Extended Abstracts of the 2009 International Conference on Solid State Devices and Materials, Sendai, 2009, pp613-614

First-principles Study of Rectifying Properties of Pt/TiO_2 Interface

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1. Introduction

Reversible resistance-switching phenomena in transition metal oxides have attracted considerable attention in fundamental research field as well as in commercial application one for resistance switching random access memory (ReRAM). Among transition metal oxides, TiO_2 has been also expected as memristive switching material [1,2] and diode polarity switching material [3], and the rectifying behavior of $Pt/TiO_2/Pt$ structures is required for both switching. Recently, the rectifying property of Pt/TiO_2/Metal structures has been investigated [4] and it is concluded that TiO_2 in contact with Pt top electrode (TE) would be well oxidized, causing the Schottky barrier at the TiO_2/Pt-TE interface, and the interface between bottom electrode Pt and TiO_2 is considered to be in an ohmic contact state. Although it has been proposed that the stoichiometry near interfaces affects the conductive property, the microscopic origin is not yet clear. In this paper, we investigate the electronic property of the Pt/anatase-TiO_2 interfaces by means of the first-principles method. Particular attention has been paid to the band-offset at the interface and the formation energy of oxygen vacancy.

2. Computational Detail

The present calculations were performed by using our in-house computational code QMAS [5]. We adopted the projector augmented-wave (PAW) method [6-8] with GGA+ U [9] (U_{eff}=U-J=5.0 eV for Ti-3d orbitals). The plane-wave energy cutoff was set to 20.0 hartree. We deal with the simple interface between fcc-Pt(001) and anatase-TiO_2(001). Our supercell consists of five Pt layers epitaxially built on nine TiO_2 layers with the vacuum of 15 Å as shown in Fig. 1. The x and y dimensions are fixed at one of the optimized lattice parameters of bulk anatase (3.832Å). This reflects an experimental condition that a metal electrode is deposited on top of TiO_2. The theoretical lattice mismatch between Pt and anatase-TiO_2 is 2.3 %. For a reduced interface, oxygen atoms in the interfacial TiO_2 (1) layer are taken out, which corresponds to $Pt/Ti/TiO_2$ system.

3. Electronic Structure of Pt/TiO_2 Interface

Figure 2 (a) shows the layer-projected local density of states (LDOS) for the stoichiometric interface. The LDOS of the TiO_2 (6) layer, near the middle of TiO_2 slab, is very similar to the DOS of the bulk anatase and the Fermi level is lying in the middle of band gap. The conduction-band offset from the Fermi energy is 0.80 eV and this interface is a Schottky contact. In the LDOS of the TiO_2 (1) layer at the interface, one can observe energy states in the band gap. These states are called MIGS (metal induced gap states). These states are appreciable in the interface layer only, and decay strongly in the subinterface layer. The partially occupied MIGS at the Fermi energy are expected to accommodate excess electrons introduced by the removal of oxygen atoms, which would make reduction easier at the interface. This will be discussed further in the next section. Figure 2 (b) shows the LDOS for the reduced interface. The LDOS of the TiO_2 (6) layer is very similar to the DOS of the bulk anatase as is for the stoichiometric interface. The Fermi level, however, is lying just bellow the bottom of the conduction band, indicating that this interface is almost an ohmic contact.

4. Oxygen Vacancy Formation near Interface

As mentioned above, the interface would be more easily reduced than the bulk region due to the existence of MIGS. In order to confirm this, we calculated the formation energy of an oxygen vacancy as a function of the distance from the interface (Fig. 3). An oxygen vacancy is introduced by removing one oxygen atom from a 2×2 lateral (xy) supercell. The smaller the value is, the easier it is to create an oxygen vacancy. It is found that the formation energy is the lowest in the TiO_2 (1) layer. The formation energy saturates within the three TiO_2 layers and that in the bulk-like region is almost the same as the value of 5.25 eV in the bulk anatase. Figure 4 shows the LDOS for the system with an oxygen vacancy in TiO_2 (1) layer and TiO_2 (3) layer. When the oxygen vacancy is away from the interface, the vacancy state can be observed in the band gap (Fig. 4 (b)). On the other hand, no vacancy state is found in Fig. 4 (a) since the excess electrons introduced by the removal of an oxygen atom are accommodated in the MIGS.

5. Conclusions

First-principles calculations have been performed to investigate the rectifying properties at Pt/TiO_2 interface. The effect of oxygen deficiency at the interface on the

band-offset has been studied. We discuss the electronic properties of Pt/TiO_2 interfaces for a stoichiometric state and a reduced one. We found that the MIGS are appreciable in the interface layer only, and an oxygen deficiency near interfaces largely affects the band-offset. We also found that the formation of an oxygen vacancy is easier at the interface than in the bulk region. The present results provide a strong theoretical support for the proposition that the oxygen deficiency near interfaces plays a key role in the rectifying properties.

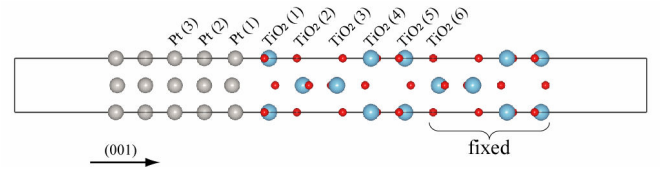

Fig. 1 A schematic picture of the supercell of the Pt/TiO_2 interface. The model system consists of five Pt layers and nine layers of TiO_2. When optimizing atomic positions, atoms in the five TiO_2 layers are fixed.

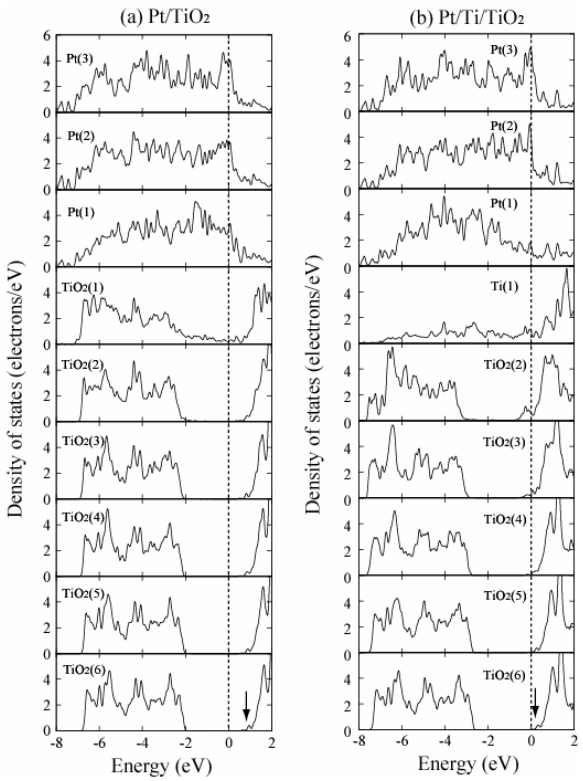

Fig. 2 The LDOS for each Pt and TiO_2 layer (a) for the stoichiometric interface and (b) for the reduced one. The labels for layers are the same as in Fig. 1. The Fermi level is chosen as zero energy. The arrow indicates the conduction-band minimum in TiO_2 (6) layer as a guide to the eye.

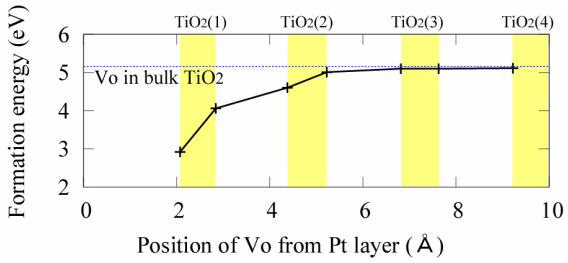

Fig. 3 Formation energies of an oxygen vacancy as a function of the distance from Pt layer.

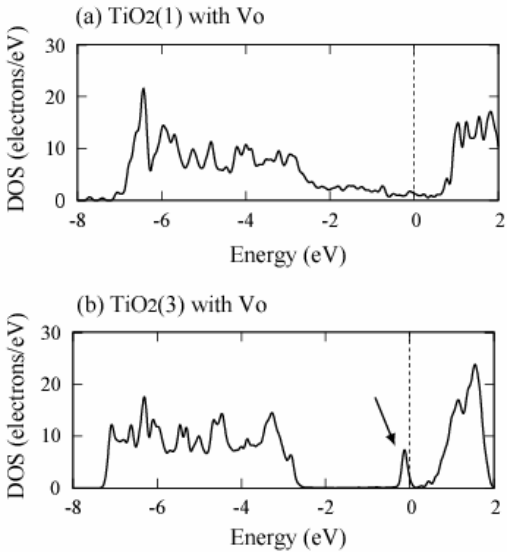

Fig. 4 The LDOS for the system with an oxygen vacancy in (a) TiO_2 (1) layer and (b) TiO_2 (3) layer. The Fermi level is chosen as zero energy. The arrow indicates the vacancy state.

Acknowledgements

The authors would like to thank Dr M. Kohyama and Dr S. Tanaka for helpful discussions on recent theoretical studies of metal/oxides interfaces. We also would like to thank Dr H. Akinaga, Dr H. Shima, Dr N. Zhong, Dr H. Akoh, Dr A. Sawa, Dr H. Inoue, Dr H. Sato, and Dr P. Xiang for discussions.

References

[1] D. B. Strukov et al., Nature **453** (2008) 80.
[2] J.J. Yang et al., Nature nanotechnology **3** (2008) 429.
[3] J. R. Jameson et al., Appl. Rhys. Lett. **91** (2007) 12101.
[4] H. Shima et al., Appl. Phys. Lett. **92** (2008) 043510.
[5] QMAS (Quantum MAterials Simulator), http://qmas.jp
[6] P. E. Blochl, Phys. Rev. B **50** (1994) 17953.
[7] N.A.W. Holzwarth et al., Phys. Rev. B **55** (1997) 2005.
[8] G. Kresse and D. Joubert, Phys. Rev. B **59** (1999) 1758.
[9] V.I. Anisimov et al., Phys. Rev. B **44** (1991) 943.