

## Supporting Information

# Electronic and Optical Properties of Oxygen Vacancies in Amorphous Ta<sub>2</sub>O<sub>5</sub> from First Principles

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## 1. Computational details

The amorphous Ta<sub>2</sub>O<sub>5</sub> structure was generated with the melt-and-quench method and *ab initio* molecular-dynamics simulations with the VASP code. The initial cell of crystal β-Ta<sub>2</sub>O<sub>5</sub> with 12 Ta<sub>2</sub>O<sub>5</sub> formula units was annealed at a temperature of 3500 K followed by a cooling step down to 1000 K and a subsequent atomistic relaxation to the equilibrium geometry as described in our previous work (ref. 17). The 84-atom amorphous cell employed in this work yields atomic configurations and electronic structures consistent with our previous study using an amorphous Ta<sub>2</sub>O<sub>5</sub> cell of 168 atoms (ref. 17). The electronic band gap of the 84-atoms amorphous structure calculated with the HSE06 functional and our choice for the mixing and range-separation parameter is 4.24 eV, which is in good agreement with our previously calculated GW band gap for the 168-atoms cell (4.26 eV with an exciton binding energy of 0.3 eV in ref. 17) and experimentally measured values (~ 4.0 eV in ref. 5).

The formation energy of oxygen vacancies for various charge states is calculated by:

$$E^f[V_O^q] = E_{tot}[Ta_2O_5 : V_O^q] - E_{tot}[Ta_2O_5 : bulk] + \mu_O + qE_F \quad (1)$$

where  $E_{tot}[Ta_2O_5 : V_O^q]$  is the total energy of the amorphous  $Ta_2O_5$  cell containing an oxygen vacancy with charge  $q$ , and  $E_{tot}[Ta_2O_5 : bulk]$  is the total energy for the perfect cell. The parameters  $\mu_O$  and  $E_F$  are the chemical potential of an oxygen atom and the Fermi level of electrons. The Fermi level is referenced to the valence band maximum (VBM) in the bulk cell with the correction of band alignments.<sup>[1]</sup> We also evaluated the finite-size correction for charged defects in supercell calculations.<sup>[2,3]</sup> The correction for the long-range Coulomb interaction is quite small,  $\sim 0.01$  eV, due to the high dielectric constant of  $Ta_2O_5$  (24 in ref. 11), and it does not affect our conclusions.

## 2. The equilibrium Fermi level

The equilibrium Fermi level and the concentration of oxygen vacancies in each charge state are calculated self-consistently. First, the concentration of defects is related with their formation energy via a Boltzmann expression,<sup>[37]</sup>

$$c = N_{sites} N_{config} e^{-\frac{E^f}{k_B T}} \quad (2)$$

where  $N_{sites}$ ,  $N_{config}$ , and  $E^f$  are the number of sites on which defects can be formed, the number of possible configurations per site, and the formation energy, respectively. The density of electronic states considering both vacancy ( $V_O^0$  and  $V_O^{2+}$ ) and free-electron states is given by

$$DOS(E) = 2c_{V_O^0} \delta(E - E_0) + \frac{8\pi\sqrt{2}}{h^3} m^{*\frac{3}{2}} \sqrt{E - E_C} \quad (3)$$

where  $c_{V_O^0}$ ,  $E_0$ ,  $E_C$ , and  $m^*$  are the concentration of neutral oxygen vacancies, the energy of mid-gap defect levels introduced by the neutral vacancy, the CBM energy, and the effective

mass of electrons, respectively. Our results for the charge distribution of electrons and the occupancy of defect levels for each oxidation states show that extra electrons from  $V_O^{2+}$  behave as free carriers with the effective mass of the CBM, while the density of neutral oxygen vacancy states at  $E_0$  is modeled as the Dirac delta function. The number of extra electrons,  $n_e$ , as a function of Fermi level due to  $V_O^0$  and  $V_O^{2+}$  is given by

$$\begin{aligned}
n_e &= \int_0^{\infty} DOS(E) \times f(E) dE \\
&= \int_0^{\infty} 2c_{V_O^0} \delta(E - E_0) \frac{1}{1 + e^{\frac{E - E_F}{k_B T}}} + \frac{8\pi\sqrt{2}}{h^3} m^{*\frac{3}{2}} \sqrt{E - E_C} \frac{1}{1 + e^{\frac{E - E_F}{k_B T}}} dE \\
&\approx 2c_{V_O^0} \frac{1}{1 + e^{\frac{E_0 - E_F}{k_B T}}} + 2 \left( \frac{m^* k_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{-\frac{E_C - E_F}{k_B T}}
\end{aligned}$$

(4)

where the energy of the VBM is zero. Since each  $V_O^0$  and  $V_O^{2+}$  introduces two electrons, the number of extra electrons is equal to

$$n_e = 2c_{V_O^0} + 2c_{V_O^{2+}}.$$

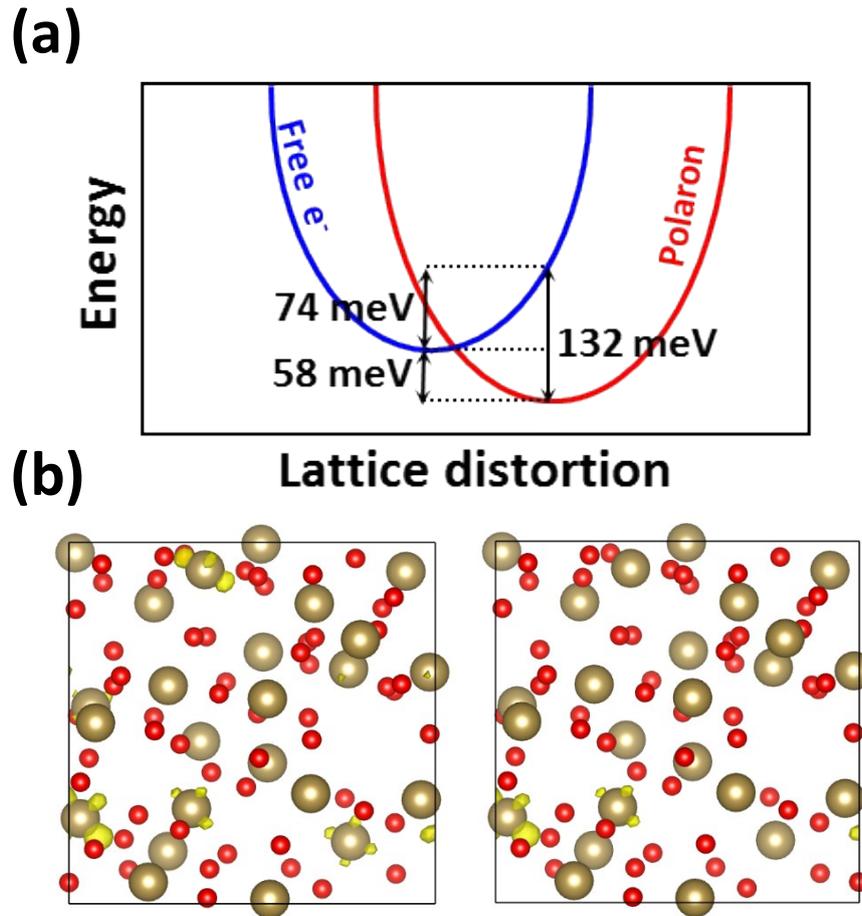
(5)

The equilibrium Fermi level is calculated self-consistently from Equation S1, S2, S4 and S5 at room temperature, which is similar to typical experimental growth conditions with radio-frequency sputtering. The estimated error in the calculation of defect formation energies by our approach based on density functional theory is approximately 0.1 eV. The defect concentrations were calculated from the formation energy via a Boltzmann expression (Equation S2) and are sensitive to the estimated error of the calculation. Since the defect

concentration is exponentially related with the formation energy, the estimated error in the calculated equilibrium concentration is approximately one to two orders of magnitude at room temperature. However, the concentration of charged vacancies is very low under O-rich conditions (lower than  $10^{10} \text{ cm}^{-3}$ ), and the difference between the concentrations of neutral and charged vacancies under O-poor conditions is much larger than the estimated error. Therefore, despite this error, our estimates and conclusions for the nature of vacancies that can exist at experimentally relevant concentrations and their stable charge state are not affected. We note that the chemical potential of oxygen atoms,  $\mu_O$ , in Equation S1 is an important additional parameter that affects the formation energy. The chemical potential of oxygen is determined by the growth conditions within the range of two extreme cases, the extreme O-rich (Ta-poor) and extreme O-poor (Ta-rich). The value of  $\mu_O$  under extreme O-rich conditions, which is the upper limit, is equal to half of the total energy of an  $\text{O}_2$  molecule. Under extreme O-poor conditions, corresponding the upper limit to  $\mu_{Ta}$  is the total energy of bulk Ta, which imposes a lower limit on  $\mu_O$  according to

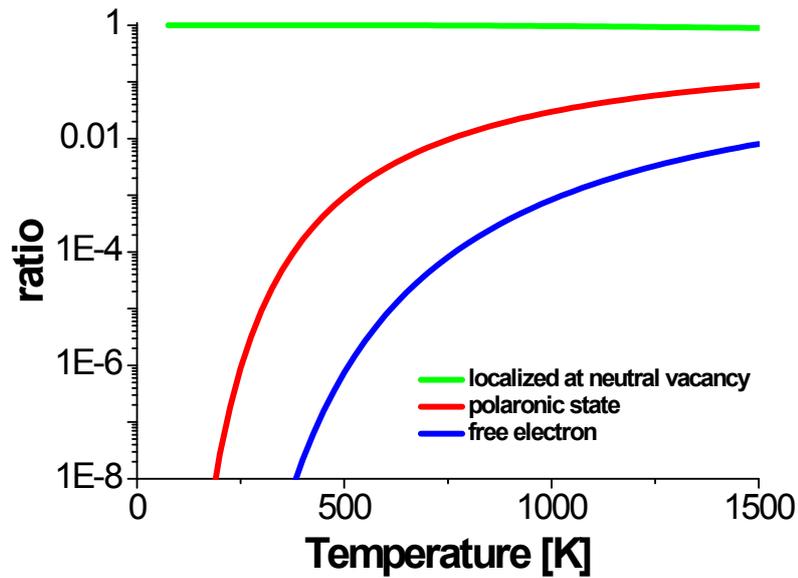
$$2\mu_{Ta} + 5\mu_O = E_{tot}[\text{Ta}_2\text{O}_5 : \text{bulk}]. \quad (6)$$

### 3. Polaron in bulk amorphous $\text{Ta}_2\text{O}_5$



**Figure S1.** (a) Calculated configuration coordinate diagram for a delocalized electron and a polaron in amorphous  $\text{Ta}_2\text{O}_5$ . The ground-state configuration of the polaron has lower energy by 58 meV than the delocalized electron. (b) Charge distributions of an extra electron in unrelaxed (left) and relaxed (right) cells. The charge distribution of excess electron becomes more localized after relaxation, giving rise to the formation of polarons. The value of the isosurface was chosen to enclose 10% of the electron density in both cases.

### 3. Excess-electron behavior in amorphous $\text{Ta}_2\text{O}_5$ with oxygen vacancies



**Figure S2.** Calculated ratio of occupation numbers of electrons localized at a neutral vacancy, in the polaronic state, and in the free-electron state. Oxygen vacancies act as deep donors in amorphous Ta<sub>2</sub>O<sub>5</sub> and most carriers are localized at neutral vacancies, but a certain fraction of carriers in Ta<sub>2</sub>O<sub>5</sub> form polarons at high temperatures.

### Reference

- [S1] C. G. Van de Walle, J. Neugebauer, *J. Appl. Phys.* **2004**, 95.
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- [S3] C. Freysoldt, J. Neugebauer, C. G. Van de Walle, *Phys. Status Solidi B* **2011**, 248.