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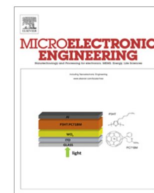

Ab initio calculations of materials selection of oxides for resistive random access memories

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ABSTRACT

The energies of various atomic processes in resistive random access memories (RRAM) are calculated for four typical oxides, HfO_2, TiO_2, Ta_2O_5 and Al_2O_3, to define a materials selection process. Oxygen vacancies have the lowest defect formation energy in the O-poor limit, and to dominate the processes. A band diagram defines the operating ranges of Fermi energy and O chemical potential. It is shown how scavenger metals can be used to vary the O chemical potential and thus vary the O vacancy formation energy. The high stability of amorphous phase of Ta_2O_5 is relevant to the high endurance of its RRAM.

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Resistive random access memory (RRAM) is a main challenger non-volatile memory technology to Flash memory. However, a wide range of material systems are presently being studied, which use various different switching mechanisms [1–6]. A working technology would favor oxide materials as they are compatible with CMOS process technology. Developing a working technology also requires materials selection, so that effort is focused on the most useful materials rather than dissipated over too many. Materials selection requires us to understand which material properties control each aspect of device performance, such as switching speed, resistance window, retention time and endurance. The favored materials are based on the formation of a conductive filament of oxygen vacancies across a film of a wide gap oxide. The device switches between a low resistance state (LRS) and a high resistance state (HRS). To date, there have been various models of the switching process [3–18]. The switching process is understood at a basic level, and there are various compact models of this process such as the 'hour-glass' model [11–13]. However, there is limited understanding of the energetics of atomic processes [14,15] relevant to materials selection, for increasing memory endurance, retention, widening the resistance memory window, or the ultimate scalability [19]. We desire something similar to that for high K oxides for gate stacks where the materials parameters became defined [20–22]. Here, we summarize the calculated energy levels and formation energies of O vacancies and interstitials in four key oxides HfO_2, TiO_2, Ta_2O_5 and Al_2O_3 to understand which processes are critical for memory operation.

An oxide-based RRAM consists of an oxide layer between two electrodes with a thin metal layer next to one electrode that scavenges oxygen ions from the oxide to form O vacancies. This scavenging metal can differ from the metal in the oxide. Switching is initiated by a forming step, during which the oxygen vacancies coalesce into a filament between the electrodes, as shown in Fig. 1(a). Various experiments have shown that oxygen vacancies are the mobile species in these systems [14] and it is supported by calculations.

We first consider the nature of the filament. The temperature coefficient of resistance of the LRS determines if the filament is metallic or semiconducting. The data of Gao [23] and Muraoka et al. [24] suggests that it is metallic. The metallic condition sets the minimum density of vacancies (n) in the filament, from Mott's criterion [25–27] for the metal–insulator transition, as $n^{1/3} = 1/a_H$. Here, a_H is the Bohr radius of the vacancy wavefunction, which can be calculated for that oxide [27,28]. This criterion is shown in Fig. 1(f). This criterion is more general than considering vacancy–vacancy interactions as in some other approaches [16–18]. The forming process creates the vacancies and assembles them into a filament. This occurs by the drift of charged vacancies, aided by the field-enhancement around the tip of the growing filament (Fig. 1e). Once the charged vacancies have entered the metallic filament, they are no longer subject to the electric field, so there is no force on them.

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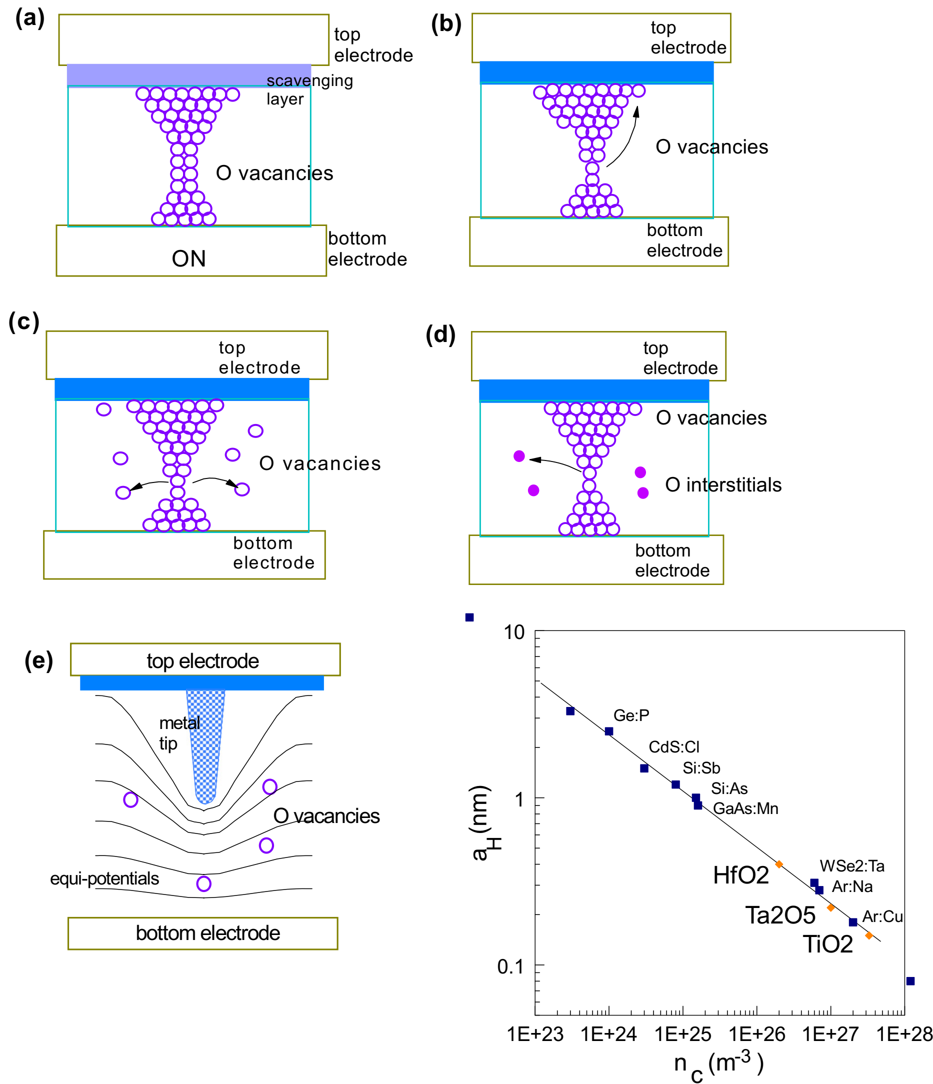

Fig. 1. Schematic of the switching process. (a) Low resistance state. (b) High resistance state (HRS), vacancies move toward electrode. (c) HRS and vacancies disperse into the insulating matrix. (d) HRS where vacancies recombine with O interstitials in the matrix. (e) Equipotential lines showing field enhancement around the metal tip of a growing filament. Diffusive drift of charged vacancies under the electric field. (f) Defect density vs. Bohr radius at metal–insulator transition.

The SET and RESEST processes are shown in Fig. 1(b–d). This shows how during reset to the HRS, the vacancies can either (b) move towards electrodes leaving a narrower filament, (c) disperse from the filament into the resistive bulk oxide, or (d) recombine with O interstitials. The hour glass model represents vacancies next to each electrode as two reservoirs [11]. In this model (b), the vacancies move from one reservoir to the other, conserving their number, and so maximizing endurance. On the other hand, in mechanisms (c) and (d), vacancies leave the reservoirs and then return. Their number may not be conserved from one cycle to another, unless exactly the same number of vacancies return to the filament [11]. This would affect endurance.

To compare oxides, we calculated their electronic structures of their defects using the ab initio plane wave pseudopotential method with the CASTEP code. Norm-conserving pseudopotentials are used with a plane wave cut-off of 780 eV. Due to the band gap error of density functional theory, the defect energy levels are calculated by the screened exchange hybrid functional [28]. The defect formation energies are calculated for each state using the supercell method [29–34]. The models contain typically 150 atoms, and can be amorphous or crystalline within the supercell. The atomic structures are relaxed for each charge state. Further details are given in Ref. [30].

The relative importance of the processes (b–d) in Fig. 1 can be estimated from the defect formation energies in their various charge states. To appreciate the factors involved, Fig. 2(a) plots the formation energy of various defects in HfO_2 against the Fermi energy (E_F), in the standard O-rich limit (O_2 at atmospheric pressure, $\mu_O = 0$ eV), the condition used in many simulations. Here, μ_O is the O chemical potential [29]. Fig. 2(a) suggests that the O interstitial is the lowest cost defect in these conditions and would therefore be dominate properties [15]. This would be contrary to our current understanding. The reason this is not right is that the metal electrodes or the metal scavenging layer next to the electrodes in fact shifts μ_O of the film towards the *O-poor* limit, which is near μ_O of the scavenging metal/oxide equilibrium. This is a key point. If Hf is the scavenging metal, this would lower μ_O by a huge 5.9 eV compared to $\mu_O = 0$. This reduces the O vacancy formation energy in its neutral state from 6.1 to 0.2 eV, that is to nearly 0 eV [29]. In contrast, the interstitial formation energy becomes very large, and this defect becomes irrelevant near equilibrium. The same effect occurs in the other three oxides of interest, as

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