Theoretical Design of Desirable Stack Structure for Resistive Random Access Memories

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Electric field-induced resistive random access memories (RRAMs) have recently attracted a great deal of attention as promising candidates for the next generation of nonvolatile memories. One of the main issues for RRAM is to understand fundamental aspects of the switching mechanism. We here proposed the RRAM switching mechanism and desirable memory structures on the basis of *ab initio* modeling [1,2,3,4]. We focused on binary oxide-based RRAMs (OxRRAMs) because of its low cost, high scalability, fast switching, and low power consumption. The OxRRAM shows filamentary-type resistive switching, where the oxygen vacancy is considered to form conductive filaments; the formation and disruption of these filaments are thus the mechanisms responsible for the ON-OFF switching. The key issue is, therefore, to reveal electronic roles in the formation and disruption of the vacancy filaments. For this purpose, we performed *ab initio* calculations in the framework of density functional theory (DFT) on three binary oxides.

Our *ab initio* calculations demonstrated the cohesion-isolation nature of the vacancy, depending on the charge states, which is inherent in binary oxides. As shown in Fig. 1 [1], there is a strong dependence of the average charge per vacancy on the cohesive energy of vacancy filaments in TiO_2, HfO_2, and Al_2O_3; for all oxides, the cohesive energy is less than zero when the vacancies take 0 or 1+ charge states, while it is greater than zero for 2+ charged vacancies, indicating the inherent nature of the vacancy cohesion-isolation induced by charge injection/removal in the binary oxides. Because of this nature, charge injection and removal determine the thermodynamic stability of the vacancy filament and the diffusion in OxRRAMs; injection of electrons induces the vacancy cohesion that stabilizes the filament, whereas removal of the electrons favors the vacancy isolation that destabilizes the filament. However, electron removal makes the energy barrier of the vacancy diffusion processes small enough to be overcome by Joule heating.

Detailed analysis of the electronic structures of vacancy filaments in TiO_2, HfO_2, and Al_2O_3 showed that the physical mechanism of vacancy cohesion-isolation upon charge injection/removal is the formation of bonding-like electronic states between the vacancies [2,3,4]. The charge injection and removal that lead to occupation of the bonding-like states can be controlled by shifting of the system Fermi level via an applied voltage during memory operation. We thus derived the physical concept in which the vacancy cohesion-isolation phase transition upon charge injection/removal is one of the main factors that governs the switching processes of OxRRAMs, as schematically shown in Fig. 2 [1].

Based on the physical concept obtained from the *ab initio* modeling, we proposed a desirable OxRRAM three-layer stack structure (Fig. 3 [1]). The oxygen chemical potential has been shown to be a key parameter in stacking engineering. The desired structure of the three-layer RRAM consists of (1) a vacancy-source layer with an extraordinarily low oxygen chemical potential, (2) a vacancy-control layer with a thickness that is thinner than the penetration depth of the oxygen chemical potential, and (3) a vacancy-barrier layer with the thickness that is as thin as allowing direct electron tunneling. The guiding principles was applied to the optimization of the $TiN/Al_2O_3/HfO_2/Hf/TiN$ RRAM stack, leading to an asymmetrical vacancy filament shape that can be used to improve the memory characteristics, such as ON/OFF ratio [1,3].

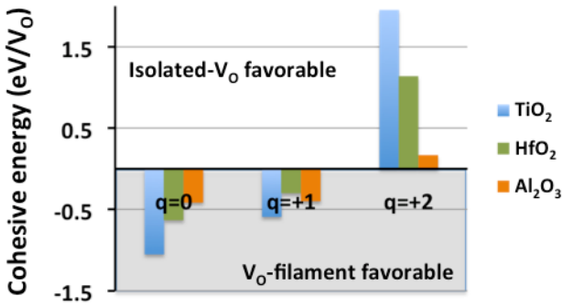

Figure 1: Cohesive energy of vacancy filaments in TiO_2, HfO_2, and Al_2O_3 as a function of vacancy charge state [1].

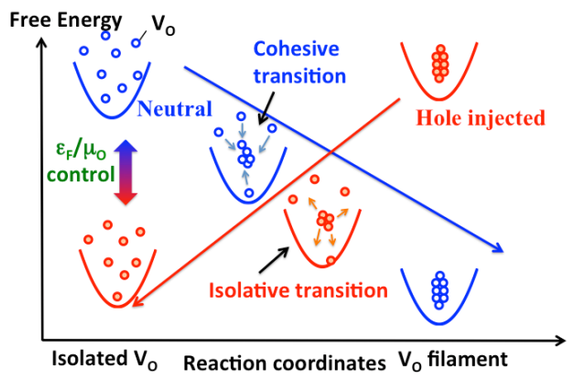

Figure 2: Schematic picture of the phase transition of the vacancy cohesion-isolation by charge injection and removal [1].

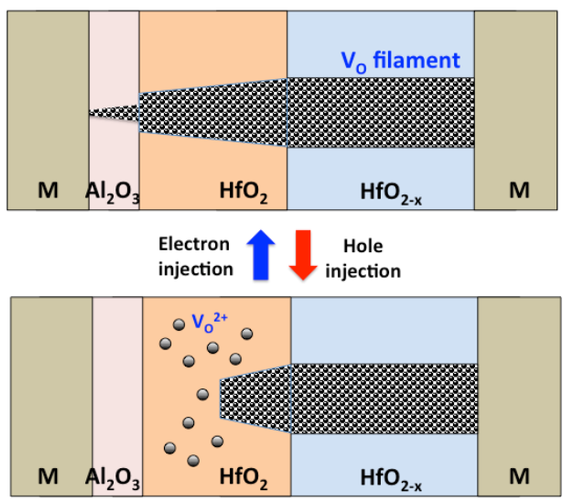

Figure. 3: Schematic picture of three-layer stack structure [1].

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