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An accurate theoretical study on intrinsic defect energetics in rutile TiO_2

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Abstract: An accurate theoretical study on the intrinsic point defects in rutile TiO_2 was carried out by first-principles calculations using plane-wave pseudopotential method. The structural parameters of defect-free bulk rutile TiO_2 were calculated, which are close to experimental data. And the effects of point defects on the geometry structures were analyzed. To get accurate value of formation energy and charge transfer levels, several technical details must be considered, such as the position of E_{VBM} originating from supercell size and electrostatic interactions between the charged defects, and band-gap error etc. The formation energies of the point defects in various charge states were given as a function of Fermi level for the two limiting values of extreme O-rich conditions and extreme Ti-rich conditions. Under extreme Ti-rich conditions, Ti^{4+} interstitial and V_O^{2+} have very low formation energy, and wound thus exist in significant quantities, namely, producing the intrinsic n-type TiO_2. The stability of these point defects is traced back to the multivalence of titanium. Under extreme reducing condition, Frenkel defect comprised of Ti_i^{4+} and V_{Ti}^{4-} would be formed in TiO_2.

Key words: first-principles; TiO_2; point defect; formation energy

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1 Introduction

Titanium dioxide has received a lot of attention as a promising material in several applications, including white pigment, photocatalysis[1], dye-sensitized solar cells[2], and nanoscale electronic devices[3−4]. Rutile has the simplest and best known structure and point defects easily yield in a perfect rutile matrix after sputtering and annealing by varying temperatures and oxygen partial pressures, which directly determine the physical and chemical behavior of TiO_2. For example, regular rutile TiO_2 is an insulator in nature and can not dissociate H_2O directly, but becomes semi-conductive with oxygen-deficiency and can adsorb H_2O dissociatively on the defect site[5]. In another example, leakage currents in the TiO_2 insulator are often explained on the basis of gap states originating from various point defects.

Recently, there have been many studies of the electronic and structural properties of point defect TiO_2, both of experimental[6−11] and theoretical aspects [12−13], the question which type of defect is dominant in region of oxygen deficiencies is still subject to debate. YAGI et al[8] and LEE et al[9] reported that defects are mostly Ti interstitial ions and ionization of Ti interstitial donors takes place at lower oxygen partial pressures ($p(O_2)$). The thermoelectric power data reported by NOWOTNY et al[10] confirmed that oxygen vacancies are the predominant ionic defects that are compensated by electrons. BAUMARD and TANI[11] have mentioned that Ti vacancies may also be present in TiO_2. The more source of information can be taken by first-principles calculations using accurate theoretical method, such as KOUDRIACHOVA[12] simply presented the investigations of the geometry structure of point defects in TiO_{2-x}, and CHO et al[13] examined atomic relaxations around the point defects and related features in the electronic structure. They seem to have focused on neutral charge states. However, their studies did not consider the chemical potential and Fermi level as controlling variables for defect formation energies. Thus, we argue that a theoretical investigation covering simultaneously charged defects of rutile TiO_2 is still in need, with particular emphasis placed on the

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technical aspects of accurate formation energy calculations.

2 Calculation models and methods

First-principles calculations were performed in the framework of density functional theory (DFT) within the generalized gradient approximation (GGA) using the Perdew−Burke−Ernzerhof (PBE) exchange correlation potential[14], and utilizing the plane−wave total energy pseudopotential method as implemented in castep code[15]. The ion-electron interaction is modeled by ultrasoft pseudopotentials in the Vanderbilt form. The valence atomic configurations are $3s^2 3p^6 3d^2 4s^2$ for Ti, $2s^2 2p^4$ for O atom. We use a 5×7×2 k-point set and cut-off 380 eV for the calculations of the stoichiometric and intrinsic point defects structure in rutile TiO_2. The convergence criteria for the structure optimization and energy calculation were set to (a) a SCF tolerance of 2.0×10^{-6} eV/atom, (b) an energy tolerance of 2.0×10^{-5} eV/atom, (c) a maximum force tolerance of 0.5 eV/nm, and (d) a maximum displacement tolerance of 2.0×10^{-4} nm. Using above-mentioned methods can yield satisfactory results in our recent studies[16−17].

To calculate the formation energies of point defects, a supercell consisting of a 2×2×2 periodic repetition of the primitive unit cell was used. In our calculations, the defects considered included oxygen vacancies and interstitials, and titanium vacancies and interstitials. To introduce an isolated vacancy, an interior Ti or O atom is removed from the supercell. In the case of an isolated interstitial, an atoms of Ti or O atom is put into the supercell, where the normally vacant octahedral site is considered as a possible interstitial site. Due to the large cation-anion size mismatch and strong ionicity of TiO_2, antisites are unlikely to form in TiO_2. For calculations of the defective supercells, the nearest and next-nearest atoms located within a radius of 0.38 nm from defects were allowed to relax.

3 Results and discussion

We begin with the experimental lattice parameters to get the crystal cell, and optimizing the bulk structure of rutile TiO_2. The calculated results using Monkhorst k-points 5×7×2 and E_{cut} of 380 eV show that the lattice constants are slightly overestimated using a typical feature of GGA methods. But the overestimated is always less than 2%. The calculated crystal parameters shown in Table 1 are in good agreement with the experimental values[18]. The PBE functional is usually the most reliable, since it performs well for both small and extended systems[19].

We analyzed the effects of point defects on the geometry structures. For an isolated O vacancy, after relaxation, the total energy is lowered by 0.6 eV and each of the nearest-neighbor Ti atoms moves 0.01−0.015 nm away from the vacancy toward its remaining O neighbors. This is due to the effectively positive charges of the O vacancy site which interact repulsively with nearby cations. As a Ti atom is missing here, the surrounding O atoms relax outward, leading to increase the Coulomb binding by reducing the apical Ti-O distances (d_{ap}) from the 0.199 8 nm to 0.184 0 nm, and the equatorial Ti-O distances (d_{eq}) from the 0.195 5 nm to 0.179 9 nm. The results also show that the interstitial Ti has little effect on the host lattice, and the interstitial O would spontaneously bind to the lattice oxygen, resulting in an O_2 dimer substituting on one O site. Our results are qualitatively similar to those of Ref.[13], although some differences were evident in the interpretation of those results. To the extent that quantitative differences occur they don't consider the charge states of point defects, referring to the ion radius and electrostatic interactions between charged defects.

In thermodynamic equilibrium the concentration c of point defects is given by the expression $c=N_{site}N_{config}\cdot\exp[-E_f/(kT)]$[20]. Here, E_f is the defect formation energy, and lower E_f means to higher defect concentration c, which directly determines the physical and chemical behavior of TiO_2. In other words, defects with lower formation energies are more likely to form. The formation energy of a defect in charge state is define as:

$$E_f(D^q)=E_{tot}(D^q)-E_{tot}(\text{perfect})+n_{Ti}\mu_{Ti}+n_Q\mu_Q+q(E_f+E^q_{VBM}) \tag{1}$$

where $E_{tot}(D^q)$ is a total energy of a supercell with the

Table 1 Calculated structural parameters for crystalline TiO_2 compared to experimental values of Ref.[18], and theoretical values of Ref.[19]

Source	a/nm	c/nm	d_{ap}/nm	d_{eq}/nm	B_0/GPa
Ref.[18]	0.4587	0.2954	0.1976	0.1946	216
This work	0.463 4(+1.0%)	0.295 9(+0.2%)	0.199 8(+1.1%)	0.195 5(+0.5%)	203±2.0
Ref. [19]	0.454 6(−0.9%)	0.292 5(−1.0%)	0.195 2(−1.2%)		249
	0.467 9(+2.0%)	0.298 5(+1.0%)	0.202 1(+2.3%)		200

The differences between calculated and experimental values of structural parameters are showed as a percentage in parentheses.

defect, E_{tot}(perfect) is the total energy for the equivalent supercell containing only bulk TiO_2. Here n_{Al} and n_O are the numbers of Ti and O atoms removed from or added to the perfect supercell to introduce a vacancy or interstitial. For example, n_{Al}=0 and n_O=−1 for an O vacancy, and n_{Al}=0 and n_O=+1 for an O interstitial. For each defect species, its charge q varying from neutral to fully ionized states was considered.

In order to succeed, a certain number of difficult problems had to be solved. Firstly, E_{VBM}^q values of defective supercells were obtained from the one of the perfect supercell and a difference ΔV in average potentials (V_{av}) between the perfect supercell and a bulk like environment in defective supercells as follow:

$$E_{VBM}^q = E_{VBM}^{perfect} + \Delta V \tag{2}$$

The first term of the right-hand side of Eqn.(2) can be contained by

$$E_{VBM}^{perfect} = E_T(\text{perfect};0) - E_T(\text{perfect};+1)$$

where E_T(perfect; 0) is the total energy of the neutral perfect supercell. E_T(perfect; +1) is that of the +1 charged perfect supercell, which corresponds to the situation that one electron is removed from the VBM of the neutral perfect supercell.

Secondly, the calculated band gap (E_g) is in much smaller than the experimental one of 3.0 eV. The difference between theory and experiment (ΔE_g=0.85 eV) could affect formation energies of intrinsic defects in TiO_2. When a defect induces extra occupied levels below the CBM, which are composed of cation orbitals similar to the conduction band, its formation energy will be underestimated since the energy position of the CBM itself is underestimated. This situation corresponds to oxygen vacancy and Ti interstitial in TiO_2. In such case, it is assumed as crude correction that the conduction band is rigidly shifted upward to match the experimental E_g. Then formation energies were corrected by adding a value of $m\Delta E_g$, where m is the number of electrons at defect-induced levels in E_g.

Thirdly, the chemical potentials depend on the experimental growth conditions, which can be Ti-rich or O-rich (or anything in between). Under extreme Ti-rich conditions, $\mu_{Ti} = \mu_{Ti[bulk]}$. Similarly, extreme O-rich conditions place an upper limit on μ_O given by $\mu_O = \mu_{O(O_2)}$. Using the following expression:

$$\mu_{Ti} + 2\mu_O = E_{tot}(TiO_2) \tag{3}$$

The upper limit on μ_{Ti} then results in a lower limit on μ_O:

$$\mu_O^{min} = E_{tot}(TiO_2) - \mu_{Ti(bulk)} \tag{4}$$

Similarly, the upper limit on μ_O results in a lower limit on μ_{Ti}:

$$\mu_{Ti}^{min} = E_{tot}(TiO_2) - \mu_{O(O_2)} \tag{5}$$

Also, the formation enthalpy $\Delta H_f[TiO_2]$ can be obtained by

$$\Delta H_f(TiO_2) = \mu_{Ti} - \mu_{Ti(bulk)} + 2(\mu_O - \mu_{O(O_2)}) \tag{6}$$

From Eqns.(3), (4) and (6), the range of μ_O is represented as

$$\frac{1}{2}\Delta H_f(TiO_2) + \mu_{O(O_2)} \leqslant \mu_O \leqslant \mu_{O(O_2)} \tag{7}$$

Our calculated value for $\Delta H_f[TiO_2]$ obtained from Eqn.(6) is −9.63 eV per TiO_2 or 3.2 eV per atom, which is comparable to the experimental value of (9.6±0.8) eV per TiO_2[21]. The formation energy of point defects in various charge states at the VBM (E_F=0 eV) under extreme O-rich conditions ($\mu_O = \mu_{O(O_2)}$) and extreme T-rich conditions ($\mu_{Ti} = \mu_{Ti(bulk)}$) are given in Table 2 under several corrections.

Table 2 Point defect formation energies in TiO_2 with Fermi level at VBM. Both O-rich (μ_O=0) and Ti-rich (μ_O=−4.814 eV) conditions are shown

Defect	Charge state	E_F	
		O-rich	Ti-rich
V_O	0	7.427	2.613
	+1	4.336	−0.474
	+2	1.438	−3.376
V_{Ti}	0	5.811	15.437
	−1	4.126	13.752
	−2	2.582	12.208
	−3	1.204	10.830
	−4	0.143	9.771
O_i	0	4.355	9.169
	+1	5.480	10.294
	+2	6.520	11.333
Ti_i	0	13.641	4.015
	+1	9.097	−0.531
	+2	4.764	−4.916
	+3	1.064	−8.562
	+4	−1.517	−11.153

Fig.1 shows the formation energies of various point defects in TiO_2 as a function of the Fermi energy under the O-rich and Ti-rich growth conditions, respectively. Filled circles denote the position of thermodynamic transition levels $\varepsilon(q_1/q_2)$, which is defined as the Fermi-level position where charge states q_1 and q_2 have equal energy. As the name implies, the level would be observed in experiments where the final charge state can fully relax to its equilibrium configuration after the transition.

From Fig.1(a), we see that when E_F is near the

VBM (i.e., p-type material), $E_F(Ti_i^{4+})$ and $F_f(V_O^{2+})$ are both negative, so Ti_i and V_O will form spontaneously. On the other hand, when E_F is the midgap (intrinsic material and /or at high temperature), $E_F(Ti_i,+4)$ still negative while $E_F(V_O^{2+})$ has positive small value about 0.5 eV, so Ti_i will be more abundant under these conditions. Ti_i is not only easy to form, but also produces a donor levels: Its lowest defect transition level is $\varepsilon_{Ti_i}(+4/+3) = E_{CBM}-0.41$ being inside the band gap, so it is ionized only when E_F is below this position. Hence, Ti_i have two charge states +4 and +3. Similarly, V_O has a donor level below the CBM at $\varepsilon_{V_O}(+2/0)=E_{CBM}-0.36$ eV.

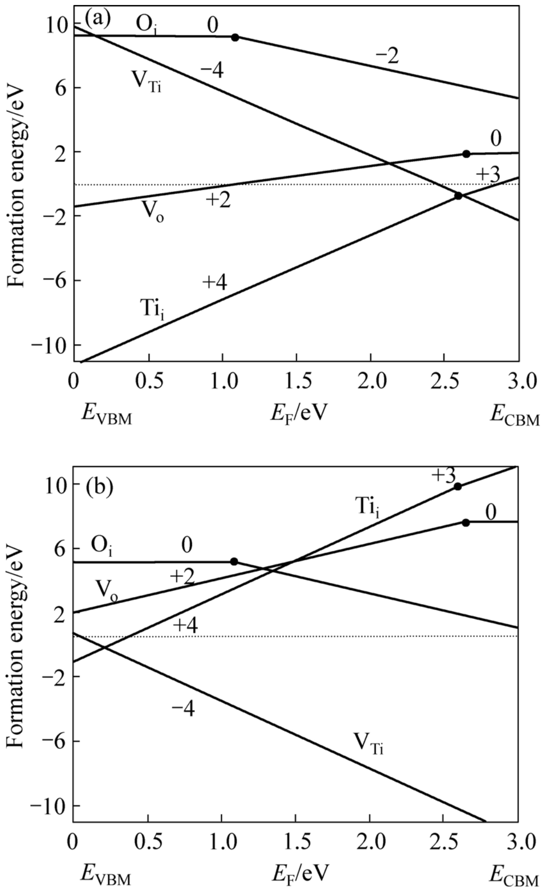

Fig.1 Formation energies of intrinsic point defects as function of Fermi level under Ti-rich (μ_O=−4.814 eV) (a) and O-rich (μ_O=0 eV) growth conditions(b), respectively. For each defect species, only lowest-energy charge states with respect to E_F are shown. Zero energy of E_F corresponds to valence-band minimum, while 3 eV indicates conduction-band minimum using experimental E_g value

The donor level of Ti_i in TiO_2 is deeper than Sn_i in SnO_2 because the outer electrons of the Ti atom are more strongly bound than that of the Sn atom, which indicate TiO_2 has more strongly covalence than SnO_2. They will play significant role in increasing absorbance in the visible region and electron traps, resulting in the improvement in photocatalytic activity under visible-light irradiation. As E_F moves towards the CBM the formation energy of acceptlike (negatively charged) intrinsic defects such as V_{Ti} and O_i is decreased. Were these "electron killers" to form spontaneously, they would compensate the electron-producing intrinsic donor defects, i.e., Ti_i and V_O. However, this does not happen since V_{Ti} and O_i hardly form as they have high formation energies, the high formation energies of V_{Ti} and O_i result from the large electrostatic repulsion between the negatively charged oxygen atoms at the vertices of Ti-centered octahedron.

To understand why Ti interstitial has a low formation energy we investigate the structural changes in the lattice of TiO_2 upon introducing this defect. In the rutile phase of TiO_2, each Ti^{4+} center is surrounded with six O^{2-} ions in octahedral coordination, and each O^{2-} ion is surrounded by three Ti^{4+} ions in trigonal-planar coordination. Like the substitutional Ti site in TiO_2, the interstitial site is also coordinated by six oxygens. This ion Ti_i of +4 and/or +3 charged state is small enough to fit in the space around the interstitial site so as to make it almost octahedrally coordinated, similar to the situation for host Ti atoms. Another reason for the ease of forming Ti_i in TiO_2 is that Titanium has two stable oxidation states, Ti(IV) in TiO_2 and Ti(II) in TiO. Introduction of Ti ion makes the oxygen coordination in TiO_2 become similar to that in TiO. It is well known that in this structure, each titanium atom is surrounded by an oxygen octahedron, because of the highly symmetric distribution of titanium atoms, no distortion takes place, leading to an fcc lattice. Because both oxides are stable, the formation of Ti_i is not energetically costly, so Ti_i can form easily.

From the Fig.1(b), we see that the thermodynamic transition levels $\varepsilon(q_1/q_2)$ are similar to that of Fig.1(a). On the other hand, when E_F is near the VBM, the formation energies of V_{Ti} and Ti_i is low. However, V_{Ti} and Ti_i have equal energy at E_F=0.21 eV, indicating that the Frenkel defect comprised of Ti_i^{4+} and V_{Ti} would form in TiO_2. In fact, V_{Ti} hardly form as Ti_i would compensate the electron-producing intrinsic accept defects, i.e., V_{Ti} and O_i. On O-rich conditions, the concentration of V_{Ti} and O_i would be very low, namely, producing the intrinsic p-type TiO_2 is quite difficult.

4 Conclusions

1) First-principles plane-wave pseudopotential calculations were performed to study the formation energies of intrinsic point defects in TiO_2. Various charge states for individual point defects were considered, and their formation energies were calculated.

2) Under the Ti-rich conditions, the fully ionized states of Ti_i and V_O has low formation energy, so Ti_i and V_O will be more abundant and will coexist and dominate

in the defect structure of TiO_2 under these conditions. Ti_i has a donor level below the CBM at 0.41 eV, so Ti_i have two charge states +4 and +3.

3) On O-rich conditions, the Frenkel defect comprised of Ti_i^{4+} and V_{Ti} would form in TiO_2. However, the concentration of V_{Ti} and O_i would be very low.

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