Defect levels of SnO₂

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A theory of the major chemical trends of impurity and vacancy levels in SnO_2 is presented, based on a tight-binding Green's-function calculation. Our results account for the shallowness of levels associated with substitutional Sb_{Sn} and F_O centers and the unrelaxed oxygen vacancy. The behavior of defects in SnO_2 and SiO_2 is contrasted and discussed in terms of their bulk electronic structures and different coordinations.

 SnO_2 is a refractory oxide with a wide 3.6-eV optical gap and a conduction-band minimum of low effective mass,^{1,2} so it has important applications as a transparent water-stable electrode and as a conducting ceramic.³ Substitutional antimony or fluorine doping or a deficiency of oxygen produce shallow levels in SnO_2 while similar centers in the isovalent oxide SiO_2 are deep or inert. In this note we use the results of a tight-binding Green's-function calculation to predict the relative ordering of deep levels associated with *s*- and *p*bonded substitutional impurities in SnO_2 . We then show why Sb_{Sn} and F_O sites and the oxygen vacancy V_O are shallow in SnO_2 and contrast this with the behavior of defects in SiO_2 in terms of differences in bonding and lattice relaxation at defect sites.

SnO₂ is 6:3 coordinated and fairly ionic. Thus, its Γ_1^+ conduction-band minimum is largely Sn *s*-like while its Γ_3^+ valence-band maximum is O-like and localized on the $p\pi$ states lying normal to the plane of the three O-Sn bonds.¹ SiO₂ is 4:2 coordinated and also has an O $p\pi$ -like upper valence band. While the bonding in SiO₂ can be represented in terms of covalent bonds, the higher coordination of SnO₂ is consistent with more ionic bonding.

Deep levels arise if the defect potential is sufficiently strong. In this limit it is believed that the central-cell potential alone determines the energy levels.⁴ As for SiO_2 ,⁵ we calculate the energies of deep levels by the tight-binding⁶ Green's-function method, retaining only the central-cell potential and neglecting initially any lattice relaxation. The Sn site is distorted octahedral D_{2h} , so we expect levels of s-like A_1^+ , and p-like B_1^- , B_2^- , and B_3^- symmetry. The oxygen site is distorted trigonal $C_{2\nu}$ giving one s- and p-like A_1 level and p-like B_1 and B_2 levels. The variations of defect energy with impurity potential are shown in Figs. 1 and 2. An element forms a deep level if a solution is found in the gap for that defect potential, otherwise the long-range part of any Coulombic potential binds shallow levels. The figures place impurity levels in a specific order allowing chemical trends to be identified and possible systematic errors to be recognized from limited experimental data.

The curve for Sn site impurities is A_1^+ and donor-like (Fig. 1). The *p*-like donor curves (not shown) lie above the A_1^+ curve for all potentials, so are unoccupied, and all the acceptorlike parts of the curves lie entirely in the valence band. The heavier group V elements like Sb are predicted to be shallow, as seen experimentally,³ while the lighter P is

predicted to be just deep. All Sn site acceptors are predicted to be shallow. This is in disagreement with experiments where group III impurities in SnO_2 and tetragonal GeO₂ are deep.⁷ However, these centers are complex, the hole is localized on one of the six oxygen sites adjacent to the impurity, as discussed shortly.

The important levels associated with substitutional impurities at the oxygen site are the $B_1 \pi$ -like acceptor levels and A_1 s-like donor levels. The B_1 acceptor levels lie above all other acceptorlike levels and so trap any holes. As the B_1 state is π , nonbonding and impuritylike, its energy lies close to that of the impurity p orbital. Figure 2 predicts most oxygen-site acceptors to be deep. Fluorine is the only possible oxygen-site donor, and its A_1 level is calculated to be shallow (not shown), as seen experimentally.³ Other halogens cannot act as donors because their p orbital energies lie above that of oxygen and they are too electropositive.

A vacancy corresponds to an infinite defect potential in the tight-binding method. We find all levels of the neutral vacancies to be resonances in the bands (Fig. 3). The tin vacancy V_{sn} is not found experimentally because of its large charge. V_0 is usually positively charged, and its Coulombic well now binds shallow levels, as seen experimentally.²

It is instructive to compare the present results with those of Ekenberg, Robertson, and Dow^5 for SiO₂ as in general



FIG. 1. Predicted energies of deep A_1^+ levels at the Sn site, between the valence-band maximum (VBM) and conduction-band minimum (CBM). The *p*-like B_1^- , B_2^- , and B_3^- levels (not shown) all lie higher.

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FIG. 2. Predicted energies of deep levels of *p*-like $B_1(\pi)$, B_2 , and A_1 symmetry at the O site.

impurities behave quite differently in SnO₂ and SiO₂ in spite of Sn and Si both being tetravalent. In detail, for the vacancies, SnO_2 : V_0 is a shallow donor³ while SiO₂: V_0^+ is very deep;⁸ for isochoric impurities $SnO_2:Sb_{Sn}$ is shallow while $SiO_2:P_{Si}$ is deep, and $SnO_2:F_O$ is shallow while F does not produce gap states in SiO₂. In contrast trivalent impurity centers like SnO₂:In_{Sn} and SiO₂:Al_{Si} are both deep with the hole localized on an adjacent oxygen in each case.^{7,9} We now account for these differences in terms of the bulk electronic structures and different coordinations. SnO₂ has a gap $E_g = 3.6$ eV, and its conduction-band minimum has an effective mass $m_e = 0.3$ m (Ref. 2) and 90% Sns content,¹ so shallow donors are truly delocalized, with radius ~ 20 Å. In SiO₂, $E_g = 9$ eV and even nominally shallow levels have sizeable binding energies (~ 1.5 eV, Ref. 8) and are quite localized. The valence-band maximum is made of oxygen π states in both compounds and consequently has a very high effective mass, over 10 m for SiO₂ and we calculate over 20 m for SnO₂. Thus, nominally shallow hole states are strongly localized in both compounds.

The trends in donor levels associated with pentavalent impurities depend on the impurity potential or "threshold" at which the cation A_1^+ curve enters the gap. More negative values favor shallower impurities. We find correctly that



FIG. 3. Schematic energy levels of V_0 for (a) unrelaxed vacancy in SnO₂, (b) unrelaxed vacancy in SiO₂, (c) relaxed V_0^+ center in SiO₂ (E' center).

the isochoric centers $SnO_2:Sb_{Sn}$ and $SiO_2:P_{Si}$ are shallow and deep, respectively, for two reasons. Firstly, the impurity potential is less for Sb_{Sn} , -2.9 compared to -4.2 eV for P_{Si} , and secondly, the threshold is greater in SnO_2 , -3.3 compared to -2.0 eV in SiO₂. The low threshold of SnO_2 arises from its remarkable broad conduction minimum. In contrast the A_1 threshold of SiO_2 is much higher, largely because of its higher electron mass. The delocalization of $SnO_2:Sb_{Sn}$ minimizes relaxation, while the localization of $SiO_2:P_{Si}$ enhances the tendency of neighboring atoms to relax.

We calculate the levels of unrelaxed V_0 in both SnO₂ and SiO_2 to be shallow (Fig. 3). Experimentally, V_0^+ is shallow in SnO₂ but very deep in SiO₂. V_0^+ is a model for the E' center observed by ESR in SiO₂.¹⁰ The single defect electron is found to be preferentially localized on only one of the two Si dangling bonds of the vacancy, and it is assumed that the positive Si site has relaxed away from the vacancy towards a planar configuration. The low oxygen coordination allows such relaxation to occur in SiO₂ by bond rotation without any change in bond length, but this would not be possible in the SnO₂ lattice. The relaxation strongly affects the associated levels, and the occupied level of $SiO_2: V_0^+$ is very deep, near midgap. The depth of $SiO_2: V_0^+$ is largely attributable to self-energy shifts in our model of this center.⁸ Self-energy shifts are introduced at Si sp³ hybrids of a dangling bond to model the absence of the bulk Si-O overlap repulsion. Just as deep states are bound by large central-cell potentials, strong self-energy shifts at dangling bonds can force these levels deep. The shifts are much smaller in SnO_2 than in SiO_2 (Ref. 11) and are insufficient to create a deep vacancy state. Thus, $SnO_2: V_0^+$ remains shallow.

The doping of SnO_2 by V_0 is also related to the different response of the SnO_2 and SiO_2 lattices to gross oxygen defficiency. While the tin coordination around an oxygen vacancy in SnO_2 is that of the bulk, oxygen defficiency in amorphous SiO_2 occurs by breaking chemical order, by the formation of covalent Si–Si bonds. These maintain a saturated valence so E_f remains in midgap.

 SnO_2 :F₀ is shallow donor level in SnO_2 but fluorine in SiO_2 has no gap level. We suggest that this indicates that fluorine enters a true substitutional site in SnO_2 but not in SiO_2 ; it takes advantage of the low O coordination by substituting two nonbridging \equiv Si-F sites for one bridging oxygen:

$$2HF + = Si - O - Si = \rightarrow = Si - F + F - Si = + H_2O$$

Valence is saturated at such fluorine centers and no gap levels result.

The similar behavior of trivalent impurities in SiO₂ and SnO₂ is largely due to O $p\pi$ states forming the upper valence band of both oxides. In both oxides Al_{Si} or In_{Sn} centers cause the hole to localize on one of the adjacent oxygens.^{7, 10} We calculate that SnO₂:In_{Sn} should be shallow. However, such a state is strongly localized due to the high hole mass of $p\pi$ states. Electron-lattice coupling further localizes the hole onto a single oxygen π orbital in both compounds. It is reassuring that calculations based on the extreme opposite model of charged ions also concludes that the holes are trapped in $p\pi$ states.⁷

In conclusion, SnO_2 is a good *n*-type semiconductor in

the 6:3 and 4:2 coordinated polymorphs of GeO_2 and SiO_2 would be most interesting.

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