

Exploring the role of nitrogen incorporation in ZrO₂ resistive switching film for enhancing the device performance

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Abstract

The role of nitrogen doping on the resistive switching (RS) performance in nitrogen doped ZrO₂ memristive device is investigated. The Pt/N:ZrO₂/TiN resistive random access memory (RRAM) shows smaller switching voltage, larger memory window as well as improved uniformity. Moreover, the multilevel storage capability can be successfully obtained by varying the compliance current in the SET process for the memory cell. Combining with first-principle method, both formation energy (E_{vf}) and migration energy (E_{m}) of oxygen vacancy (V_{O}) show noticeable decrease in N doped ZrO₂ supercell, which relate to the lower forming voltage and operating voltage. The density of states indicate that the oxygen vacancy midgap defect states can be removed as a result of N dopant, which neutralizes the excess defects in ZrO₂ switching layer and may reduce the densities of the potential filaments. Herein the uniformity can be improved. All the theoretical results show reasonable agreement with the improved experimental RS performance for Pt/N:ZrO₂/TiN device.

1. Introduction

Resistive random access memory (RRAM) is the focus of development as a promising candidate for next-generation nonvolatile memory in terms of its excellent scalability, high-speed operation and simple structure [1]. Among the numerous oxide materials that exhibit resistive switching properties, ZrO₂ has recently attracted significant attention for fabricating high-quality RRAM devices [2]. In recent years, it has been reported that nitrogen has often been used to improve device properties in both experimental and theoretical studies. It is believed that the V_{O} is the origin of the ON-OFF operation and N also plays an important role in oxide-based RRAM [3].

In this work, it is aimed to investigate the role of N incorporation on the V_{O} properties in ZrO₂-based RRAM. The E_{vf} and E_{m} in ZrO₂ are significantly decreased by N incorporation which lead to lower forming voltage and operation voltage RRAM devices. Furthermore, we reveal that N atoms favorably couple with V_{O} in ZrO₂ which induces a more stable conductive filament by preventing V_{O} diffusion. The results clearly explained how N incorporation improves the performance of ZrO₂-based RRAM.

2. Calculation methods and experiments

The first-principles calculations [4] based on the density

functional theory (DFT) is performed on monoclinic ZrO₂ (m -ZrO₂). Four different models (A, B, C, and D) have been constructed in 96 atoms m -ZrO₂ supercell by substituting two O atoms with N atoms and removing one O atom as shown in Fig. 1(a). Based on the formation energy of oxygen vacancy [5], the E_{vf} can be calculated as,

$$E_{\text{vf}} = E(V_{\text{O}}) - E(\text{bulk}) + \mu_{\text{O}}$$

where $E(V_{\text{O}})$ is the total energy of each model containing a V_{O} , $E(\text{bulk})$ is the total energy of ZrO₂ bulk crystal with or without N atoms, and μ_{O} is the chemical potential of an oxygen atom. To simulate the vacancy diffusion, one oxygen ion is moved from the lattice site to the neighboring vacant sites in ZrO₂. Transition state search is used to calculate E_{m} in ZrO₂.

In the experiments, undoped and N-doped ZrO₂ memory devices are fabricated on TiN/SiO₂/Si substrates by radio frequency magnetron sputtering in Ar atmosphere and N₂/Ar mixed atmosphere. Lastly, the same Pt electrode with 200 nm thickness was deposited by magnetron sputtering.

3. Results and discussion

Figs. 1(a)-(b) show the E_{vf} and E_{m} for all models in ZrO₂. The E_{vf} is significantly reduced by introducing N atoms, which indicates that the V_{O} formed easily in N doped ZrO₂-based RRAM. The E_{vf} of Model C and Model D are higher than that of Model B by 0.25 and 0.32 eV, respectively. The E_{m} is decreased in N doped ZrO₂ and increases with migration distance. These results indicate that the most stable configuration is Model B and N atoms tend to couple with the V_{O} . Therefore, N incorporation would improve the reliability of RRAM by suppression of V_{O} diffusion.

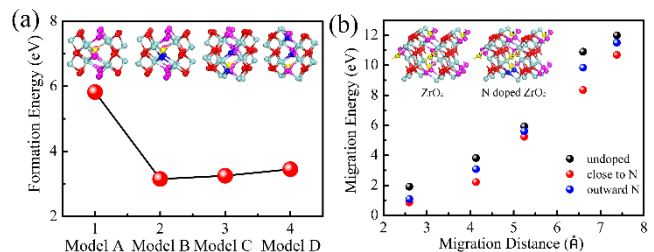


Fig. 1 (a) The formation energy of oxygen vacancy in ZrO₂, (b) V_{O} migration energy as a function of migration distance. The gray, blue, pink, red, and yellow balls denote zirconium, nitrogen, 3-fold oxygen, 4-fold oxygen and the V_{O} site, respectively.

Figs. 2(a)-(b) describe the calculated band structure and density of states (DOS) of Model A and B. The original V_{O}

defect state in the bandgap of Model A in Fig. 2(a) is removed as a result of N doping, leaving some N non-bonding states near the valence band of ZrO_2 , as illustrated in Fig. 2(b). The original neutral V_O introduces two excess electrons, which fill the valence states of N atoms and form a closed shell electronic configuration. Herein, the V_O becomes a V^{2+} center and pushes the original defect state up into the conduction band [6]. It is suggested that V_O defect states in bandgap is nullified by the presence of tow N atoms and thus the neutralization of V_O defect states may eliminate the excess conductive paths and potential filaments.

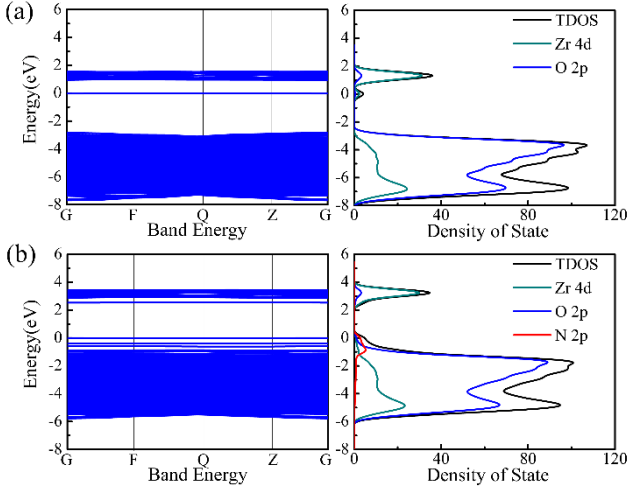


Fig. 2 The band structure and density of states for (a) Model A and (b) Model B.

Electron localization function (ELF) [7] was calculated to measure electron pairing by defining,

$$\text{ELF} = \frac{1}{1 + [D(r)/D_h(r)]^2}$$

where the term $D(r)/D_h(r)$ normalizes the same-spin probability by the uniform-density electron gas as reference, and ELF is a dimensionless value restricted to the range of [0,1]. The ELF value at 0~0.5 and 0.5~1 indicate low electron density areas and high electron density areas, respectively. Fig. 3 indicates that N atoms tend to grab electrons from V_O and thus neutralizes the defect states of oxygen vacancies, which may eliminate the excess conductive paths.

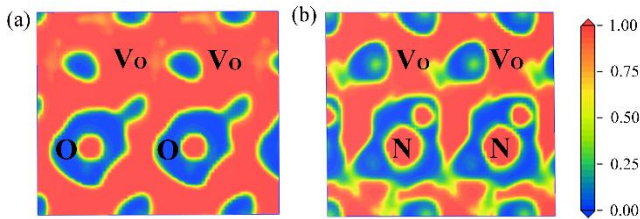


Fig. 3 ELF for (a) undoped ZrO_2 and (b) N doped ZrO_2

Fig. 4(a) presents the I-V curves of the forming process for the undoped and N-doped ZrO_2 device. The forming voltage reduced from 7.2 to 3.6 V in N doped ZrO_2 device,

which shows reasonable agreement with the lower E_vf in N-doped ZrO_2 . Fig. 4(b) illustrates that the SET voltage reduces from 0.61 to 0.52 V in the N-doped device, which is consistent with the lower E_m in N-doped ZrO_2 .

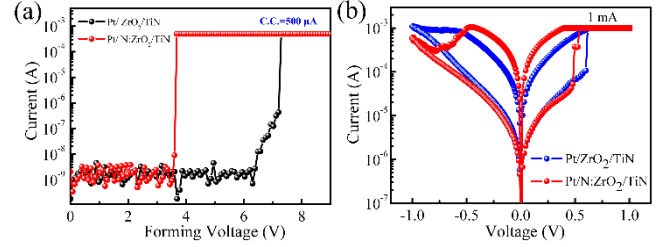


Fig. 4 (a) The forming I-V characteristics for ZrO_2 device and N: ZrO_2 device, (b) Typical I-V curves with one cycle for ZrO_2 device and N: ZrO_2 device.

Fig. 5 shows the multilevel RS I-V curves for the Pt/N: ZrO_2 /TiN device with different compliance currents. Controlling the compliance currents in the set process to read at 0.2 V, three LRS were obtained by applying different compliance currents. The smallest resistance window of LRS/HRS is about 12.5, which means that the LRS/HRS ratio is capable of memory application and the three LRS are clearly distinguished.

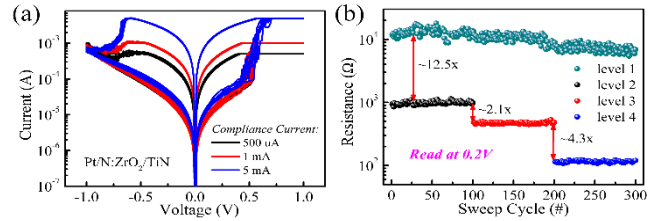


Fig. 5 (a) Typical I-V characteristics for the Pt/N: ZrO_2 /TiN RRAM device under different compliance currents, (b) The HRS and LRS of the TiN/N: ZrO_2 /Pt RRAM device with different compliance currents.

3. Conclusions

In summary, the role of N incorporation into ZrO_2 -based RRAM has been investigated by using first-principles calculations. N doping can nullify the V_O defect states in the mid bandgap of ZrO_2 , and thus eliminates the alternative conductive paths. The reduced V_O formation energy and migration energy in N doped ZrO_2 can explain the lower forming voltage and SET voltage in RRAM device.

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