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SUPPORTING INFORMATION

First-Principles Description of Oxygen Self-Diffusion in Rutile TiO_2: Assessment of Uncertainties due to Energy and Entropy Contributions

Heonjae Jeong[1], Edmund G. Seebauer[2], and Elif Ertekin[1]

[1]Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States

[2]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States

*Corresponding author:

ertekin@illinois.edu (E. Ertekin)

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1. DFT Computational Details

1.1 Chemical Potential of Atomic Species

The chemical potential is given by $\mu_i = \mu_i{}^0 + \Delta\mu_i$ where $\mu_i{}^0$ is the chemical potential of the atomic species in the standard condition and $\Delta\mu_i$ represents the temperature and pressure variance. We constrain our analysis to $\Delta\mu_{\mathrm{O}} = -0.23$ eV/atom and $\Delta\mu_{\mathrm{Ti}} = -9.27$ eV/atom, based on the oxygen partial pressure (~10^{-5} Torr) corresponding to the previous isotope diffusion experiments [1]. The oxygen chemical potential (μ_O) is given by

$$\mu_{\mathrm{O}}(T,P) = \frac{1}{2}\mu^0_{\mathrm{O}_2} + \Delta\mu_{\mathrm{O}} = \frac{1}{2}\mu^0_{\mathrm{O}_2} + \Delta\mu^0_{\mathrm{O}}(T) + \frac{1}{2}\left(k_{\mathrm{B}}T\ln\left(\frac{P_{\mathrm{O}_2}}{P^0_{\mathrm{O}_2}}\right)\right), \qquad \text{(S1)}$$

where $\mu^0_{\mathrm{O}_2}$ is the oxygen chemical potential under the standard condition (25 °C and 1 atm). The chemical potential under the standard conditions is given by $\mu^0_{\mathrm{O}_2} = h^0_{\mathrm{O}_2} + ZPE^0_{\mathrm{O}_2} - Ts^0_{\mathrm{O}_2}$ where $h^0_{\mathrm{O}_2}$ is the oxygen gas enthalpy at (T = 0 K and P = 0 atm) and $ZPE^0_{\mathrm{O}_2}$ is the zero-point energy. Both $h^0_{\mathrm{O}_2}$ and $ZPE^0_{\mathrm{O}_2}$ are obtained directly from DFT. Since DFT-PBE is known to overbind the oxygen molecule, we correct the DFT-computed total energy $E^{0,\mathrm{DFT}}_{\mathrm{O}_2}$ by $h^0_{\mathrm{O}_2} = E^{0,\mathrm{DFT}}_{\mathrm{O}_2} + \Delta E^{\mathrm{corr}}_{\mathrm{O}_2}$ [2]. The entropic contribution ($Ts^0_{\mathrm{O}_2}$) is obtained from the standard thermodynamic tables [3]. In Eq. S1, the term $\Delta\mu^0_{\mathrm{O}}(T)$ is the temperature dependent term of the oxygen chemical potential at the reference pressure (1 atm) and is also obtained from the standard thermodynamic tables [3], and the term $\frac{1}{2}(k_{\mathrm{B}}T\ln\left(\frac{P_{\mathrm{O}_2}}{P^0_{\mathrm{O}_2}}\right))$ is the pressure dependence where P_{O_2} is the partial pressure of oxygen gas and $P^0_{\mathrm{O}_2}$ is the standard state pressure of 1 atm.

1.2 Finite Size Effect Error Analysis of Charged Defect Formation Energy

The uncertainty for interaction between charged defect images arise from due to using a computational limited supercell size with periodic boundary conditions. The charged defect interactions are electrostatic and rather long-ranged. The finite size effect (FSE) error of defect formation energy (DFE) is estimated by extrapolation to the dilute limit based on the Makov and Payne approximation [4] but with fitting coefficients obtained from supercell extrapolation [5–7] as

$$E_T\left(\frac{1}{L}\right) = E_T\left(\frac{1}{L} \to 0\right) - \frac{C_1}{L} - \frac{C_2}{L^3}, \qquad \text{(S2)}$$

where L is the lattice constant for supercell, and C_1 and C_2 are extrapolation fitting parameters. C_1/L is the Madelung energy which depends on interactions between the point defect charge and the neutralizing background charge. C_2/L^3 is the localized charge distribution, which is related with dipole-dipole interaction.

Fig. S1 illustrates extrapolation for the DFE to correct the FSE in rutile TiO_2. For our extrapolation to dilute limit, we employ three supercells: 3×3×4 containing 216 atoms, 4×4×5 containing 480 atoms, and 5×5×6 containing 900 atoms. We observed that the DFE converges rapidly, resulting in approximately a −0.5 eV finite size correction to the DFE computed for the smaller 2×2×3 supercell used in the main manuscript.

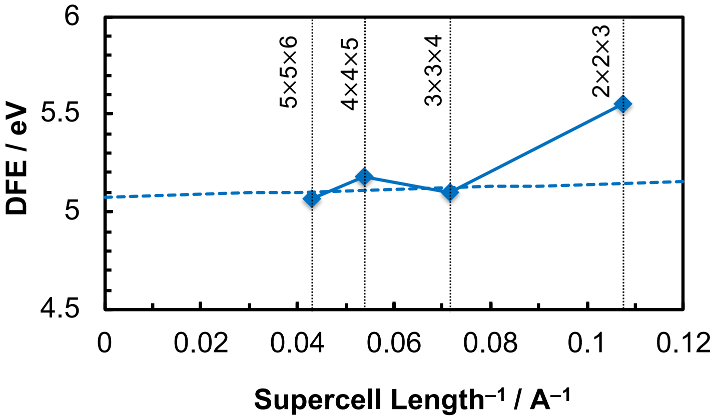

Figure S1. Supercell extrapolation for the DFE as a function of the supercell length to correct doubly charged interstitial oxygens interaction due to FSE. The blue dash line represents the extrapolated DFE value of the three biggest supercells by linear fits to the data (blue diamond symbol).

2. Maximum-Likelihood (ML) Estimation

2.1 Band gap

Fig. S2 shows the temperature coefficient β at the experimental temperature range of 600−750 °C determined by maximum-likelihood (ML) estimation [8,9] that can improve the quality of data. Based on the optical density data [10], the ML estimated temperature coefficient $\bar{\beta}$ is in a fairly good agreement with the previous literature of 0.7×10^{-3} eV/K [11]. Consequently, band gap is represented as $E_g = 3.1-(0.7\pm0.11)\times10^{-3}$ T in the temperature interval of 600−750 °C. For example, the value of E_g at 700 °C is around 2.42 eV. The main source of error likely arises from systematic errors originating from monochromator calibration or optical detection.

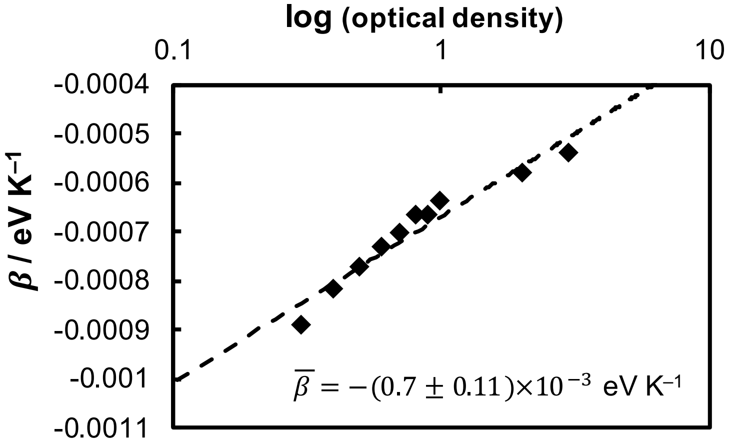

Figure S2. ML estimation for temperature coefficient $\bar{\beta}$ as a function of optical density [10].

2.2 Effective Mass of Electrons

Maximum-likelihood (ML) estimation [8,9] was carried out to determine the positon of the Fermi level E_F in conjunction with the effective mass of electrons m_0. Prior to obtaining E_F, m_0 must be determined. The key parameters are tabulated below from previous literature. The average of effective mass $\overline{m_0}$ and the weighting factor w_i obtained as the inverse of the error variance $1/\sigma_i^2$ was aggregated from literature. Consequently, the ML effective mass of electrons m_0 is represented as $(\bar{y} \pm \bar{\sigma})m_e^*$ according to $\bar{y} = \sum_i w_i\, y_i / \sum_i w_i$ and $\bar{\sigma} = 1 \Big/ \sqrt{\sum_i 1/\sigma_i^2}$, respectively. The ML estimation yields an effective mass of $(8.44 \pm 1.00)m_e^*$ and yields E_F of 1.58 ± 0.003 eV.

Table S1. ML estimation for effective mass of electrons m_0

	m_0	$\log(\overline{m_0})$	σ_i ($\log m_0$)	w_i	$\log(\overline{m_0})$* w_i
Breckenridge et al. [12]	30−100	1.74	0.26	14.63	25.44
Frederikse [13]	12−32	1.29	0.21	22.04	28.49
Thurber et al. [14]	20−35	1.42	0.12	67.72	96.33
Acket et al. [15]	5−13	0.91	0.21	23.23	21.06
Baumard et al. [16]	8−10	0.95	0.05	425.91	405.28
Cristea et al. [17]	2−8	0.60	0.30	11.04	6.64
DeFord et al. [18]	5−20	1	0.30	11.04	11.04
Kormann et al. [19]	5−13	0.91	0.21	23.23	21.06
Yagi et al. [20]	7−8	0.87	0.02	1189.39	1039.64
Hendry et al. [21]	8−190	1.59	0.68	2.11	3.36

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