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Scattered distribution of oxygen vacancies in anatase TiO_2 film; first-principles study on VMCO-memory characteristics

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Abstract

Because of the scalability, vacancy modulated conductive oxide (VMCO) memory made of anatase-TiO_2 oxide is promising among various ReRAM. In this work, we show that the uniform distribution of oxygen vacancies in TiO_2-VMCO memory is stable under the change of voltage application during the device operation, by the first-principles calculation. This occurs owing to the repulsive Coulomb interaction between ionized vacancies and large barrier for vacancy diffusion. The result will help to understand the operation and reliability of VMCO memory.

1. Introduction

Due to the small energy consumption and high-speed operation, resistive random access memories (ReRAM) are one of promising candidates for next-generation non-volatile memory devices [1]. ReRAM often use the resistivity change of insulating oxide layers by voltage application as a memory. Among various ReRAM, the vacancy modulated conductive oxide (VMCO) memory made of anatase-TiO_2 oxide attracts intensive attraction because its resistivity shows the area-size dependence and thus the device can be scalable, i.e., the device can be easily integrated. Such scalability is believed to reflect the uniform distribution of oxygen vacancies in TiO_2 layers [2]. However, it has not been clear how the uniform distribution of oxygen vacancies is realized and how such vacancy distribution changes under the change of voltage application during the device operation.

In this work, by using the first-principles calculations, we study the formation and stability of oxygen-vacancy distribution in different voltage conditions and answer the above-mentioned fundamental questions.

2. Calculation Model and Method

To simulate the distribution of oxygen vacancies (V_Os) in anatase TiO_2, we adopt a $(3 \times 3 \times 1)$ large bulk unit cell including 36 Ti and 72 O atoms, which is shown in Fig. 1(a). Vacancies are produced in this cell by removing 1-10 O atoms. Atom positions and electronic structures of various V_O distributions are calculated by the standard first principles method in the density functional theory, using the VASP code. We employ the LDA+U exchange-correlation functional with U^d=7.4 for Ti atoms and U^p=8.4 eV for O atoms to reproduce the TiO_2 band gap [3]. The 500eV energy cutoff is adopted for the plane-wave expansion of wave functions, while the $4\times4\times4$ k-points are used for the Brillouin-zone integration. To study the dissociation and incorporation of a vacancy in V_O cluster, we adopt the nudged elastic band (NEB) method and calculate the adiabatic diffusion potential of a vacancy. Other calculation details are described in our previous publications [4,5].

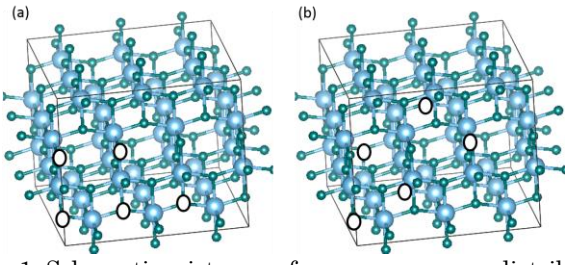

Fig.1 Schematic pictures of oxygen-vacancy distribution in anatase TiO_2; (a) condensed distribution and (b) scattered distribution. Blue and green balls indicate Ti and O atoms, respectively. Oxygen vacancies (V_Os) are denoted by open circles. There are five V_O in a unit cell.

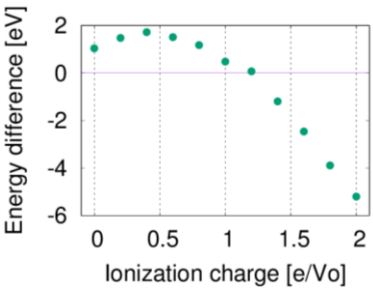

Fig.2 Energy difference between condensed and scattered oxygen-vacancy distributions, i.e., (a) and (b) in Fig.1, as a function of ionization charge per a vacancy. The case of five V_O is displayed.

3. Results and Discussions

Stability of oxygen-vacancy distributions

We first examine the stability of V_O distribution. We prepare two kinds of distributions, as shown in Figs. 1(a) and 1(b). The former is the V_O-condensed distribution, where five V_Os are located nearby in the unit cell, while the latter represents the V_O-scattered distribution, where the same numbers of V_Os are located uniformly in the cell. Figure 2 shows the calculated energy difference between these distributions, E(scattered)-E(condensed), as a function of ionization charge per a vacancy. Note that the V_O is known to be easily ionized positively, around +2, when the positive

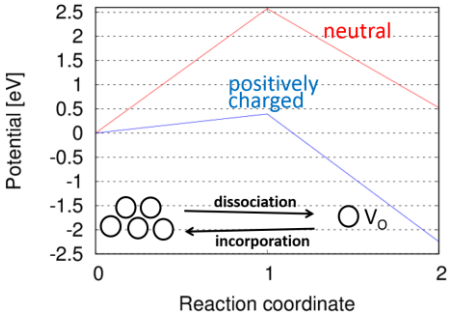

Fig.3 Dissociation and incorporation potential of oxygen vacancy around condensed vacancy cluster, for the neutral and positively ionized cases.

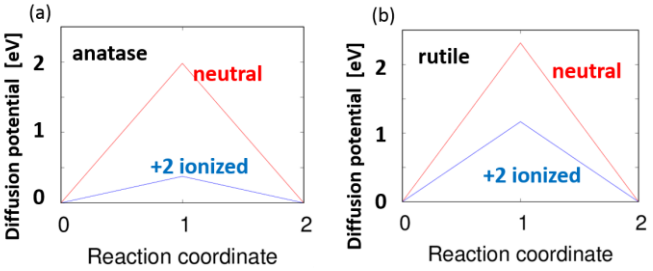

Fig.4 Diffusion potentials of a single oxygen vacancy in (a) anatase and (b) rutile TiO_2, for the neutral and +2-ionized cases.

voltage is applied to TiO_2. When the V_O distribution is located in neutral condition, the condensed distribution has lower energy around 0.3eV/V_O than the scattered one. However, when the positive voltage is applied and the ionization per V_O becomes larger than +1, the scattered distribution becomes stable. This transition occurs because there appears a repulsive Coulomb interaction between ionized V_Os and the V_Os prefer to separate from each other. In this way, for a number of V_Os, the cluster forms are stable in the neutral condition, while scattered distribution is stable when the Vos are positively ionized.

Dissociation/ incorporation of V_O around V_O clusters

Next, to clarify the dynamical stability of V_O clusters, we study the dissociation and incorporation processes of a V_O around V_O clusters. Figure 3 shows the potential of a single V_O corresponding to such processes around V_O cluster, in the neutral and positively-charged cases. In the neutral case, the potential barriers from both left and right sides are around 2eV, indicating the difficulty of both processes. In the charged case, the potential markedly decreases, around 0.4eV from left side, indicating the easy dissociation. Considering the energy at the right point is low, this decrease occurs due to the repulsive Coulomb interaction between a single V_O and V_O cluster; the energy decreases with increasing the distance between a V_O and V_O cluster.

Diffusion of a single V_O in TiO_2

Then, we consider the diffusion of a single V_O in bulk TiO_2. The diffusion potentials are shown in Fig. 4(a) for the

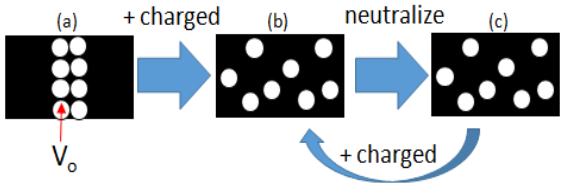

Fig.5 Schematic picture to explain the change of oxygen-vacancy distribution during the change of voltage application to TiO_2 film.

neutral and +2-ionized cases. It is clearly seen that the +2-charged V_O has small barrier, around 0.4eV, and easily diffuses in TiO_2. By analyzing electronic structure, we found that such decrease of barrier is caused by small elastic strain during the diffusion reflecting the small ionic radius of positively-ionized O atoms around V_O.

From all the results in the above, we can imagine how the V_O distribution changes during the voltage application, as shown in Fig.5. Even when the Vos are first generated as a condensed cluster like Fig.5(a), the positive voltage application promotes the dissociation of V_Os from the cluster and the V_O diffusion in TiO_2, and eventually realizes the uniform V_O distribution like Fig.5(b) to diminish the repulsive Coulomb interaction. When the positive voltage is turned off or the reverse voltage is applied, the V_Os hold their scattered positions like Fig.5(c) because their diffusion has large barriers as seen in Fig.4(a). When the positive voltage is applied again, they still hold their positions like Fig.5(b). This result indicates that the uniform distribution of V_Os is stable during the device operation.

Finally, we shortly comment on the case of rutile TiO_2 insulating layers. The formation energy of V_O is larger (+5.8eV) in rutile than in anatase (+5.3eV). In addition, the diffusion barrier is large even when positively charged as shown in Fig.4(b), indicating the difficulty of uniform V_O distribution. Thus, the anatase TiO_2 is favorable from the viewpoint of VMCO memory.

4. Conclusions

By the first-principles calculations, we showed that oxygen vacancies in anatase TiO_2 produce uniform distribution and hold the uniformity during the device operation, which indicates the long-time stability of TiO_2 VMCO memory.

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References

[1] B. Govoreanu et al., VLSI Symp. Tech. Digest, p.T132 (2015)
[2] J. Ma et al., IEDM Tech., p.564,(2016)
[3] S.L. Dudarev et al.,Phys.Rev.B **57**,1505(1998)
[4] T. Nakayama et al., ECS Trans. **86**, 69 (2018).
[5] R. Nagasawa et al., Jpn.J.Appl.Phys.**57**,04FB05 (2018).