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First-Principles Study of Oxygen Vacancy and Hydrogen Impurity Effects in the Pseudo-hexagonal Ta_2O_5

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Resistance random access memory (ReRAM) is one of the most promising candidates for future non-volatile memory devices to replace conventional flash memory. ReRAM has attracted much attention because of its simple structure, high speed operation, low power consumption, and high density integration.[1] Among the candidates for resistive materials for ReRAM applications, conventional binary transition metal oxide (TMO) is particularly attractive because they can be easily mass produced. In particular, Ta_2O_5-based ReRAM devices showed superior endurance properties and switching performances.[2] The resistance switching behavior is controlled by the applied voltage or current pulse at the electrodes. Lattice defects in the bulk oxide or near the interface with the electrode are currently believed to play an important role in the switching between the resistive off state to a more conductive on state. Based on experimental observations, several resistance switching models have been suggested so far for TMO-based devices.[3] However, the underlying principles of the switching mechanism are still lacking a detailed understanding. In this study, the structures and energies of Ta_2O_5 were calculated using density-functional theory. The electronic interactions are described within GGA+U formalism, where on-site Coulomb corrections are applied on 5d orbital electrons of Ta atoms (U^d) and 2p orbital electrons of O atoms (U^p). The results are improved when the correlation correction is introduced additionally on O 2p orbitals by employing GGA+U^d+U^p approach. Using this combined approach, based on the bulk properties, as structural stability, crystal structure symmetry, and band-gap, the pseudo-hexagonal referenced as “asymmetric” by previous authors[4] was found to be a quite stable polymorph of Ta_2O_5 and proposed as a new candidate for resistive switching applications. The supercell structure (2x2x4) of the pseudo-hexagonal Ta_2O_5 is illustrated in Fig. 1(a). Fig. 1(b) shows x-ray diffraction (XRD) pattern of Ta_2O_5 film and diffraction data calculated by GGA+U^d+U^p in the pseudo-hexagonal Ta_2O_5. The diffraction data of the pseudo-hexagonal Ta_2O_5 are comparable to the experimental result. Both the experimental result and diffraction data of the orthorhombic *cmmm* and triclinic *p1* Ta_2O_5 are not consistent with one another. All our three proposed structures are much more stable than δ- and β-Ta_2O_5. Not only the band-gap energies of δ- and β-Ta_2O_5 calculated by GGA+U^d+U^p are in good agreement with those of PBE0 by Nashed *et al.*,[5] but also the band-gap energies of all our three proposed structures obtained by GGA+U^d+U^p agree well with the experimental band-gap energy. It is well known that the oxygen vacancies play an important role in the electrical conductivity of Ta_2O_5. To simulate the oxygen vacancy in the pseudo-hexagonal Ta_2O_5, we employed GGA+U^d+U^p in the calculation of the electronic structure of 2x2x4 supercell incorporating one oxygen vacancy. The total density of states calculated in the pseudo-hexagonal Ta_2O_5 with one neutral oxygen vacancy is shown in Fig. 2(a). The oxygen vacancy causes a defect state in the band gap. This electron-occupied state is situated at 2.5 eV above the top of the valence band. This is also in good agreement with the experimental x-ray photoelectron spectroscopy spectrum from a previous report.[6] The partial density of states of Ta and O atoms in the same structure are shown in Figs. 2(b) and 2(c). The defect state generated by the oxygen vacancy is formed mostly by 5d orbitals of Ta atoms with a small contribution of O 2p states. Furthermore, the effects of the hydrogen impurity on the electronic structures were also investigated, as shown in Fig. 3. The hydrogen impurity extends the defect state region in the band gap and is found to be preferentially located in the neighborhood of the oxygen vacancy. The hydrogen impurity also reduces the oxygen vacancy formation energy, which is predicted to have an influence on lowering forming voltage.

References

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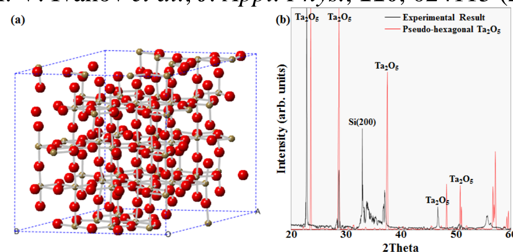

Fig. 1. (a) Structure of the pseudo-hexagonal Ta_2O_5. Small yellow ball denotes Ta atom and big red one O atom. (b) XRD pattern of Ta_2O_5 film and diffraction data calculated in the pseudo-hexagonal Ta_2O_5.

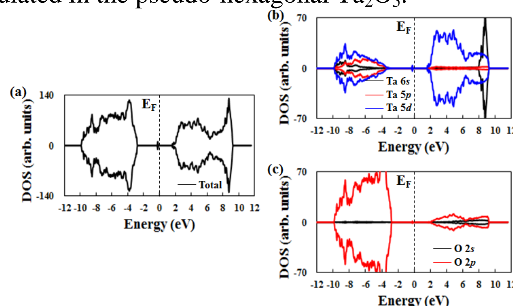

Fig. 2. (a) Total density of states and partial density of states of (b) Ta and (c) O atoms calculated in the pseudo-hexagonal Ta_2O_5 with one neutral oxygen vacancy.

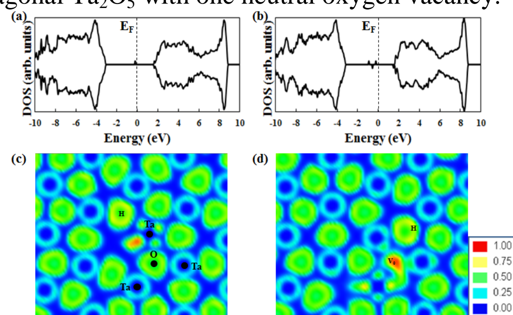

Fig. 3. (a-b) Total density of states and (c-d) electron localization function (ELF) calculated in the pseudo-hexagonal Ta_2O_5 (a, c) without/(b, d) with one neutral oxygen vacancy and with one hydrogen impurity. ELF: showing the missing electrons in the blue region and the highly localized ones in the red region.