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First-Principles Investigations of the Metal Doping Effects in TiO_2 ReRAM

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Abstract

We systematically study the metal doping effects in TiO_2 ReRAM using ab-initio density functional (DFT) calculations. Based on the oxygen vacancy filament model, the effects of various metal dopants on the electronic structures and vacancy formation energies are studied. It is shown that most metal dopants can reduce the forming voltage through decreased V_O formation energy. Some dopants show vacancy compensation phenomena, which can be utilized to reduce the reset current. The reduction of forming voltage and reset current by doping may help to improve the variations of ReRAM devices.

Introduction

Transition metal oxide ReRAM has been identified as one of the most promising candidates for next generation non-volatile memory, with its advantages of fast switching speed, high density, low operating power and CMOS compatibility [1,2]. One of the major challenges of ReRAM is the large variations of device characteristics due to the randomness of conductive filament formation [3]. Also, the reset current (I_{RESET}) needs to be reduced for low-power applications. As an important technique in semiconductor process, doping has been widely explored to cope with these challenges [3-4]. However, a systematic understanding of ReRAM doping effects still lacks. In this work, we theoretically study the roles of the various metal dopants in the resistive switching of TiO_{2-x}, which is considered a prototypical material for ReRAM [5]. The results provide insights to the selection and incorporation of dopants in ReRAM device design.

Model and Method

In TiO_2, it is believed that resistance change is caused by the formation/rupture of a conductive filament, modeled here as an oxygen vacancy (V_O) chain in the [001] direction of a 3x3x4 supercell of rutile TiO_2 [1]. In order to study the doping effects, 9 different metal dopants (Fig. 1a) are selected to replace one Ti atom in the supercell (Fig. 1b). Single oxygen vacancy is first created at 2 positions near the dopant to study the dopant-vacancy interaction (Fig. 1c). Then a conductive filament with one Ti atom replaced by the metal dopants is studied (Fig. 1d). Density functional calculations with projector-augmented wave method (PAW), local density approximation and on-site Coulomb corrections (LDA+U) are performed with VASP [6] to study the electronic structures of the doped systems. The applied exchange and correlation parameters, U^d=8eV, U^p=6eV and J= 0.6eV, are discussed elsewhere [1,2].

Results and Discussions

Fig. 2 shows the electron density of states of the 3x3x4 supercell with one substitutional dopant, before and after an oxygen vacancy is created next to it. The valence electron configuration of each dopant is outlined. Out of the 9 dopants, Zr and Hf have similar valence electrons as Ti. Thus they don't induce a defect state in the TiO_2 bandgap. When an oxygen vacancy is created next to the dopant, a defect level very similar to the bulk TiO_2 case is created in Hf. For Zr, the defect states are spin-polarized and split in energy. Metals with less valence electrons than Ti (Sr and Al) act as P-type dopants in TiO_2. When an oxygen vacancy is created, the two excess electrons from Ti atoms will compensate the dopant and the defect states in the bandgap are not filled. The other five dopants (V, Cr, Co, Ni, Cu) are all 3d transition metals with increasing number of valence electrons. The defect state first locates close to CBM, and then goes deeper into the bandgap as the atomic number increases. When an oxygen vacancy is created, the excess electrons first introduce its own defect level (V, Cr), then begins to compensate the dopant to form closed d-shell and eliminate the bandgap states (Co, Ni, Cu). From the above analysis, it can be concluded that the electronic property of dopant-vacancy complex is largely determined by the valence electron configuration of the dopant.

Fig. 3 shows the defect formation energies [7] of the dopants, and of the oxygen vacancy with the presence of dopants. The Ti-like dopants (Zr and Hf) slightly decreases the oxygen vacancy formation energy due to their larger atomic radii. The P-type dopants and 3d transition metal dopants all decrease the V_O formation energy, which is consistent with the strong oxygen gettering ability of Ti [8]. The trend of V_O formation energy change can be summarized as: larger difference between the dopant and Ti valence electrons will cause larger reduction in V_O formation energy.

These observations can be interpreted together with the DOS calculations to guide the ReRAM device design. For example, most dopants can act to reduce the forming voltage of TiO_2 ReRAM, but some of them (like Sr) have too low formation energies which could inhibit reversible switching. The oxygen vacancies strongly bound to these dopants are likely to form permanent conductive paths. There could be a trade-off between the formation energy and reset current. This argument is supported by the studies of vacancy filament containing metal dopants. As shown in Fig. 4, the formation energy of oxygen vacancies in a metal doped filament is calculated, and the same energy trend to the single vacancy case is retained. The effects of dopant on a single vacancy and a vacancy filament are directly correlated. On the other hand, if the goal is to reduce the reset current, the dopants with defect state compensation by V_O (such as Al and Co) should be selected. They tend to form less conductive vacancy filaments in TiO_2 and reduce I_{RESET}. To sum up, the variations of ReRAM devices can be improved by doping through the reduction of both V_{FORM} and I_{RESET}.

Finally, we wish to point out that the addition of dopants will modify the percolative properties of the oxide film and the device performances, an interesting aspect yet to be studied [9].

Conclusions

This work focuses on the interactions between dopants and oxygen vacancies in TiO_2 ReRAM. The roles of various metal dopants were thoroughly investigated with DFT calculations for the first time. It is revealed that dopants can reduce the formation energies of oxygen vacancy, as well as modify the electronic structures of the system. Both effects can be utilized to improve ReRAM forming and reset characteristics.

References

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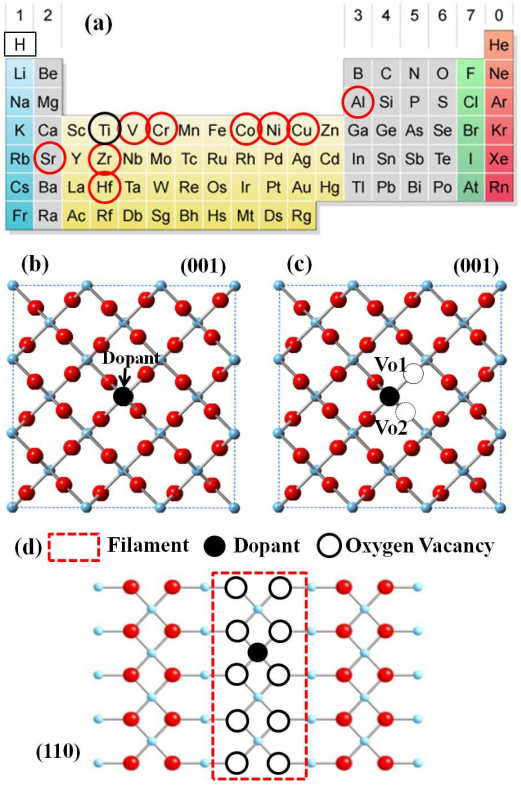

Fig. 1 Schematics of the metal doping configurations in TiO_2. (a) Selected metal dopants; (b) Dopant in 3x3x4 TiO_2 supercell; (c) Oxygen vacancy introduced at two non-equivalent positions next to the dopant; (d) Dopant in vacancy filament.

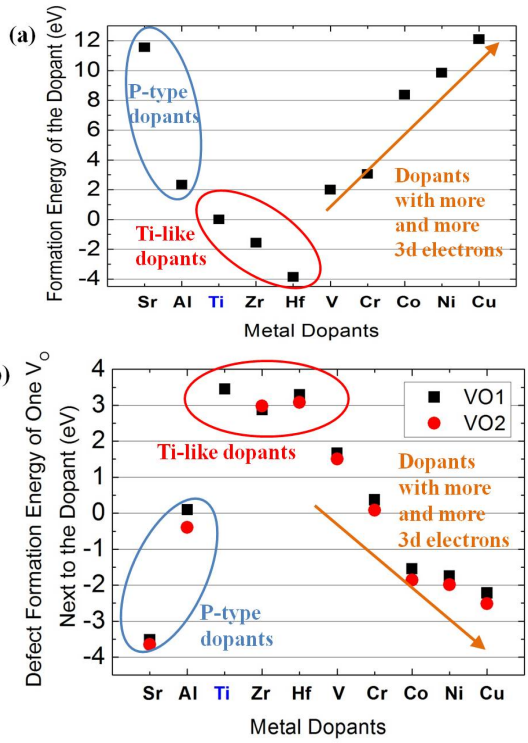

Fig. 3 Formation energies of (a) the dopants and (b) the oxygen vacancy created at two non-equivalent positions next to the dopants. Here we focused on substitutional dopants.

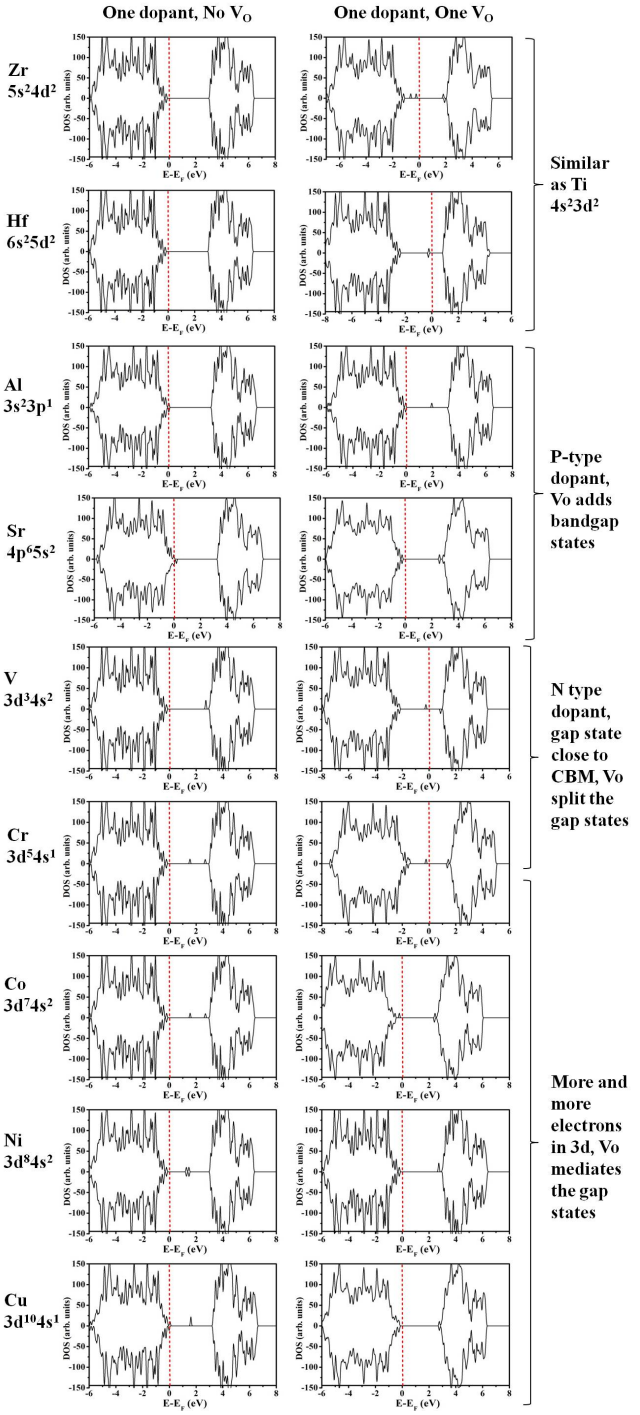

Fig. 2 Spin polarized density of states (DOS) calculated for the supercells with various dopants and zero/one oxygen vacancy.

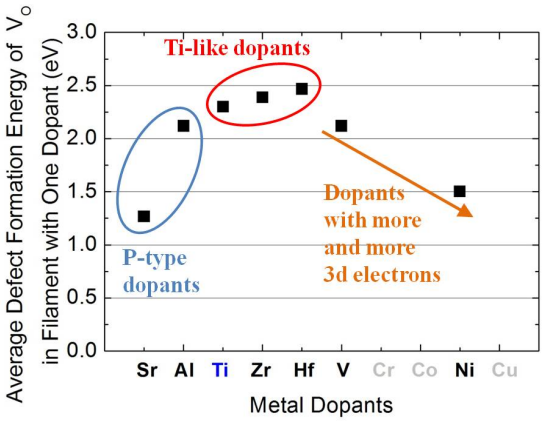

Fig. 4 Defect formation energies of one oxygen vacancy in the vacancy filament doped with selected metal dopants. Similar trend to the single vacancy case is observed.