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Diffusion mechanisms of native point defects in rutile TiO_2: *Ab initio* total-energy calculations

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The structural energetics and diffusion mechanisms of the two most important point defects in rutile TiO_2, the oxygen vacancy (V_O) and the titanium interstitial (Ti_I), are examined using the *ab initio* pseudopotential total-energy method. The two defects are found to be somewhat competitive in energy, with V_O being more favorable in a larger range of the stoichiometry. The Ti_I, on the other hand, is shown to be the major diffusive species, since its low migration barrier is significantly smaller (by ~1 eV) compared to that of V_O. The diffusion mechanisms of Ti_I parallel and perpendicular to the crystal c axis are found to be different with a surprisingly larger barrier along the more open [001] direction, which was originally thought to be the easier channel for Ti self-diffusion. These theoretical findings are in excellent quantitative agreement with existing experimental data.

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As a model transition-metal oxide with a relatively simple crystal structure, and as a wide spread catalyst and catalyst support, rutile TiO_2 has been receiving a great deal of attention in recent fundamentally and technologically motivated research studies.[1] Defects in transition-metal oxides control a wide range of their physical and chemical properties. In the particular case of TiO_2, it has been well known for some time that many of its important properties, such as catalytic activity, occurrence of the strong metal-support interaction, and oxide growth rates in electrochemical cells, are affected by point defects.[2] More recently, there has also been growing evidence for diffusing point defects in bulk rutile playing a major role in surface and interface related phenomena when high-temperature annealing is involved.[1,3] Bulk-assisted surface reoxidation,[4,5] self-limiting growth of Pt particles encapsulated by TiO_x species,[3,6] and surface reconstructions[7] are some examples. A detailed understanding of the structural energetics and diffusion mechanisms of the relevant native point defects is, therefore, a problem of both scientific and technological interest.

Naturally occurring rutile TiO_{2-x} is almost always reduced (i.e., $x>0$), which suggests that the dominant native point defects should be the oxygen vacancy V_O and the titanium interstitial Ti_I (there is no experimental evidence for the titanium antisite, in agreement with our finding of a large formation energy for this defect). The question of which of these defects plays a more important role as a function of sample stoichiometry, and especially in bulk-to-surface diffusion related phenomena, has been somewhat controversial. While earlier works have favored the anion vacancies as the more dominant defect, in 1999 Henderson suggested,[4] based on his experimental studies, that cation interstitials might be playing a more important role in bulk-assisted surface reoxidation of rutile (110). The diffusion mechanism of the Ti_I has also been controversial. In 1965, Huntington and Sullivan made the reasonable suggestion that it should be easier for Ti_I to diffuse along the open [001] channels of rutile TiO_2.[8] In the mid-1980s, the experimental data of Hoshino *et al.*, however, showed that the activation enthalpy for Ti_I diffusion was smaller along the less open [110] or $[1\bar{1}0]$ channels.[9] From a theoretical point of view, there have only been few recent first-principles studies on these defects[10] (due to large computational demand), which have either been limited to small system sizes or dealt with the energetics and/or electronic structures of neutral defects. While these studies have provided useful information, charged defects and, more importantly, their diffusion mechanisms in the bulk have not yet been addressed, despite the experimental evidence for their critical role in bulk-assisted surface phenomena and existing controversies. In this paper, by performing large-scale *ab initio* calculations, we examine the structural energetics and diffusion mechanisms of the V_O and Ti_I in neutral and charged states and interpret our findings on the basis of earlier suggestions and experimental data.

Our calculations for V_O and Ti_I defects in rutile TiO_2 were performed using the *ab initio* pseudopotential total-energy method as implemented in VASP.[11] We used ultrasoft pseudopotentials with a cutoff energy of 300 eV, $2\times2\times2$ Monkhorst-Pack k-point grids, and Perdew-Wang parametrization of the generalized gradient approximation. Defect formation energies were determined from calculations on large $3\times3\times5$ supercells along the [100], [010], and [001] directions, respectively, composed of 270 atoms. For the diffusion profiles, we used 240-atom $5\times2\times4$ supercells along the [001], [110], and $[1\bar{1}0]$ directions, respectively. We compared the results for the migration barrier of Ti_I^{4+} along [001] from this slightly smaller supercell with those from a 270-atom supercell and found them to agree within 0.03 eV. Since the $3p$ semicore electrons of Ti were treated as valence electrons, the calculations required self-consistent solutions of ~1000 bands at each of the four k points (with no symmetries imposed). As such, the present calculations represent some of the most computationally demanding *ab initio* modeling studies of defects in transition-metal oxides. Our tests also showed that the spin-polarization effects were negligible.

We start with the pattern of the atomic relaxations due to

V_O and Ti_I. In general, both V_O and Ti_I create long-ranged and anisotropic relaxations, making it necessary to use large supercells. For V_O, the most significant displacements extend along the [110] and [001] directions of the equatorial plane encompassing the vacancy. The three Ti nearest neighbors (nn) have the largest outward displacements of 0.31 Å. The next largest Ti displacements of 0.125 Å (four of them) are observed quite far away (5.5 Å) from V_O. The largest O displacement of 0.14 Å is observed for the nearest O neighbor of V_O and is inward. For Ti_I, starting with small random displacements of the bulk atoms and an interstitial slightly off the center of the octahedral hole, we found a stable position, in which the interstitial is sixfold coordinated by O and Ti atoms (shown later in Figs. 2 and 3 when discussing diffusion profiles). The major atomic displacements occur in the planes perpendicular to [001], the largest ones being observed in the plane passing through Ti_I. The two nn Ti are pushed away from their ideal positions by 0.3 Å, creating two Ti-Ti bonds, which are 10% smaller than that in bulk Ti. Of the six nn O atoms, the closest four relax away from the interstitial by 0.24 Å, while the other two relax toward it by 0.21 Å.

Next, we examine the formation energies. From total-energy calculations on 270-atom supercells and using the standard grand canonical formalism,[12] we find the formation energies of neutral V_O and Ti_I as $4.93\ \mathrm{eV}+\Delta\mu_O$ and $8.84\ \mathrm{eV}+2\Delta\mu_O$, respectively. Here, $\Delta\mu_O=\mu_O-\frac{1}{2}E_{O_2}$ denotes the deviation of the oxygen chemical potential from its 0 K molecular value. From total-energy calculations on bulk Ti, TiO_2, and O_2 (we find the correct triplet ground state), the heat of formation for rutile TiO_2 is calculated as 10.16 eV, in good agreement with the experimental result of 9.8 eV.[13] The corresponding theoretical range for $\Delta\mu_O$ is found to be $-5.08\ \mathrm{eV}<\Delta\mu_O<0$. Considering the experimentally accessed range of pressures p and temperatures T can further restrict the range for $\Delta\mu_O$. If we neglect the vibrational and rotational terms, μ_O can be related to p and T via $2\mu_O=E_{O_2}+kT\ln(pV_Q/kT)$, where k is the Boltzmann constant and V_Q is the canonical volume.[12] Using $10^{-20}\ \mathrm{Pa}<p<10^5\ \mathrm{Pa}$ and $200\ \mathrm{K}<T<1400\ \mathrm{K}$ (the full experimentally accessed range[9,14]), we find a more restricted range of $-4.2\ \mathrm{eV}<\Delta\mu_O<0$. The formation energies of $V_O^{(0)}$ and $Ti_I^{(0)}$ as a function of stoichiometry are shown in Fig. 1(a). We can see that while $V_O^{(0)}$ is a lower-energy defect for a large portion of the sample stoichiometry, Ti_I is competitive in energy in the O-poor region. We also considered various positive charge states of the two defects.[15] The formation energies of V_O^{q+} and Ti_I^{q+} relative to neutral defects as a function of electron chemical potential μ_e are shown in Figs. 1(b) and 1(c) for $q=1,2$ and $q=1-4$, respectively. Although there are small regions in which other charge states are lower in energy, the most relevant charge states are (2+) and (4+) for V_O and Ti_I, respectively, for a wide range of μ_e. As such, most of our computations for the diffusion mechanisms were performed for these charge states, as will be presented next.

In bulk rutile TiO_2, the channels along the equivalent [110] and $[1\bar{1}0]$ directions are significantly less open than those along the [001]. As a result, the diffusion of small ions has been shown to exhibit a significant anisotropy.[9] Whether

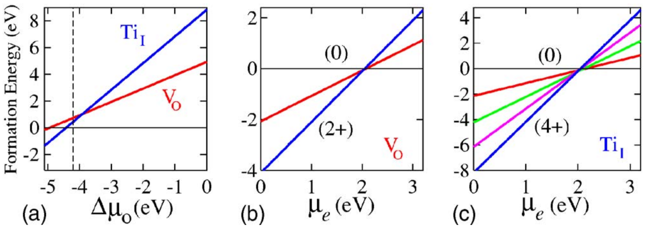

FIG. 1. (Color online) (a) Formation energies of neutral V_O and Ti_I defects as a function of stoichiometry given by $\Delta\mu_O$. The vertical dashed line denotes the lower range of $\Delta\mu_O$ from experimentally accessed O partial pressures and temperatures. (b) and (c) Relative formation energies (with respect to neutral defects) of charged V_O and Ti_I defects, respectively, as a function of the electron chemical potential μ_e referenced to the valence-band maximum. The slopes of the lines give the charge states of the defects.

the anisotropy is significant for Ti self-diffusion has not been clear. Therefore, we first examine the Ti_I^{4+} diffusion along both [001] and [110]. The diffusion profiles of Ti_I^{4+} were obtained by fixing the coordinates of the diffusing atom only along the diffusion direction and allowing the other two coordinates as well as the rest of the atoms in the supercell to relax. The results for the diffusion along [001] are displayed in Fig. 2(a). The diffusion for both neutral (not shown here) and charged defects is through the interstitial region, in which the interstitial diffuses along the open [001] channels, while the lattice atoms relax around the defect to accommodate the induced stress, as shown in Figs. 2(b)–2(d). The barrier for Ti_I^{4+} is 0.37 eV, while it is 0.7 eV for Ti_I^{0}.[16] The smaller barrier for the diffusion of the charged defect is correlated by its reduced size compared to the neutral defect.

Given the large discrepancy in the openings of the two inequivalent directions, [001] and [110], one would expect to

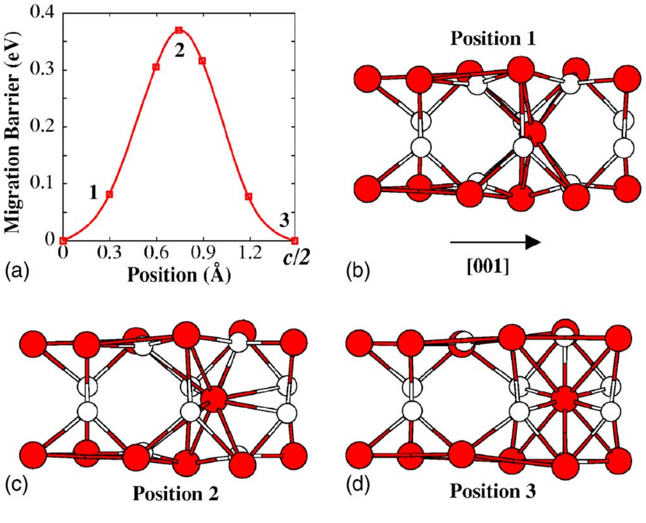

FIG. 2. (Color online) (a) Diffusion profile of Ti_I^{4+} along [001]. The squares correspond to the actual calculations, which have been fitted to a smooth curve. Due to the symmetry of rutile, only a path of length $c/2$ is considered. (b)–(d) Snapshots of the diffusing Ti_I^{4+} and a portion of the surrounding bulk at the positions 1, 2, and 3 given in (a). Position 3 is the interstitial Ti configuration discussed in the text. Ti and O atoms are represented by gray (red) and white circles, respectively.

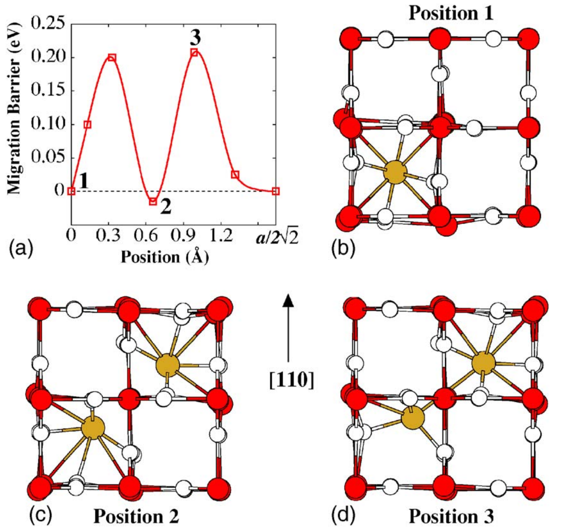

FIG. 3. (Color online) (a) Diffusion profile of Ti_I^{4+} along [110]. Due to the symmetry of rutile, only a path of length $a/2\sqrt{2}$ is considered. (b)–(d) Snapshots of the diffusing Ti_I^{4+} and a portion of the surrounding bulk at the positions 1, 2, and 3 given in (a) showing the interstitialcy mechanism of Ti_I^{4+} along [110]. Position 1 is another view of position 3 in Fig. 2. Position 2 is the (slightly lower-energy) interstitialcy configuration. The diffusing Ti_I and the bulk Ti which gets kicked out are shown by light gray (gold) circles. The rest of the Ti and O atoms are represented by gray (red) and white circles, respectively.

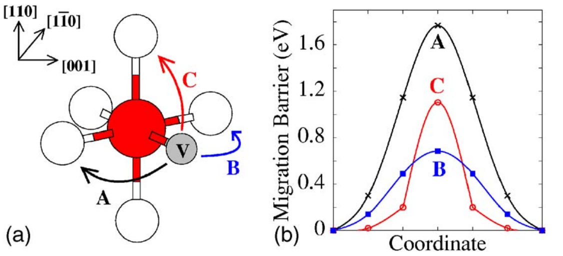

FIG. 4. (Color online) (a) A ball and stick model of the TiO_6 octahedron in rutile. The "atom" labeled by V is the oxygen vacancy in the equatorial plane. Its diffusion is considered along the paths A, B, and C. (b) Migration barriers of V_{O}^{2+} along the three paths shown in (a). The points (stars, circles, and squares) correspond to actual calculations which have been fitted to smooth curves.

find a much higher-energy barrier of the interstitial along the less open [110] channels. The [001] direction was indeed suggested about four decades ago as the main diffusion channel of Ti_I.[8] However, our *ab initio* calculations for the Ti_I^{4+} diffusion along the [110] direction, shown in Fig. 3(a), are *not* in agreement with this reasonable suggestion. The energy barrier of 0.225 eV along [110] is significantly lower than the barrier of 0.37 eV along [001]. Although this finding might at first seem somewhat counter-intuitive, it *is* actually in excellent agreement with extensive experimental measurements from about two decades ago. In particular, Hoshino *et al.*[9] measured the activation enthalpies for the Ti self-diffusion in rutile TiO_2 along [001] (∥, parallel to the c axis) and [110] (⊥, perpendicular to the c axis). Since the activation enthalpy Q is the sum of the defect formation energy and the migration barrier E^m, the difference in the measured activation enthalpies ($\Delta Q_{\parallel,\perp}$) along the two directions can be directly compared with the difference of our calculated migration barriers ($\Delta E^m_{\parallel,\perp}$). That is, $\Delta Q_{\parallel,\perp} = Q_\parallel - Q_\perp = E^m_\parallel - E^m_\perp = \Delta E^m_{\parallel,\perp}$. The experimentally measured difference in the activation enthalpies $\Delta Q_{\parallel,\perp}$ and our calculated $\Delta E^m_{\parallel,\perp}$ are +0.1 and +0.145 eV, respectively, indicating excellent agreement between experiment and theory in terms of both the sign and the magnitude of the energy difference.

The calculated migration barriers of Ti_I^{4+} along the two inequivalent directions naturally raise the question of why [110] is the preferred channel for Ti self-diffusion compared to the more open [001] channels. The answer to this lies in the difference in the diffusion mechanisms of Ti_I along the two channels. Figures 3(b)–3(d) show snapshots for the positions of the diffusing Ti_I^{4+} along [110] corresponding to the points on the migration barrier curve in Fig. 3(a). It is clear that the diffusion of Ti_I^{4+} along [110] is not via the interstitial mechanism as in the [001] case but through the *interstitialcy* (or sometimes called as kick-out) mechanism, in which the diffusing atom kicks out one of bulk Ti atoms and takes its lattice position. The atom kicked out of its bulk position then becomes the new interstitial. This mechanism for the Ti self-diffusion was indeed suggested by the tracer diffusion experiments of Sasaki *et al.*[9] During the interstitialcy diffusion, as shown in the migration barrier [Fig. 3(a)], a new minimum energy configuration is achieved for Ti_I^{4+}, where there are two Ti interstitials and one Ti vacancy [Fig. 3(c)]. This new configuration is slightly favored (by 15 meV) over the interstitial position described earlier. As shown in Fig. 3, the diffusion mechanism of Ti_I^{4+} along [110] is controlled by the continuous making and breaking of the Ti-O bonds.

Finally, we consider the diffusion of V_{O}^{2+}. The four O atoms in the equatorial plane of a TiO_6 octahedron do not form 90° angles. Therefore, as shown in Fig. 4(a), we investigated the diffusion of V_{O}^{+2} by moving the oxygen vacancy (in effect, the O atom) along two inequivalent paths in the equatorial plane (path A along [001] and B along $[1\bar{1}0]$), in addition a third path C which involves moving it from the plane to the apex position of the octahedron. The corresponding migration barriers are shown in Fig. 4(b). The barrier of 1.77 eV along [001] is the highest, which suggests that a direct V_{O} diffusion along this direction is highly unlikely. A direct diffusion of V_{O} along $[1\bar{1}0]$, on the other hand, has a much smaller barrier of 0.69 eV, as the diffusing O atom can still make bonds with two neighboring Ti atoms, unlike the diffusion along [001]. The migration barrier along the third path C is 1.1 eV. Given the symmetry of the rutile structure, the maximum barrier to migration of V_{O}^{+2} along any direction of the crystal will be 1.1 eV, since the direct migration along [001] (1.77 eV barrier) can be avoided by using a combination of the other two paths B and C. However, a migration barrier of 1.1 eV for V_{O}^{+2} is still much larger than that for Ti_I^{4+}. This finding is in very good agreement with Henderson's suggestion[4] that the Ti cations are the major diffusive species responsible for the bulk-assisted reoxidation of the rutile (110) surface.

In summary, we have modeled the two major point defects, V_O and Ti_I, in bulk rutile TiO_2 by performing *ab initio* calculations with large supercells. We have shown that the Ti interstitials with small migration barriers are the major diffusive species compared to oxygen vacancies. Our calculations indicate that the diffusion mechanisms of Ti_I^{4+} parallel ([001]) and perpendicular ([110]) to the *c* axis are different, with a surprisingly larger barrier along the more open [001] channels. Our results show that a Ti interstitialcy mechanism along [110] will be dominant in oxygen-deficient TiO_{2-x} samples, which is in excellent quantitative agreement with experimental data.

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[15] We neglected multipole corrections arising from the compensating background charge due to the large dielectric constant of TiO_2. In large supercells of 270 atoms, the correction due to valence-band maximum alignment for charged defects has also been estimated to be negligible.

[16] Based on our observations for the (4+) and (0) charge states, we expect the diffusion barriers for the intermediate charge states (3+), (2+), and (1+), not considered here, to fall between 0.37 and 0.7 eV. We do not, however, expect to see a change in the mechanism.