Revisit of the band gaps of rutile SnO$_2$ and TiO$_2$: a first-principles study

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Abstract: From the recent experimentally observed conduction band offset and previously reported band gaps, one may deduce that the valence band offset between rutile SnO$_2$ and TiO$_2$ is around 1 eV, with TiO$_2$ having a higher valence band maximum. This implication sharply contradicts the fact that the two compounds have the same rutile structure and the Γ_3^+ VBM state is mostly an oxygen p state with a small amount of cation d character, thus one would expect that SnO$_2$ and TiO$_2$ should have small valence band offset. If the valence band offset between SnO$_2$ and TiO$_2$ is indeed small, one may question the correctness of the previously reported band gaps of SnO$_2$ and TiO$_2$. In this paper, using first-principles calculations with different levels of computational methods and functionals within the density functional theory, we reinvestigate the long-standing band gap problem for SnO$_2$. Our analysis suggests that the fundamental band gap of SnO$_2$ should be similar to that of TiO$_2$, i.e., around 3.0 eV. This value is significantly smaller than the previously reported value of about 3.6 eV, which can be attributed as the optical band gap of this material. Similar to what has been found in In$_2$O$_3$, the discrepancy between the fundamental and optical gaps of SnO$_2$ can be ascribed to the inversion symmetry of its crystal structure and the resultant dipole-forbidden transitions between its band edges. Our results are consistent with most of the optical and electrical measurements of the band gaps and band offset between SnO$_2$ and TiO$_2$, thus provide new understanding of the band structure and optical properties of SnO$_2$. Experimental tests of our predictions are called for.

Key words: SnO$_2$; TiO$_2$; band gap; band offset; dipole-forbidden transition

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1. Introduction

Post-transition-metal oxides, such as In$_2$O$_3$ and SnO$_2$, have been extensively used as transparent conducting oxides (TCOs), a unique class of materials that combine the high electrical conductivity and optical transmission in the visible or near-infrared spectral range, which are needed in various optoelectronic devices, such as solar cells, flat-panel displays, light emitting diodes (LEDs) and transparent transistors[1–7]. Obviously, one of the most critical properties of these materials is related to their band gaps that essentially determine their transparency. However, the determination of band gaps of these TCOs has not been a trivial work. For instance, early experimental measurements on In$_2$O$_3$ revealed a strong optical absorption at 3.75 eV and a much weaker absorption at 2.62 eV[8]. Initially, the former absorption was attributed as the direct band gap of In$_2$O$_3$, while the latter was attributed to the indirect transitions. Although this interpretation seems able to explain some of the experiments, the indirect transitions in In$_2$O$_3$ has never been confirmed by first-principles calculations[9, 10], hindering further understanding of the band structure and optical properties of this material. More recently, by combining the experimental measurements and theoretical calculations, Walsh *et al.*[11] identified that In$_2$O$_3$ actually possesses a direct

fundamental gap of 2.9 eV and a much larger optical gap of 3.7 eV. The large discrepancy between the fundamental and optical gaps was attributed to the inversion symmetry of its bixbyite structure and the resultant dipole-forbidden transitions between the valence band maximum (VBM) and conduction band minimum (CBM) states. This argument, capable of explaining various theoretical and experimental results, has now been commonly accepted.

In contrast to the case of In$_2$O$_3$, the band gap problem of SnO$_2$ is still not fully understood, largely because of the lack of detailed experimental measurements. Analogous to bixbyite In$_2$O$_3$, rutile SnO$_2$ also has the inversion symmetry and the dipole-forbidden transitions between the band edge states. As a result, one may expect different fundamental and optical gaps of SnO$_2$ as well, which, however, has never been reported in experiments. The single-photon and two-photon absorption experiments showed an optical gap of SnO$_2$ at ~3.60 eV, which has been widely taken as its "band gap"[12–14]. Moreover, the recent theoretical calculations, based on the density functional theory (DFT) and GW approximation, identified a fundamental gap of 3.65 eV for SnO$_2$[15, 16], which is nearly equal to its optical gap. Sabino *et al.*[17] attributed the coincidence between the measured fundamental and optical gaps to the intense illumination used in experiments, so that the very weak absorption in the vicinity of Γ point at the band edges was detected. Based on this argument, they also predicted that a much larger optical band gap of 4.34 eV should be detected, if the low illumination condition is satisfied. However, up to now, no
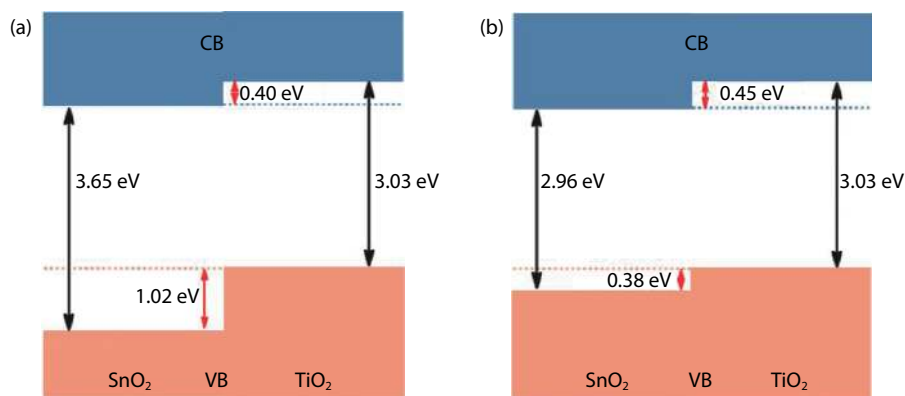
Fig. 1. (Color online) Band gaps and band alignments between rutile SnO_2 and TiO_2. In (a) the band gaps of SnO_2 is taken from Ref. [15] and the CB band alignment is taken from Ref. [19], while in (b) both of them are calculated in this work. The band gap of TiO_2 is always set to its experimental value (taken from Ref. [20]).

experimental demonstration of this difference between fundamental and optical gaps has been reported.

Despite the absence of direct measurements on its fundamental gap, more insight can be obtained from the recent experiments where SnO_2 was employed as the electron transport layer (ETL) in both dye-sensitized and perovskite solar cells to replace the commonly used TiO_2[18, 19]. The band alignment measurements[19] showed that the CBM of SnO_2 is about 0.4 eV lower than that of TiO_2, which facilitates the electron transport. Assuming the fundamental gaps of SnO_2 and TiO_2 as 3.65 and 3.03 eV[20], respectively, we can easily deduce that the VBM of SnO_2 is ~1.02 eV lower than that of TiO_2, as illustrated in Fig. 1(a). This result, however, is quite puzzling and contradicts the small VBM offset one would expect in this system[21–23], because the two compounds are isovalent semiconductors with the same rutile structure and similar lattice constants, and moreover, the Γ_3^+ VBM state is almost a pure oxygen p state, which only couples weakly with the cation d state but does not couple to the cation p state. Therefore, this VB offset anomaly is difficult to understand if the fundamental gap of SnO_2 is taken as ~3.65 eV, as previously reported.

To address this issue, in this work, we revisit the band gap problem for the rutile SnO_2 by using first-principles calculations. Different-level computational methods and functionals, such as PBE, PBE + G_0W_0, HSE06 and HSE06 + G_0W_0 are employed and the results are carefully compared. We find that the HSE06 calculations yield a VB offset of 0.38 eV between SnO_2 and TiO_2, generally obeying the common-anion rule. The fundamental gap is calculated to be 2.96 eV, which is much smaller than the previously reported value. The conduction band (CB) offset is then found to be 0.45 eV, in good agreement with experiments[18, 19]. Moreover, similar to In_2O_3, our calculations reveal that the direct optical transition between the band edges of SnO_2 is parity forbidden and the optical gap between the lower-lying VB states and CBM is 3.69 eV, which can well explain its optical absorptions[12–14]. On the other hand, by employing the HSE06 + G_0W_0 method, the fundamental gap of SnO_2 is found to be 3.76 eV that is close to the value reported previously[16, 17, 24]. However, with the same method, the fundamental gap of TiO_2 is calculated to be 3.68 eV, significantly larger than the experimental result of 3.03 eV[20]. In fact, we find that the fundamental gap of SnO_2 is always similar to that of TiO_2, independent of the computation-

al methods and functionals employed, which implies that the HSE06 + G_0W_0 calculations may overestimate the fundamental gap of SnO_2, which has been the case also found in other sp semiconductors[25]. The estimated error of HSE06 + G_0W_0 calculation is about 0.8 eV, which in turn results in a fundamental gap of SnO_2 as ~3.0 eV, in good agreement with the HSE06 calculations.

2. Theoretical calculation

Our calculations are carried out using the projector augmented wave (PAW) method[26] and the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional[27] within the density functional theory (DFT) as implemented in VASP[28]. For both SnO_2 and TiO_2, a 520 eV cutoff energy is used for the plane wave basis set and a Γ-centered $4 \times 4 \times 6$ k-point sampling of the Brillouin zone is employed. Since the band gaps of these compounds are sensitive to their lattice constants, experimental lattice constants ($a = 4.737$ Å and $c = 3.186$ Å for SnO_2[29], $a = 4.594$ Å and $c = 2.958$ Å for TiO_2[30]) are adopted for the electronic structure calculations. During the structural relaxation, the atomic coordination is fully relaxed until the Hellman–Feynman force on each atom is less than 0.01 eV/Å. To compare the influence of different computational methods and functionals on the band gaps, the Perdew–Burke–Ernzerhof (PBE)[31], GW[32] with the PBE (PBE + G_0W_0), and HSE06 + G_0W_0 calculations are also performed.

3. Results and discussion

Fig. 2(a) illustrates the tetragonal rutile structure for both SnO_2 and TiO_2 with the space group $D_{4h}^{14}(P4_2/mnm)$. As shown in Fig. 2(a), each cation atom (Sn or Ti) binds with six O atoms, forming a distorted octahedron, while each O atom is trigonally coordinated to three cation atoms. The calculated projected density of states (PDOS) are given in Fig. 2(b). We find that the Γ_1^+ CBM state of SnO_2 is mainly composed of Sn 5s and O 2s states, while the Γ_3^+ VBM state is mainly composed of O 2p states. For TiO_2, on the other hand, the CBM has mostly Ti 3d character, while the VBM is still the Γ_3^+ state dominated by O 2p states with minor Ti 3d character. The above analysis indicates that the well-known common-anion rule[21, 22] should apply to this system, i.e., the VBM offset between these two compounds should be relatively small. To verify this expectation, we construct a SnO_2/TiO_2 heterojunction consisting of six
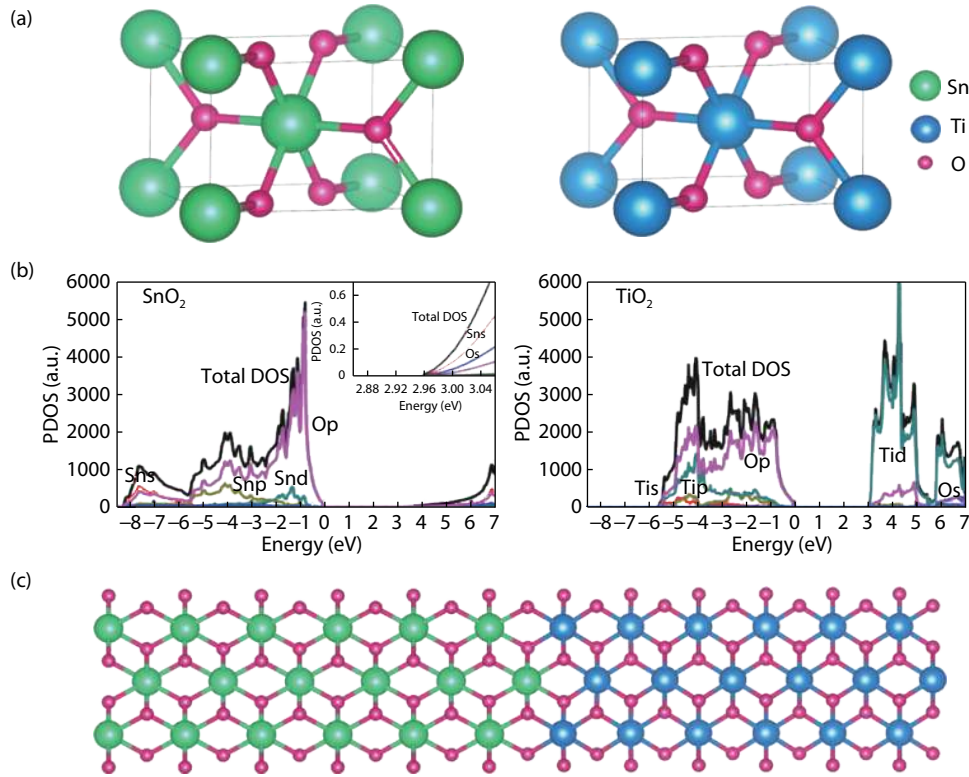
Fig. 2. (Color online) (a) Primitive unit cells and (b) calculated total and partial density of states for rutile SnO_2 and TiO_2. The green, blue and purple balls represent Sn, Ti and O respectively. (c) Side view of the atomic configuration for SnO_2/TiO_2 heterojunction (top panel).

SnO_2 (001) and six TiO_2 (001) layers, as shown in Fig. 2(c), to calculate the VB offset between SnO_2 and TiO_2 using the method described in Ref. [33], that is

$$\Delta E_V(SnO_2/TiO_2) = (E_V - E_{CL})_{TiO_2} - (E_V - E_{CL})_{SnO_2} + \Delta E_{CL}. \quad (1)$$

The first two terms on the right-hand side are the core-level to VBM energy separations for pure bulk TiO_2 and SnO_2, respectively, and the third term ΔE_{CL} is the difference of core-level binding energy between SnO_2 and TiO_2 in the SnO_2/TiO_2 superlattice. Since the lattice mismatch between SnO_2 (001) and TiO_2 (001) layers is very small (< 2%), here we set the lattice constants of the superlattice as the average of those of SnO_2 and TiO_2 and fully relax the atomic coordination in the superlattice with a Γ-centered $4 \times 4 \times 1$ k-mesh until the Hellman–Feynman force on each atom is less than 0.01 eV/Å.

The calculated band alignment for SnO_2 and TiO_2 is shown in Fig. 1(b). We find that the VBM of SnO_2 is 0.38 eV lower in energy than that of TiO_2, which generally follows the common-anion rule. The slightly lower VBM of SnO_2 can be attributed to the more polar Sn^{4+} ions, compared to Ti^{4+} ions. The calculated fundamental gaps of SnO_2 and TiO_2 are 2.96 and 3.15 eV, respectively, with the latter slightly larger than the experimental value of 3.03 eV[20]. Using the experimental band gap of TiO_2, one can deduce that the CBM of SnO_2 lies ~0.45 eV below that of TiO_2, which falls in line with the experimental measurements[18, 19]. It is interesting to see that the calculated fundamental gap of SnO_2 is slightly smaller than that of TiO_2, which is quite different from the experimentally measured band (optical) gap of ~3.60 eV[12–14]. To understand this discrepancy, we carefully investigate the band structure of SnO_2, as shown in Fig. 3(a). Apparently, SnO_2 has a direct fundament-

al gap located at the Γ point. Inspection of the wavefunction at the band edges indicates that the VBM and CBM states both have the even parity with Γ_3^+ and Γ_1^+ symmetries, respectively. Therefore, the electric-dipole transition between these two states is forbidden. Table 1 gives the corresponding transition matrix elements. We can see that the transition probability between the VBM and CBM at the Γ point is exactly zero. As the k-point is slightly off the Γ-point, the transition matrix elements between the VB and CB states are still negligibly small, indicating very weak optical transitions in this region. In contrast, we find that the pronounced optical transitions can occur from the low-lying VB states to the CBM at the Γ point, leading to an optical gap 0.74 eV larger than the fundamental gap. As shown in Fig. 3(a), the low-lying VB states have the Γ_5^- symmetry with oxygen and cation p characters, so the optical transitions from these states to the CBM state are allowed. As shown in Fig. 3(b), the calculated absorption coefficient indicates a very slow increase above 2.96 eV and a sharp increase above 3.70 eV, in good agreement with the band structure analysis. From these calculations, we can conclude that SnO_2 should have a relatively small fundamental gap of ~3.0 eV and a much larger optical gap of ~3.7 eV, with the latter accounting for the "band gap" observed in optical absorption experiments[12–14].

It should be noted that the fundamental gap of SnO_2 obtained here is quite different from the values reported by the previous calculations[15–17]. For instance, based on the HSE03 + G_0W_0 calculations, Schleife et al.[15] reported a fundamental gap of SnO_2 as 3.65 eV that is similar to observed optical gap. They attributed the near coincidence between the fundamental and optical gaps to the dipole-allowed transitions in the vicinity of the Γ point, as depicted by the green arrow in Fig. 3. Sabino et al.[17] further explained that the detection of these
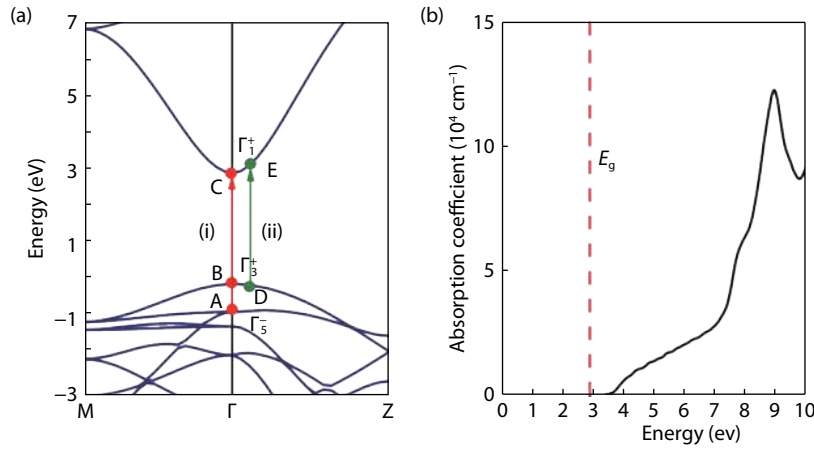
Fig. 3. (Color online) (a) Band structure of SnO$_2$ along two high symmetry lines M–Γ–Z. (b) Optical absorption coefficient of SnO$_2$. The valence band maximum is set at zero. In (a), the red and green arrows represent the possible optical transitions at Γ-point and away from Γ-point, respectively.

Table 1. The calculated optical transition matrix elements (in arbitrary units) between the valence band states and conduction band states for rutile SnO$_2$. Three transition paths are considered: two are at Γ-point and one is at the vicinity of Γ-point, as shown in Fig. 3. The energy for the valance (E_{VB}) and conduction band states (E_{CB}) are calculated with respect to the VBM and their energy difference is $\Delta E = E_{CB} - E_{VB}$.

Transition path	E_{VB} (eV)	E_{CB} (eV)	ΔE (eV)	p_x, p_y, p_z (a.u.)
B–C	0.00	2.96	2.96	(0.0 0.0 0.0)
D–E	−0.03	3.10	3.13	(0.3 0.3 0.0)
A–C	−0.74	2.96	3.69	(76.6 69.6 0.0)

weak transitions can be attributed to the intense illumination used in experiments. To compare with these previous calculations, we also employ the GW formalism combined with the hybrid functional calculations (HSE06 + G$_0$W$_0$), together with some other methods, such as PBE and PBE + G$_0$W$_0$, with the calculated fundamental gaps of SnO$_2$ and TiO$_2$ given in Table 2. For the HSE06 + G$_0$W$_0$ calculations, the fundamental gap of SnO$_2$ is found to be 3.76 eV that is consistent with the previous calculations. However, with the same method, the fundamental gap of TiO$_2$ is calculated to be 3.68 eV, apparently larger than the experimental results[20]，which indicates that the HSE06 + G$_0$W$_0$ calculations cannot describe the band structure well, at least for TiO$_2$. More interestingly, we can see from Table 2 that the calculated fundamental band gap of SnO$_2$ is always similar to that of TiO$_2$, although different computational methods and/or functionals result in different band gap values. This trend suggests that the HSE06 + G$_0$W$_0$ calculations, as employed in the previous work, may also overestimate the fundamental gap of SnO$_2$, which has also been the case found in other sp semiconductors[25].

One may argue that the hybrid functional and/or GW approximation may have different impacts on the fundamental gaps of SnO$_2$ and TiO$_2$, because of the different component of their CBM states, as shown in Fig. 1(b). To clarify this point, we consider a series of metal oxides, including ZnO, CdO, Ga$_2$O$_3$, In$_2$O$_3$ and GeO$_2$, for which the CBM and VBM components are all similar to that of SnO$_2$. Table 3 gives the calculated fundamental gaps by the HSE06 + G$_0$W$_0$ method, together with the available experimental data. We find that although the HSE06 +

Table 2. Calculated fundamental band gaps (eV) of rutile TiO$_2$ and SnO$_2$ using different calculation methods and functionals.

Method	PBE	HSE06	PBE + G$_0$W$_0$	HSE06 + G$_0$W$_0$
TiO$_2$	1.75	3.15	3.33	3.68
SnO$_2$	1.23	2.96	2.87	3.76

Table 3. The calculated fundamental band gaps by HSE06 + G$_0$W$_0$ method ($E_g^{cal.}$), the experimental band gaps ($E_g^{exp.}$), and their difference (ΔE_g) for ZnO, CdO, Ga$_2$O$_3$, In$_2$O$_3$, GeO$_2$ and SnO$_2$.

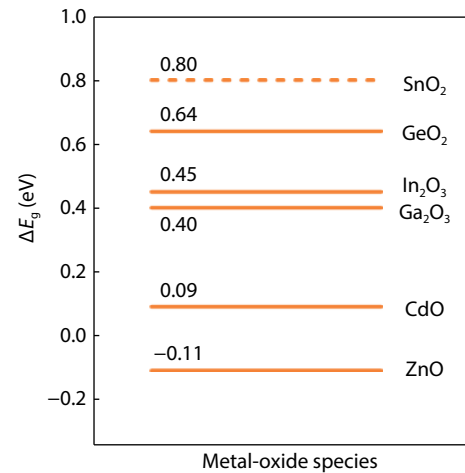| Metal oxide	ZnO	CdO	Ga$_2$O$_3$	In$_2$O$_3$	GeO$_2$	SnO$_2$
$E_g^{cal.}$ (eV)	3.33	1.18	5.30[34]	3.35[34]	5.14	3.76
$E_g^{exp.}$ (eV)	3.44[35]	1.09[36]	4.90[37]	2.90[11]	4.50[38]	–
ΔE_g (eV)	−0.11	0.09	0.40	0.45	0.64	–

Fig. 4. (Color online) Differences between the HSE06 + G$_0$W$_0$ calculated and experimentally measured band gaps $\Delta E_g = E_g^{cal.} - E_g^{exp.}$ for a series of oxides.

G$_0$W$_0$ calculations can result in reasonable fundamental gaps for IIB oxides ZnO and CdO, which have large d orbital component at the VBM, it significantly overestimates the band gaps of IIIA oxides Ga$_2$O$_3$, In$_2$O$_3$ and IVA oxides GeO$_2$, which have similar band edge wavefunction characters as SnO$_2$. We find the differences between the calculated and experimentally meas-
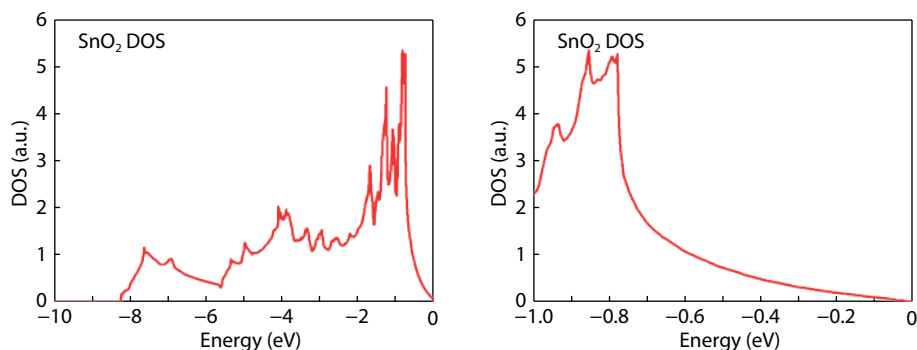
Fig. 5. (Color online) Calculated DOS of SnO$_2$ for the valence bands below VBM level. The right-hand side shows the DOS with enlarged energy scale below the VBM at $E = 0$ eV.

ured fundamental gaps $\Delta E_g = E_g^{cal.} - E_g^{exp.}$ increase monotonically as the occupied d orbital binding energy increases, e.g., from ZnO to Ga$_2$O$_3$ and to GeO$_2$ or from CdO to In$_2$O$_3$, as summarized in Fig. 4. From this trend, it is reasonable to expect that the HSE06 + G$_0$W$_0$ calculations would also overestimate the fundamental gap of SnO$_2$. By a simple linear extrapolation, we can roughly estimate the overestimation is ~0.8 eV, which gives an error-corrected fundamental gap of SnO$_2$ as ~3.0 eV, in accordance with the HSE06 calculations.

Recently, a hard X-ray photoelectron spectroscopy (HAXPES) measurement showed that the sharp increase of the VBM occurs at ~3.6 eV below the Fermi energy for undoped SnO$_2$[39]. To confirm that this is consistent with our prediction that the fundamental band is only 2.9 eV, we have plotted the total DOS of SnO$_2$ with high resolution, as shown in Fig. 5. We see that the sharp increase of the band edge DOS occurs at 0.7 eV below the VBM, corresponding to the A points in the band structure (see Fig. 3), that is, it gives also the optical band gap, not the fundamental band gap. This is consistent with the fact that due to the specific band structure of SnO$_2$ (Fig. 3), the HAXPES signal near the VBM is low, so can be easily missed by the HAXPES measurement by weak signal.

4. Conclusion

In conclusion, we have performed a systematic first-principles calculations and symmetry analysis to revisit the long-standing band gap problem for SnO$_2$. Different-level computational methods and functionals, such as PBE, PBE + G$_0$W$_0$, HSE06 and HSE06 + G$_0$W$_0$ are employed. We find that in all these calculations the band gap of SnO$_2$ is similar or slightly smaller than that of TiO$_2$. The HSE06 calculations yield a fundamental gap of 3.0 eV and a much larger optical gap of 3.6 eV for SnO$_2$, which is consistent with recent experimental measurement of the band alignment between SnO$_2$ and TiO$_2$, but smaller than the previously reported fundamental band gap of 3.65 eV for SnO$_2$. The discrepancy between the fundamental and optical gaps is attributed to the inversion symmetry of rutile SnO$_2$ and the resultant dipole-forbidden transitions between the VBM and CBM, similar to what has been found in In$_2$O$_3$. On the other hand, we find that the HSE06 + G$_0$W$_0$ method, as employed in previous calculations, would overestimate the fundamental gaps of both TiO$_2$ and SnO$_2$ as well as a series of other oxides, including Ga$_2$O$_3$, In$_2$O$_3$ and GeO$_2$. More experimental tests of our predictions are called for. Because SnO$_2$ is widely used in optoelectronic devices, our new understand-ing of the band structure and optical properties of SnO$_2$ should have large impact on the future design of optoelectronic materials.

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