

Defect properties and Materials Selection for Oxide RRAM

John Robertson¹, Yuzheng Guo¹

¹ Department of Engineering, Cambridge University,
Cambridge CB2 1PZ, United Kingdom
Phone: +44-1223-748331 E-mail: jr@eng.cam.ac.uk

Abstract

Defect formation energies are calculated in various oxides to model atomic processes in oxide based RRAM.

1. Introduction

Resistive random access memory (RRAM) is a main challenger non-volatile memory technology to Flash memory [1-3]. A working technology would favor oxide materials as they are more compatible with CMOS process technology. The device operates by the formation of a conductive filament of oxygen vacancies across a film of a wide gap oxide, and switches between a low resistance state (LRS) and a high resistance state (HRS).

To date, there have been various models of the switching process [4,5], including compact models such as the 'hour-glass' model [5]. However, developing a working technology also requires materials selection, so that effort can be focused on the few most useful materials. Materials selection requires us to understand which material properties control each aspect of the device performance, such as switching speed, resistance window, retention time, endurance and the ultimate scalability. Here, we develop an understanding of the energetics of atomic processes relevant to switching. We calculate the energy levels, formation energies and migration energies of O vacancies and interstitials in five key oxides HfO₂, TiO₂, Ta₂O₅, Al₂O₃ and NiO to understand which processes are critical for memory operation.

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. The RRAM switches between two states, the LRS in which the filament is wider and more conductive, and the HRS in which it is narrower and more resistive, but is still present. The temperature coefficient of resistance suggests that the filament is metallic in the LRS.

2. Method

Now consider possible atomic processes in the SET and RESEST transitions between LRS and HRS. During reset to the HRS, Fig. 1, the vacancies can either (a) move towards electrodes leaving a narrower filament, (b) disperse from the filament into the resistive bulk oxide, or (c) recombine with O interstitials previously injected into the bulk during the forming process. The hour-glass model envisages most vacancies lying next the electrodes or in the filament, as two reservoirs [4]. During switching, the vacancies move from one reservoir to the other, conserving their number, to maximise endurance. On the other hand, in mechanisms (b) and (c), vacancies leave the reservoirs and

then return. In that case, the vacancy number may not be conserved from one cycle to another, which is eventually detrimental to endurance.

3. Discussion

The relative importance of the processes in Fig 1 can be estimated from the defect formation energies in their various charge states. Consider first HfO₂. At $pO_2=0$ eV, the O interstitial appears as the lowest cost defect, which is against experimental results. What has happened is that the metal electrodes or metal scavenging layer next to the electrodes shifts pO_2 towards the *O-poor* limit, which is near pO_2 of the metal/oxide equilibrium. For HfO₂, this greatly lowers the neutral O vacancy formation energy from 6.1 eV to 0.2 eV [6]. In contrast, the interstitial formation energy rises by this amount, and this defect becomes irrelevant. Thus, the O chemical potential is the key system parameter. In each case, it is clear that O vacancies now have low formation energy (except for Al₂O₃) [7]. In NiO, considering the O vacancy, Ni interstitial or O interstitial [8,9], the O vacancy is most important.

The second relevant parameter is the Fermi energy E_F . For each oxide, the shaded areas in Fig 2 show the relevant range of E_F , and this gives the defect's charge state.

We have assembled the data on defect charge states into band diagrams for each oxide in Fig 3, referenced to the vacuum level, and including the electrode work function. We mark on Fig 3 the Fermi level of the oxide's parent metal. For all but HfO₂, E_F lies near 4.3 eV below the vacuum level. The O vacancy is in its +2 charge state for HfO₂ and TiO₂ for $E_F = -4.3$ eV, and in its V^0 configuration for Ta₂O₅. NiO has a small electron affinity, but likely metal work functions still lie in the V^{2+} range. It is in the V^{2-} configuration for Al₂O₃, and this makes its RRAM operation different to that of the others.

We can allow the scavenger metal M' to differ from the parent metal M of the oxide, for example using Ti next to HfO₂. The formation energy of the vacancy E_{form} is raised by raising pO_2 by using a less electropositive scavenging metal, Fig 4. Raising E_{form} allows us to control the total number of vacancies in the system by increasing the cost of forming new ones. However, it might increase the forming and switching voltages, so a compromise must be reached. Changing the scavenger metal also changes E_F , which can be used to vary the defect charge state, Fig 5.

Now consider materials selection in general. TiO₂ is less favored for endurance [2] because it possesses a number of sub-stoichiometric phases TiO_{2-x} which will interfere with conservation of vacancy numbers. HfO₂, Ta₂O₅ and Al₂O₃ do not have stable, insulating sub-stoichiometric oxides, which is an advantage. Al₂O₃ has a comparatively

large O vacancy formation energy [7], and a large migration barrier energy, so that vacancy migration in its RRAM cycling is impeded. Experimentally, Ta_2O_5 shows good endurance [2,3,5]. Crystalline Ta_2O_5 has a complex layered structure [10,11]. It has three O vacancy sites, two intra-layer sites and one inter-layer site. The 2-fold coordinated intra-layer vacancy is the most stable, and it gives a $0/2+$ state near midgap. The other vacancies are less stable, and give levels near the conduction band edge.

The long endurance and retention time of Ta_2O_5 RRAM may be due to various factors; the ability of Ta_2O_5 to remain amorphous to higher temperatures than HfO_2 , its adaptive lattice for easy defect migrations in any crystalline inclusions, and that the vacancy is in V^{2+} state for typical electrode materials such as TiN.

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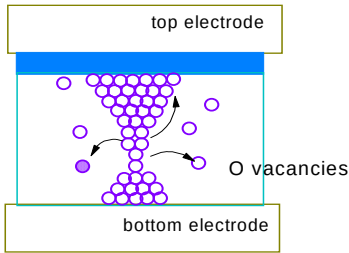


Fig. 1. Oxygen ion processes during transition to HRS.

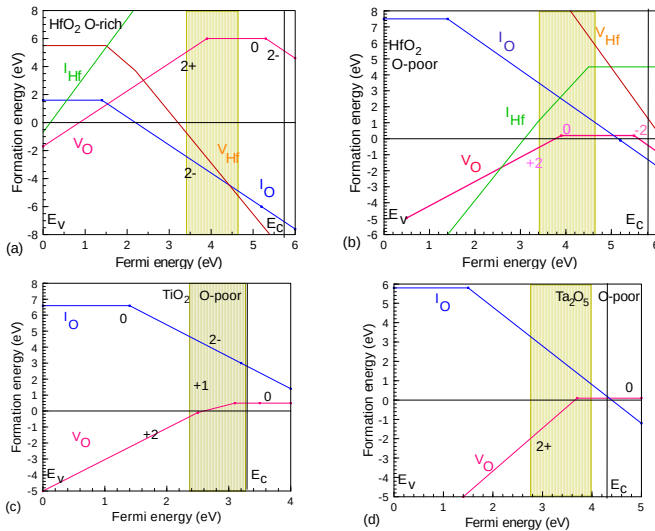


Fig. 2. Formation energy/Fermi energy diagrams for defects in HfO_2 , TiO_2 and Ta_2O_5 .

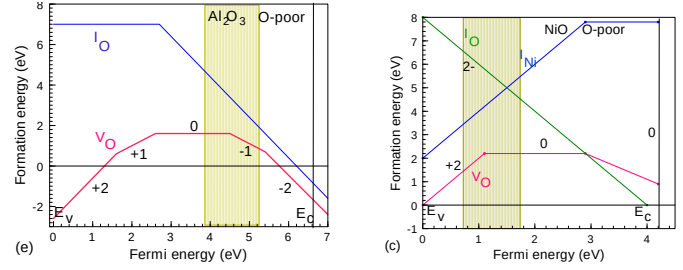


Fig. 2 (continued). Formation energy diagram for defects in Al_2O_3 and NiO .

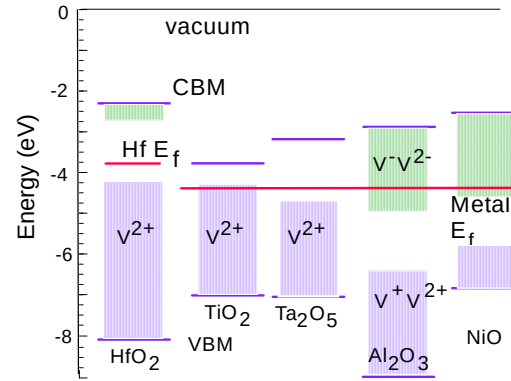


Fig 3. Vacancy charge states and band edges aligned to vacuum level for the different oxides.

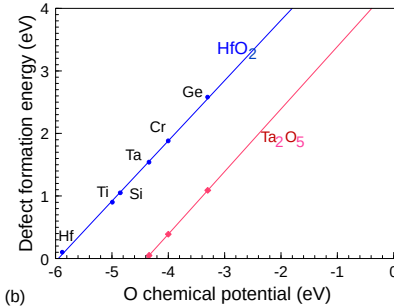


Fig 4. Increase in vacancy formation energy in HfO_2 or Ta_2O_5 by use of different scavenger metals.

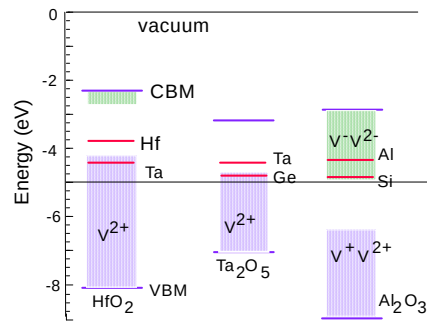


Fig. 5. Vacancy charge states and band diagram when different scavenger metal is used.