hybrid functional approach and projector augmented wave potentials as implemented in the Vienna *Ab Initio* Simulation Package (VASP) code.[10,11] The hybrid functional employed is that proposed by Heyd-Scuseria-Ernzerhof with a Hartree-Fock mixing parameter of 25% and the generalized gradient approximation for exchange and correlation as parameterized by Perdew-Burke-Ernzerhof.[12,13] The Sn 4*d* electrons are explicitly included in the valence and a plane-wave basis set is used. Convergence tests showed that all the relevant quantities (formation energies, O-H bond lengths, and vibrational frequencies) are converged at an energy cutoff of 400 eV. All integrations over the Brillouin zone are performed using a $2 \times 2 \times 2$ grid of Monkhorst-Pack special k points for a 72-atom supercell.

III. RESULTS

A. Structural parameters and bulk properties of SnO$_2$

The calculated equilibrium lattice parameters for rutile SnO$_2$ are $a=4.76$ Å, $c=3.19$ Å, and $u=0.306$, in good agreement with the experimental values of $a=4.73$ Å, $c=3.18$ Å, and $u=0.307$.[14] Our calculated formation enthalpy is also close to the experimental value as shown in Table I. Our calculated band gap is 2.96 eV, somewhat smaller than the experimental value of 3.6 eV.[5,16] Our calculations of formation energies, transition levels, and binding energies for acceptors and acceptor-hydrogen complexes are minimally affected by any band-gap error. The relevant occupied acceptor states are all valence band related and insensitive to the position of the conduction band, while for shallow-donor hydrogen the conduction-band-related states are unoccupied.

B. Formation energies and transition levels

The formation energy of an impurity determines the likelihood of it being incorporated in the lattice; for group III-A acceptors in SnO$_2$ we define[17]

TABLE I. Calculated and experimental formation enthalpies ΔH_f for SnO$_2$, Al$_2$O$_3$, Ga$_2$O$_3$, In$_2$O$_3$, and H$_2$O molecules.

Compound	ΔH_f (eV) (Calc.)	ΔH_f (eV) (Expt.)[a]
SnO$_2$	−5.42	−5.98
Al$_2$O$_3$	−16.31	−17.36
Ga$_2$O$_3$	−9.36	−11.29
In$_2$O$_3$	−8.62	−9.61
H$_2$O	−2.69	−2.51

[a]Reference 15.

$$E_f[A_{Sn}^q] = E_{tot}[A_{Sn}^q] - E_{tot}[SnO_2] + [\mu_{Sn} + E_{tot}(Sn_{bulk})]$$
$$- [\mu_A + E_{tot}(A_{bulk})] + qE_F, \qquad (1)$$

where $E_{tot}[A_{Sn}^q]$ is the total energy of a supercell containing the acceptor A_{Sn} in charge state q (0 for neutral or −1 for ionized) and $E_{tot}[SnO_2]$ is the total energy of the corresponding perfect-crystal supercell. The Fermi level E_F is conventionally referenced to the valence-band maximum (VBM). A correction to the VBM is included by aligning the electrostatic potential in a bulklike region of the defect supercell with that of the perfect bulk, as described in Ref. 17.

Since we are replacing a Sn atom with an impurity A atom, the formation energy depends on the chemical potentials μ_{Sn} and μ_A. These chemical potentials can vary according to the experimental conditions during growth or annealing, e.g., Sn-rich, O-rich, or anything in between. We reference their values to the energy per atom of the elemental phases Sn_{bulk}, (α-Sn), and A_{bulk} (fcc-Al, α-Ga, or hcp-In). μ_{Sn} and μ_A are subject to bounds to ensure the stability of SnO_2 and to avoid the formation of secondary phases A_nO_m

$$\mu_{Sn} + 2\mu_O = \Delta H_f(SnO_2), \qquad (2)$$

$$n\mu_A + m\mu_O \leq \Delta H_f(A_nO_m), \qquad (3)$$

where the oxygen chemical potential μ_O is taken with respect to the energy per atom of an O_2 molecule $[\frac{1}{2}E_{tot}(O_2)]$. The Sn-rich limit is characterized by $\mu_{Sn}=0$, $\mu_O = \frac{1}{2}\Delta H_f(SnO_2)$, and $\mu_A < \frac{1}{n}[\Delta H_f(A_nO_m) - \frac{m}{2}\Delta H_f(SnO_2)]$ (or $\mu_A < 0$); while the O-rich limit is characterized by $\mu_O=0$, $\mu_{Sn}=\Delta H_f(SnO_2)$, and $\mu_A < \frac{1}{n}\Delta H_f(A_nO_m)$. Since the formation enthalpies are negative for stable compounds, the relations above show that the lowest formation energy (i.e., the highest solubility) of an impurity A substituting on Sn sites occurs in the O-rich limit provided $m<2n$, a condition which is satisfied here since the limiting phases are Al_2O_3, Ga_2O_3, and In_2O_3. Table I shows that the calculated formation enthalpies are in reasonable agreement with experiment. Expressions similar to Eq. (1) also apply to interstitial H and H-acceptor complexes. Under Sn-rich conditions the solubilities of H-related species are limited by the formation of H_2; under oxygen-rich conditions the limit is set by the formation of H_2O, i.e., $\mu_O + 2\mu_H \leq \Delta H_f(H_2O)$.

The calculated formation energies for substitutional acceptors, interstitial hydrogen, and H-acceptor complexes are shown in Fig. 1. The isolated impurities Al, Ga, and In act as shallow acceptors in SnO_2: their ionization energies are given by the position of the transition level $\varepsilon(0/-)$ (the Fermi level value at which the formation energies of the neutral and negative charge states are equal) and are calculated to be 90 meV for Al, 70 meV for Ga, and 110 meV for In.

Isolated interstitial H is stable exclusively in the positive charge state (H_i^+) in SnO_2. Its formation energy is higher under O-rich conditions than under Sn-rich conditions due to the limit imposed on μ_H by the formation of H_2O. Isolated H_i^+ is highly mobile in SnO_2, with a calculated diffusion barrier of 0.57 eV,[8] and Coulomb attraction drives complex formation with acceptors. We investigated various configura-
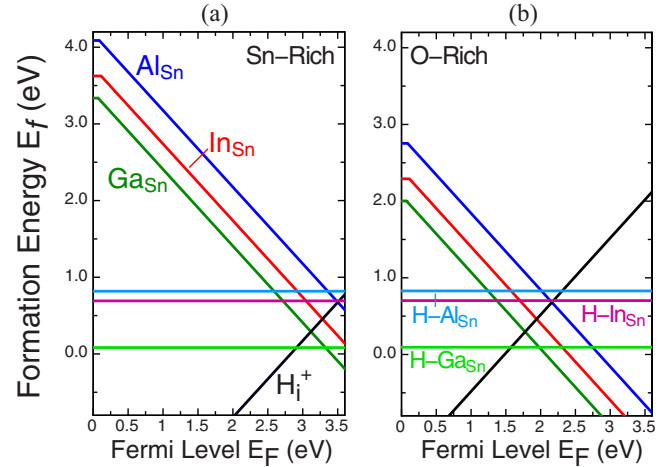

FIG. 1. (Color online) Calculated formation energies as a function of Fermi level for group III-A acceptors, interstitial hydrogen, and hydrogen-acceptor complexes in SnO_2. Results are shown for (a) Sn-rich and (b) O-rich conditions. The Fermi level varies from 0 at the VBM to 3.6 eV, which corresponds to the experimental band gap of SnO_2.

tions for acceptor-hydrogen complexes, consistently finding that H prefers to bond to an O atom next to the acceptor impurity as shown in Fig. 2 for the H-Ga$_{Sn}$ complex. Configurations where H is directly bonded to the acceptor impurity are much higher in energy. The complexes are stable exclusively in the neutral charge state (see Fig. 1) and all have low formation energies, indicating that they can be easily incorporated in SnO_2. Since H acts as a donor in SnO_2, its incorporation drives the Fermi level toward higher values thus lowering the formation energy of the acceptor (see Fig. 1). This lowering, along with the low formation energy of the complexes, enhances the acceptor solubility, which is highly desirable for p-type doping. Once such complexes are formed the H atom would have to overcome an energy barrier in order to reactivate the acceptor. To a good approximation, this activation energy is given by the sum of the binding
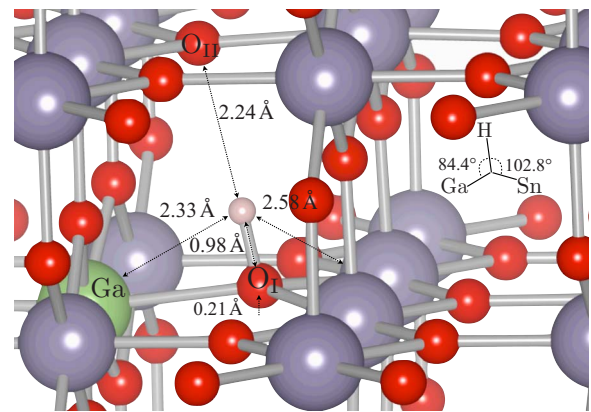

FIG. 2. (Color online) Atomic configuration of an acceptor-hydrogen complex in SnO_2 showing the hydrogen atom and a substitutional Ga$_{Sn}$. The relaxed configuration is similar to that of the isolated H_i^+ but the primary O_I-H bond length is slightly contracted while the distance to the secondary O neighbor O_{II}-H is increased.

TABLE II. Calculated properties of hydrogen-acceptor complexes in SnO_2 and comparison with isolated interstitial H_i in perfect SnO_2. E_b is the binding energy of the complex as defined in Eq. (4). A_{Sn}-H is the distance between the acceptor and the hydrogen atom, and O_I-H and O_{II}-H are the distances between H and the primary and secondary oxygen atoms. ω is the vibrational frequency of the O-H stretch mode (including anharmonic contributions).

	A_{Sn}-H d (Å)	E_b (eV)	O_I-H d (Å)	O_{II}-H d (Å)	ω (cm^{-1})
Bulk	2.42		0.98	2.11	3245
Al_{Sn}	2.31	0.53	0.98	2.22	3379
Ga_{Sn}	2.33	0.50	0.98	2.24	3412
In_{Sn}	2.42	0.22	0.98	2.12	3294

energies of the complex and the migration barrier of interstitial H.

C. Binding energies of hydrogen complexes

The binding energy is defined as

$$E_b = E_f[A_{Sn}^-] + E_f[H_i^+] - E_f[(H_i\text{-}A_{Sn})^0], \qquad (4)$$

where $E_f[(H_i\text{-}A_{Sn})^0]$ is the formation energy of the complex. A positive E_b means that the neutral complex H_i-A_{Sn} is lower in energy than the isolated H_i^+ and A_{Sn}^-. The calculated binding energies are listed in Table II; the values and trends are consistent with the Coulombic nature of the interactions between H_i^+ and A_{Sn}^-. They are quite modest and comparable to those of hydrogen-acceptor complexes in other materials. Combined with the calculated migration barrier for H_i^+,[8] the activation energy would be on the order of 0.8–1.1 eV. The most relevant comparison may be possible with the H-Mg complex in GaN, which has a binding energy of 0.7 eV and a dissociation activation energy of 1.5 eV.[18] It is well known that the removal of hydrogen and acceptor activation in Mg-doped GaN can be achieved by thermal annealing,[19] we therefore expect that the same strategy would be successful in acceptor-doped SnO_2.

Hydrogen can also be incorporated in a substitutional form on the oxygen site in SnO_2 (H_O);[8] release of this hydrogen during activation anneals could lead to compensation by oxygen vacancies. We have examined this possibility and concluded that it will not be a concern for two reasons: (1) the calculated barrier for H_O to be released from the oxygen site is 2.24 eV (Ref. 8), substantially higher than the barrier for dissociation of hydrogen-acceptor complexes. It should therefore be possible to identify a temperature window where oxygen vacancy generation is not triggered. (2) Under Sn-rich (O-poor) conditions, which are most favorable for incorporating hydrogen on the substitutional oxygen site, the formation energy of H_O is 0.8 eV larger than that of H_i (Ref. 8). As we move from Sn-rich conditions toward O-rich conditions the difference between the formation energies of substitutional and interstitial H increases, becoming as large as 3.51 eV under O-rich conditions. Moving away from Sn-rich conditions is favorable for incorporation of group III acceptors on the Sn site (see Fig. 1); this will simultaneously increase the formation energy of H_O and thus suppress its incorporation. The substitutional hydrogen concentration is

thus expected to be low under conditions that are beneficial for acceptor incorporation. For these two reasons substitutional hydrogen in SnO_2 should not be an obstacle to achieving p-type doping.

D. Lattice relaxations and experimental signatures

Our results indicate that the group III-A acceptors cause only a relatively small perturbation in the SnO_2 lattice. In the perfect crystal each Sn is bonded to six O atoms and each O is bonded to three Sn atoms. Four of the Sn-O bonds have a calculated bond length of 2.063 Å and two have a length of 2.060 Å. For the isolated Al_{Sn}^- and Ga_{Sn}^- acceptors, the Al_{Sn}-O and Ga_{Sn}-O bond lengths are smaller than the Sn-O equilibrium bond lengths by 4.7% and 2.1%. For In_{Sn}^-, the In_{Sn}-O bond lengths are greater by 3.4%. The variations in the acceptor-O bond lengths are consistent with the relative atomic sizes of Al, Ga, and In.[20]

For acceptor-hydrogen complexes, the bonding arrangement is very similar to that of isolated interstitial H in SnO_2. We find that interstitial H disrupts the planar O bonding in SnO_2 causing the primary O atom bonded to H_i (labeled O_I) to move out of the plane, as shown in Fig. 2. H_i also interacts with a secondary O atom (labeled O_{II}), which also moves out of the plane in the direction of the H atom. The introduction of an acceptor has three effects: (1) a minor contraction of the O_I-H bond; (2) a tilting of the O_I-H bond with the H moving in the direction of the acceptor (consistent with Coulomb attraction); and (3) an increase in the O_{II}-H distance. We see that these effects have direct consequences for vibrational frequencies; these are listed in Table II, along with specific values for atomic distances.

Vibrational frequencies for the stretch mode of the O-H bonds were calculated by displacing the hydrogen atom from its equilibrium position along the direction of the O-H bond. The light mass of the hydrogen leads to large anharmonicity as evident from a plot of total energy versus displacement (Fig. 3). Anharmonic contributions to the vibrational frequencies have therefore been included as described in Ref. 21.

Table II shows that the calculated vibrational frequencies of the O-H_i stretching mode in SnO_2 are similar to typical O-H stretch frequencies. For instance, the experimentally reported frequency for O-H in TiO_2 is 3277 cm^{-1}, which also possesses the same rutile crystal structure and the same interstitial configuration.[22] The variations between the frequen-
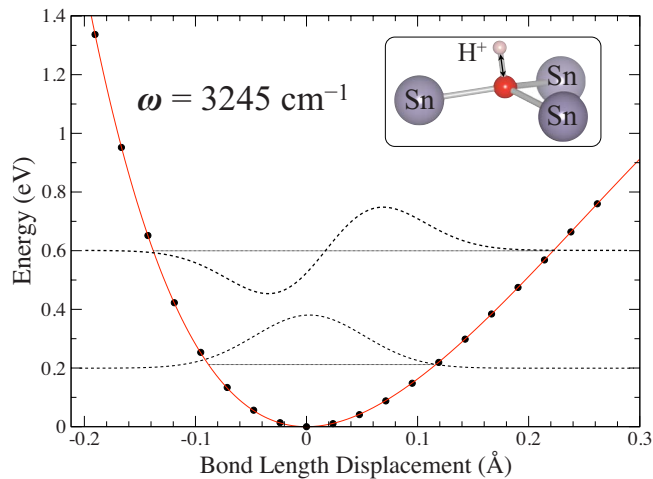
FIG. 3. (Color online) Calculated potential-energy curve for an O-H$_i$ oscillator due to interstitial H$_i^+$ in SnO$_2$ (see inset). Large anharmonicity is evident. The curve is a fourth-order polynomial fit to the calculated data points. Calculated energy levels for the ground state and first excited state are shown, with schematics of the corresponding wave functions.

cies for the various complexes can be attributed to the interaction between H and the secondary O atom O$_{II}$. While the primary bond of the hydrogen atom is clearly bonded to its first nearest-neighbor oxygen atom, some degree of bonding is also present with the secondary O atom (labeled O$_{II}$ in Fig. 2). As the interaction with this secondary O atom increases (i.e., as the O$_{II}$-H distance decreases), the vibrational frequency goes down due to a "hydrogen bonding" effect.[23]

IV. SUMMARY

In summary we find that interstitial hydrogen effectively passivates group III-A acceptors in SnO$_2$, with H bonding to an O neighbor of the acceptor impurity and forming a neutral acceptor-hydrogen complex. These complexes have low formation energies indicating they can be easily incorporated during growth in a hydrogen-containing environment. The calculated binding energies (ranging from 0.2 to 0.6 eV) indicate that dissociation and consequent activation of acceptors should be feasible by annealing. The calculated vibrational stretch modes are reported for both the bulk interstitial and acceptor-complex O-H bonds, yielding signatures for experimental identification of the complexes via vibrational spectroscopy.

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