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First-principles modeling of resistance switching in perovskite oxide material

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We report a first-principles study on SrRuO₃/SrTiO₃ interface in the presence of the oxygen vacancy. While the oxygen vacancy on the side of SrTiO₃ significantly lowers the Schottky barrier height, the oxygen vacancy close to the interface or inside the metallic electrode results in a Schottky barrier comparable to that of the clean interface. Based on these results, we propose a model for resistance-switching phenomena in perovskite oxide/metal interfaces where electromigration of the oxygen vacancy plays a key role. Our model provides a consistent explanation of a recent experiment on resistance switching in SrRuO₃/Nb:SrTiO₃ interface.

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Reversible resistance-switching phenomena in transition metal oxides such as NiO,¹ TiO₂,² and SrTiO₃ (Refs. 3 and 4) have recently been receiving attention in both fundamental researches as well as commercial applications. Relatively simple metal-oxide-metal structures and good retention properties for resistance states could be exploited for a next generation nonvolatile memory device known as resistance-switching random access memory (ReRAM). However, there are many technical issues to be addressed before the actual commercialization of ReRAM devices, and most of them are related to the lack of fundamental understanding of the switching phenomena, especially at the microscopic level. Several phenomenological models have been proposed to date; charge trap model,⁵ conducting domain model,⁶ metallic filamentary path,² Mott transition,⁷ and electrochemical migration of point defects.^{8,9} Recently, based on a systematic study on the Schottky junction formed by metallic electrode of SrRuO₃ and *n*-type semiconductor of Nb-doped SrTiO₃, Fujii *et al.* claimed that the observed resistance switching can be understood through a variable Schottky barrier model.¹⁰ An explanation at an atomistic level is yet to be found.

In this letter, based on the results from first-principles calculations, we propose a switching mechanism at the perovskite oxide/metal interface where the oxygen vacancy (V_O) plays a crucial role in changing a Schottky barrier height (ϕ_B) formed at the oxide/metal interface. For a computational package, we use Vienna *ab initio* simulation package (VASP).¹¹ We use projector-augmented-wave potentials¹² for describing electron-ion interactions and the energy cutoff for plane waves expanding electronic wave functions is set to 400 eV. For *k*-point sampling, $6 \times 6 \times 1$ and $3 \times 3 \times 1$ meshes are used for the clean and defective interface models, respectively. We employ the local density approximation for

the exchange-correlation energy of electrons. For all calculations, we relax internal positions until Hellmann-Feynman forces are reduced to within 0.03 eV/Å.

Figure 1(a) is a schematic picture of the model system used in the present work. Our model system consists of four layers of SrRuO₃ epitaxially built on eight layers of SrTiO₃. The lattice parameters are matched to those of SrTiO₃. The lattice mismatch between SrRuO₃ and SrTiO₃ is less than 1% both experimentally and theoretically. Due to the periodic boundary condition required for plane-wave calcula-

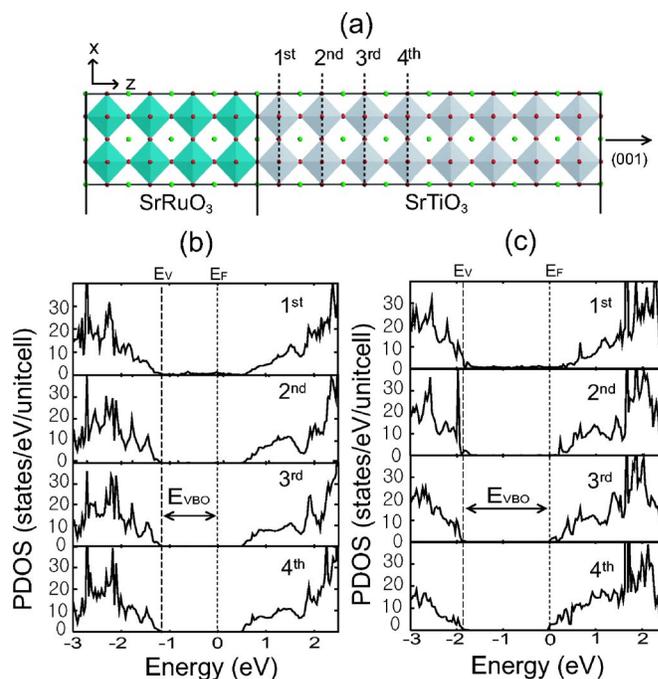


FIG. 1. (Color online) (a) A schematic picture of the unit cell of the model system. The shaded squares represent octahedra formed by oxygens. (b) Partial density of states (PDOS) for the clean interface, i.e., without any defect, projected onto each layer indicated in (a). (c) PDOS in a similar style with the oxygen vacancy present in the fourth TiO₂ layer in (a).

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high resistance region with ϕ_B comparable to that of the clean interface. LR is the low resistance region with lower ϕ_B or even Ohmic contact [see Fig. 2(b)].

Our observation of vacancy-dependent ϕ_B can explain a recent experimental observation of hysteretic I - V characteristics of the Schottky junction formed at SRO/Nb:STO interface.¹⁰ In that work, a forward bias scan drove the junction to low resistance state while the reverse bias scan resulted in high resistance states. Based on our computational results, this can be explained in terms of electromigration of V_O ; oxygen vacancies are easily generated in Nb-doped SrTiO₃ due to high growth temperatures.¹⁶ Since the effective charge of V_O is positive, the forward bias (or positive voltage at electrode) will drive V_O away from the interface or into LR in Fig. 2(b). The opposite thing will occur for a reverse bias scan and V_O now moves into HR. With the increase of the extreme value of each bias scan, the chance of electromigration of V_O also increases, resulting in a larger variation of ϕ_B . This is in qualitative agreement with the experiment. On the other hand, V_O may not be able to move easily into SrRuO₃ due to the metallic screening. Therefore, a reverse bias larger than the forward bias will be required to drive V_O into the electrode, also consistent with the experiment.

An explanation about the time scale of electromigration of V_O in actual devices is in demand. The migration barrier of V_O in the bulk SrTiO₃ was measured to be 0.67–1.27 eV (Ref. 17) and we also obtain 0.6 eV using the nudged-elastic-band method.¹⁸ A rough estimation gives ≥ 10 ms for a single hopping event of V_O at 300 K (see below), in contrast with the experiment in Ref. 10 where the switching behavior was observed for a pulse duration as small as 1 μ s. This strongly implies that the electrical bias should lower the migration barrier substantially. The first-principles description of V_O migration at the biased metal/oxide interface is beyond the scope of this work. Instead, we estimate the migration time based on a simplified model of local environments at the interface. We first note that the depletion length at the SRO/Nb-STO interface would be very small since Nb-doped SrTiO₃ is a good conductor. Using a formula known for the metal-semiconductor interface,¹⁹ the depletion length is estimated to be 5–10 nm from the interface. (The electric-field dependence of the dielectric constant of SrTiO₃ is also accounted for.) As the voltage drop occurs only along this narrow width, a large electric field will be applied in the depletion region. As a specific case, 10 V bias will result in an electric field of 1–2 V/nm, which decreases the activation energy approximately by 0.2–0.4 eV since V_O carries a nominal charge of $+2|e|$ (or oxygen carries $-2|e|$). Within the harmonic transition state theory, the average migration time τ is given by $\tau=1/[\nu \exp(-E_a/k_B T)]$, where ν is the attempt frequency and E_a is the activation energy. With $\nu \sim 1$ THz, which is a typical frequency of soft mode in SrTiO₃, the migration time at 300 K lies in the range of nanosecond to microsecond which are far shorter than ~ 10 ms for the unbiased case. This is in reasonable agreement with the experiment in Ref. 10 where the switching behavior was observed at 300 K as long as the time duration of 10 V pulse was longer than 1 μ s.

For a microscopic understanding of ϕ_B variation, we look into the macroscopic average of the local potential in the presence of V_O , as shown in Fig. 3. It is noticeable that V_O lowers the local potential around the vacancy site. This leads to a rigid downshift of local electronic structures. Accordingly, the conduction edge of the dielectric moves closer to the Fermi level that is mostly determined by the metallic electrode. On the other hand, when V_O is in close proximity of the interface or inside the electrode, free electrons screen the positive potential of V_O and the potential profile of the clean interface recovers.

In summary, we have presented a resistance-switching model based on first-principles calculations on SRO/STO interface containing V_O . The change of ϕ_B as dictated by the electromigration of V_O in response to the external bias was found to provide a consistent explanation of a recent experimental report. Although we employed a specific model of SRO/STO interface, our results also have implications for other metal/perovskite interfaces.^{8,20}

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