

Origins of Coexistence of Conductivity and Transparency in SnO₂

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SnO₂ is a prototype “transparent conductor,” exhibiting the contradictory properties of high metallic conductivity due to massive structural nonstoichiometry with nearly complete, insulator-like transparency in the visible range. We found, via first-principles calculations, that the tin interstitial and oxygen vacancy have surprisingly low formation energies and strong mutual attraction, explaining the natural nonstoichiometry of this system. The stability of these intrinsic defects is traced back to the multivalence of tin. These defects donate electrons to the conduction band without increasing optical interband absorption, explaining coexistence of conductivity with transparency.

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Most electrical conductors are opaque, and most optically transparent solids are electrical insulators. Electrical conduction in a transparent solid [1] occurs in just a few systems [2] such as the 4d metal oxides SnO₂ and In₂O₃, and is thus the rarest form of conductivity (e.g., compared to semiconductivity or superconductivity). Stannic oxide [4] SnO₂ is the prototype transparent conductor, being a wide band gap (3.6 eV) material with up to 97% optical transparency in the visible range (for films of thickness 0.1–1 μm), yet having a resistivity of 10⁻⁴–10⁶ Ω cm, considerably lower than most semiconductors (10⁻³–10⁹ Ω cm). Remarkably, nominally undoped SnO₂ has a carrier density of up to 10²⁰ cm⁻³ [1] which is comparable to that of semimetals (10¹⁷–10²⁰ cm⁻³). For these reasons, SnO₂ and its alloy with In₂O₃ is widely used technologically as a transparent electrical contact in flat-panel displays [3] and in solar cells [1].

The reason for the coexistence of electrical conductivity with optical transparency is unclear. It has been postulated for a long time [4] that transparent conductivity is related to the existence of shallow donor levels near the conduction band, formed by a large concentration of oxygen vacancies. While these levels create only *far-infrared* (Drude-like) absorption, they leave the fundamental, across-the-gap absorption intact, i.e., the material is optically transparent. Indeed, electrical conduction in undoped SnO₂ is correlated with nonstoichiometry [2,5] (as perfectly stoichiometric samples are highly resistive [6]), and with oxygen-related intrinsic defects (since the conductivity of tin oxide films changes by orders of magnitude with controlled variation of oxygen partial pressure [5]).

As widespread as this oxygen vacancy scenario is (virtually almost all papers in this field subscribe to it), this model raises a few questions: (i) Given that vacancies usually form *deep* (i.e., nonconductive) levels in the band gap of both insulators (alkali halides, SiO₂) and semiconductors (Si and GaAs), it is surprising that vacancies would form *shallow* (i.e., conductive) levels in SnO₂. (ii) Given that main-group oxides (CaO, MgO, SiO₂) tend to be stoichiometric, one wonders why SnO₂ tolerates such an enormous concentration of intrinsic, stoichiometry-

violating vacancies. Is this structural tolerance related to the multivalence of Sn? (iii) The placement of the Fermi level inside the conduction band could lead to absorption from the Fermi level into excited conduction bands that will render the material opaque. Surprisingly, electron-rich SnO₂ is still highly transparent in the visible range.

These questions are fundamental to the general understanding of the phenomenon of transparent conductivity. To address them we have carried out first-principles calculations of formation energies and electrical (donor, acceptor) levels for various intrinsic defects (oxygen vacancy V_O, tin interstitial Sn_i, tin antisite Sn_O, tin vacancy V_{Sn}, oxygen interstitial O_i) in different charge states and under different chemical potential conditions in SnO₂. Our results indicate that Sn_i plays a more prominent role than that of V_O. We find the following: (i) While oxygen vacancy produces a level inside the band gap, owing to its loosely bound outer electrons interstitial Sn produces a donor level *inside* the conduction band, leading to instant donor ionization and conductivity. (ii) Sn_i has a very low formation energy, and would thus exist in significant quantities. The unusual stability of interstitial Sn in SnO₂ (as opposed to, say, the relative instability of interstitial Si in SiO₂) is due to the multivalence of tin, i.e., Sn(IV) as in SnO₂ and Sn(II) as in SnO. Moreover, the presence of Sn_i lowers dramatically the formation energy of V_O, explaining the natural oxygen deficiency and overall nonstoichiometry of SnO₂. (iii) The absence of inter-conduction-band absorption is a consequence of a special feature of the band structure of SnO₂, manifesting a large internal gap inside the conduction band that eliminates optical transitions in the visible range.

First-principles calculations were performed in the framework of density functional theory within the local density approximation (LDA) using the Ceperley-Alder exchange correlation potential as parametrized by Perdew and Zunger [7], and utilizing the plane-wave total energy method [8] as implemented in VASP code [9]. The tin (*s*²*p*²) and oxygen (*s*²*p*⁴) atoms were modeled using ultrasoft pseudopotentials [10]. The energy cutoff for the

plane wave basis set was 496 eV. We used an approximately cubic supercell constructed from 12 tetragonal unit cell of SnO_2 (i.e., 24 molecular units), whose Brillouin zone was sampled by a $2 \times 2 \times 2$ \mathbf{k} -point mesh generated according to the Monkhorst-Pack scheme [11], yielding one, two, or four irreducible \mathbf{k} points depending on the supercell symmetry. Total energy minimization with these computational settings gives the lattice constants $a = 4.723 \text{ \AA}$ and $c = 3.179 \text{ \AA}$, and the internal parameter $u = 0.306 \text{ \AA}$ of the tetragonal unit cell of SnO_2 in good agreement with experimental values [12] of $a = 4.738 \text{ \AA}$, $c = 3.188 \text{ \AA}$, and $u = 0.307$. In defect calculations, we relaxed all ions in the supercell until the residual atomic forces are less than 0.03 eV/\AA . For charged defects, a jellium background was used, and the total energy was corrected to $O(L^{-5})$ where L is the supercell size [13].

The formation energy of a defect D in charge state q , formed by transferring n_{Sn} tin and n_{O} oxygen atoms to the atomic reservoirs, and q electrons to the Fermi sea is given as

$$\Delta H(D^q) = \Delta E(D^q) + n_{\text{O}}\mu_{\text{O}} + n_{\text{Sn}}\mu_{\text{Sn}} + qE_{\text{F}}, \quad (1)$$

where μ_{O} and μ_{Sn} are the chemical potentials of oxygen and tin, respectively, and E_{F} is the Fermi energy measured from the valence band maximum E_{VBM} . Here,

$$\begin{aligned} \Delta E(D^q) &= E(\text{SnO}_2 + D^q) - E(\text{SnO}_2) \\ &+ \frac{1}{2}n_{\text{O}}E(\text{O}_2) + n_{\text{Sn}}E(\beta - \text{Sn}) + qE_{\text{VBM}}, \end{aligned} \quad (2)$$

where $E(\alpha)$ denotes the total supercell energy of the system α . In Eq. (1), we consider SnO_2 to be in thermal equilibrium with solid β -Sn and molecular O_2 , so that $2\mu_{\text{O}} + \mu_{\text{Sn}}$ is equal to the formation enthalpy of SnO_2 . The latter is calculated to be -6.29 eV per molecular unit (being in good agreement with experimental value [14] of -6.02 eV). Thus, $\mu_{\text{Sn}} = -6.29 - 2\mu_{\text{O}}$. The range of μ_{O} can be determined by noting that (i) μ_{O} is constrained to be less than the oxygen chemical potential in O_2 . The latter is chosen as the zero of μ_{O} , hence $\mu_{\text{O}} < 0$. (ii) μ_{O} is such that SnO_2 will not decompose. Since the energy of the decomposition reaction $\text{SnO}_2 \rightarrow \text{SnO} + (1/2)\text{O}_2$ is calculated to be -3.08 eV (compared to the experimental value [14] of -3.06 eV), $\mu_{\text{O}} > -3.08 \text{ eV}$. In Eq. (1), the Fermi energy E_{F} is also an independent variable, whose value is determined by the number of free carriers. While the value of $\Delta H(D^q)$ provides an indication of whether or not the defect D^q is stable (thus, abundant), the position of the electrical (donor or acceptor) level $\varepsilon(q/q')$ is determined as the value of Fermi energy for which $\Delta H(D^q) = \Delta H(D^{q'})$, at which point the charge state will switch between q and q' .

Figure 1 shows the formation energies of various point defects in SnO_2 as a function of the Fermi energy E_{F} for

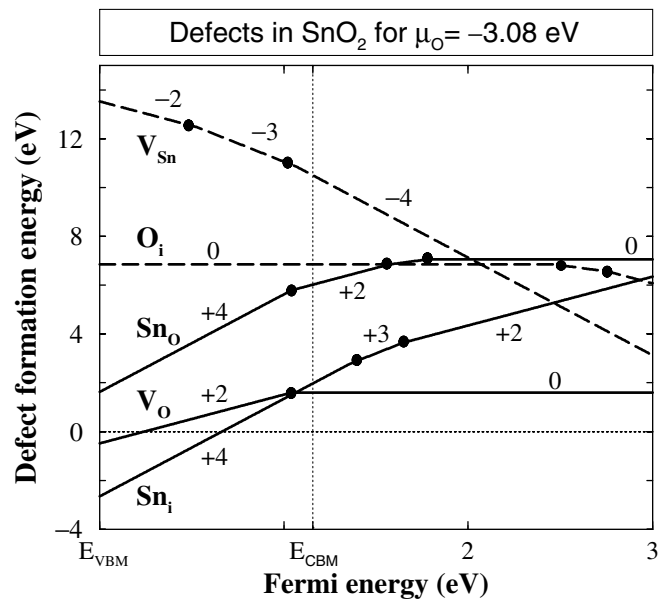


FIG. 1. Formation energy of intrinsic point defects and H impurity in SnO_2 under O-poor and H-rich conditions. The zero of Fermi energy is set to E_{VBM} , and $E_{\text{CBM}} = 1.16 \text{ eV}$ in the LDA calculation. The transition level positions between different charge states are shown by filled circles. Donors/acceptors are shown by solid/dashed lines.

the oxygen-poor limit. Filled circles denote the position of electrical levels $\varepsilon(q/q')$. We see that: (a) When E_{F} is near the VBM (i.e., p -type material), $\Delta H(\text{Sn}_i^{4+})$ and $\Delta H(\text{V}_O^{2+})$ are both *negative*, so Sn_i and V_O will form spontaneously, leading to *stable nonstoichiometry* which is the hallmark of SnO_2 . On the other hand, when E_{F} is the midgap (intrinsic material and/or at high temperature), $\Delta H(\text{Sn}_i^{4+})$ is still *negative* while $\Delta H(\text{V}_O^{2+})$ has positive small value ($\sim 0.67 \text{ eV}$), so Sn_i will be more abundant under these conditions. (b) Sn_i is not only easy to form, but also produces a shallow donor level: Its lowest defect transition level is $\varepsilon_{\text{Sn}_i}(4+/3+) = E_{\text{CBM}} + 203 \text{ meV}$ being inside the conduction band [15]. Hence, Sn_i is fully ionized. In contrast, V_O has a donor level below the CBM at $\varepsilon_{\text{V}_O}(2+/0) = E_{\text{CBM}} - 114 \text{ meV}$, so it is ionized only when E_{F} is below this position. Sn_i has a *shallow* level in SnO_2 because the outer electrons of the Sn atom are weakly bound, thus giving rise to a level within the conduction band. (c) As E_{F} moves towards the CBM the formation energy of acceptorlike (negatively charged) intrinsic defects such as O_i and V_{Sn} is reduced. Were these “electron killers” to form spontaneously, they would compensate the electron-producing intrinsic donor defects, i.e., Sn_i and V_O . However, this does not happen since O_i and V_{Sn} hardly form as they have high formation energies (Fig. 1). The high formation energy of V_{Sn} results from the large electrostatic repulsion between the negatively charged oxygen atoms at the vertices of Sn-centered octahedron. (d) The tin antisite Sn_O hardly forms due to its high formation energy, so it does not contribute to nonstoichiometry.

To understand why Sn_i has a low formation energy we investigate the structural changes in the lattice of SnO_2 upon introducing this defect. First, we show the tin interstitial fits perfectly into the SnO_2 lattice: Like the substitutional Sn site in SnO_2 , the (empty) interstitial site [marked as \mathbf{x} in Fig. 2(a)] is also coordinated by six oxygens. Because of the large size of charge-neutral Sn atom (covalent radius of 1.40 Å) its placement in the interstitial site \mathbf{x} causes a large distortion in bond angle, seen in the optimized geometry of Fig. 2(b). Thus, inserting Sn_i^0 requires a high energy (~ 6.7 eV, cf. Fig. 1). On the other hand, the stable charge state of Sn_i is 4+ (Fig. 1). This ion Sn_i^{4+} is small enough to fit in the space around the interstitial site \mathbf{x} , as seen in Fig. 2(c). Indeed, the lattice relaxes around Sn_i^{4+} so as to make it almost octahedrally coordinated, similar to the situation for host Sn atoms.

Second, we show that the reason for the ease of forming Sn_i in SnO_2 is that tin has two stable oxidation states [16], as manifested by the existence of two stable tin oxides, i.e., Sn(IV) in SnO_2 and Sn(II) in SnO. This conjecture is substantiated in Fig. 3, where the distribution of O-Sn bond lengths and O-Sn-Sn bond angles are shown for V_O^{2+} (upper panels) and Sn_i^{4+} (lower panels) defects in SnO_2 . When V_O^{2+} forms the distribution of the O-Sn bond lengths and O-Sn-Sn bond angles merely broaden around their ideal values in the SnO_2 lattice [shown as vertical dotted lines in Figs. 3(a) and 3(b)]. However, when Sn_i^{4+} forms, in addition to broadening, new peaks arise in the distributions. Remarkably, the new peaks are centered around the values of the bond lengths [Fig. 3(c)] and angles [Fig. 3(d)] in the SnO lattice (denoted by vertical dashed lines). Sn_i^{4+} in SnO_2 has six oxygen neighbors, each having four Sn neighbors. Hence, introduction of Sn_i^{4+} makes the oxygen coordination (by Sn atoms) in SnO_2 become similar to that in SnO. The new peaks in Fig. 3 assigned to SnO show that ionic relaxations improve the structural similarity in the oxygen coordination. Thus, formation of Sn_i^{4+} in SnO_2 requires a structural rearrangement which leads to a bonding environment that resembles both SnO_2 and SnO. Because both oxides are stable, the formation of

Sn_i^{4+} is not energetically costly, so Sn_i^{4+} can form easily. In contrast, oxides of elements having a single oxidation state (e.g., MgO and SiO_2) cannot tolerate such a high concentration of added interstitials, as lattice distortion carries them too far away from their stable bonding geometry, and no “fall-back” lattice configuration is available.

By calculating the energy of $\text{Sn}_i + \text{V}_\text{O}$ defect pair, and comparing to the energies of the isolated defects we determine an attraction of 3.2 eV between them. Thus, V_O and Sn_i will coexist, and dominate in the defect structure of SnO_2 . The main contribution (2.6 eV) to the attraction is due to ionic relaxations through which the structural similarity of the local environment to that of SnO is further enhanced. This is shown in Fig. 2(d) where the atoms forming a local environment that resemble the basic motif of (001) plane in SnO crystal are connected by thick lines. The structural similarity to SnO in Fig. 2(d) implies that the interstitial tin atom in SnO_2 has an effective oxidation state Sn(II). This suggests the presence of SnO fingerprints in SnO_2 as observed by x-ray and electron diffraction and Mössbauer spectroscopy [5]. Our predicted interdefect attraction, and hence the coexistence of V_O and Sn_i also explains the oxygen deficiency of SnO_2 [2,4].

We find that the formation of intrinsic defects in SnO_2 has only minor effects on the optical transparency due to special features of the electronic structure of SnO_2 : In bulk SnO_2 , the spacing between the first and second conduction bands is 4.75 eV at the Brillouin zone center. So inter-conduction-band absorption leaves the material optically transparent. This continues to be the case in nonstoichiometric SnO_2 for an electron concentration as high as 10^{20} cm^{-3} (i.e., E_F being 0.42–0.75 eV above the CBM [17]) since the dispersion of the lowest unoccupied band is less than 0.3 eV. Thus, the lowest direct optical transition would correspond to an energy above 3.7–4.0 eV, i.e., well beyond the visible range. On the other hand, the conduction-to-conduction indirect transitions are calculated to occur at 2.7–3.1 eV, and could reduce the transparency in the visible range for wavelengths smaller than 4600 Å.

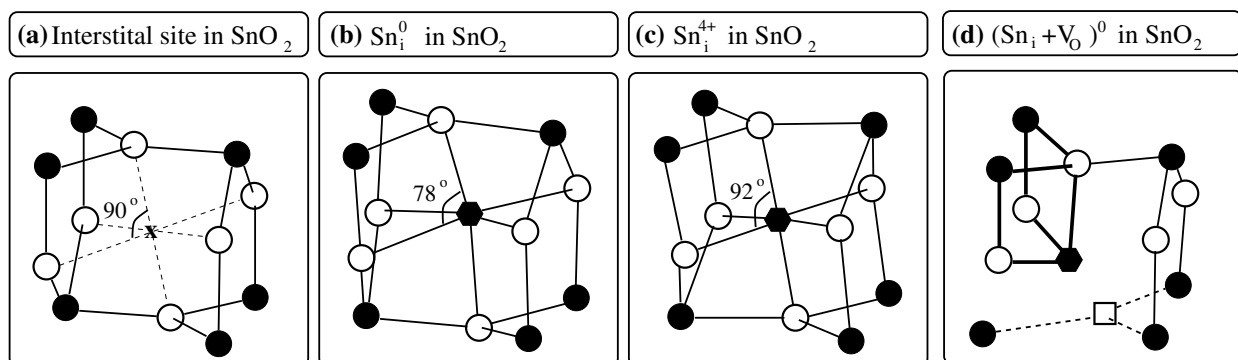


FIG. 2. (a) The empty interstitial site (denoted as \mathbf{x}), (b) neutral, and (c) fully ionized tin interstitials (shown by filled hexagon), (d) tin interstitial (filled hexagon) and oxygen vacancy (empty square) in SnO_2 . The filled/empty circles represent tin/oxygen. The atoms connected by thick lines in (d) form a SnO-like phase.

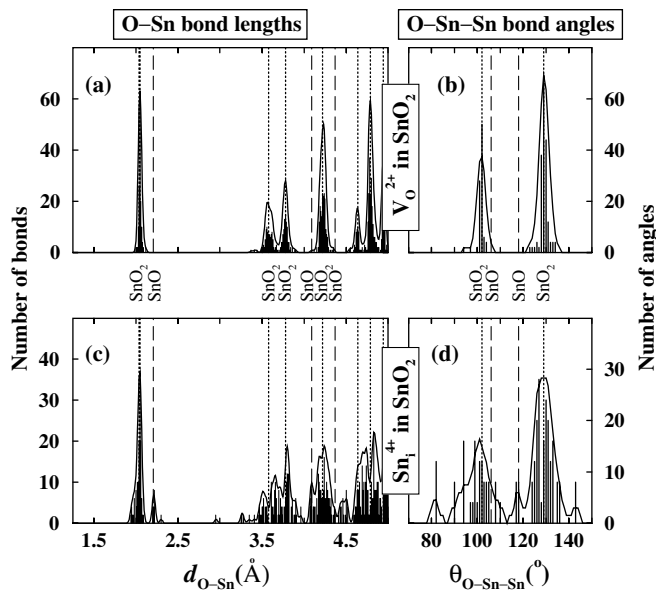


FIG. 3. O-Sn bond lengths [(a) and (c)] and O-Sn-Sn bond angles [(b) and (d)] for V_O^{2+} and Sn_i^{4+} in SnO_2 . Vertical dotted/dashed lines show the values in the ideal SnO_2/SnO lattice.

Other than this, the conduction band absorption remains small, so the optical transparency survives in the presence of the intrinsic defects.

Considering similarities in the band structures of various column-IV oxides, one wonders why SnO_2 alone is a transparent conductor in this series. It turns out that the energetic closeness and hybridization of the Pb 6s level with O 2p level makes PbO_2 a semimetal [18], i.e., not transparent. On the other hand, atomic Si 3s is very far from the O 2p level, and consequently SiO_2 is completely transparent, having a huge band gap (~ 9 eV). However, first-principles calculations [19] for V_O in SiO_2 yield a *deep* donor level at $\sim E_{CBM} - 2.2$ eV. Thus, V_O does not contribute to the electron conduction in SiO_2 , in contrast to SnO_2 . Therefore, the coexistence of conductivity and transparency in SnO_2 is unique among the column-IV oxides.

Our study of defect structure of SnO_2 provides a theory for the coexistence of conductivity with transparency in this prototype transparent conductor. Our results support the general features of an oxygen vacancy model, but also point out the previously unnoticed, but important role of tin interstitial. We show that Sn_i and V_O dominate in the defect structure of SnO_2 due to the multivalence of tin, explaining the natural nonstoichiometry of this material. That these defects produce shallow donor levels explains n -type conduction in undoped SnO_2 . The electrons released by Sn_i and V_O are not compensated owing to the absence of spontaneous formation of acceptorlike intrinsic defects (V_{Sn} and O_i), and do not make direct optical transitions in the visible range due to a large gap between the Fermi level and the energy level of first unoccupied states. Thus, SnO_2 can have a high carrier concentration with minor effects on its transparency.

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