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Non-negligible Metal Ions Diffusion in Amorphous Oxygen-Deficient Metal-Oxide Based Resistive Switches: A First Principle Study

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Abstract

Taking amorphous TaO_x and HfO_y (a-TaO_x and a-HfO_y) based resistive switches as examples, we perform systematic investigation on the ionic conductivities in a-TaO_x (x = 2, 1.5 and 1) and a-HfO_y (y = 1.5, 1 and 0.75) from first principles. Our results reveal that the self-diffusion of O is predominant in both the a-TaO_x and a-HfO_y based resistive switches, and the diffusions of both O and metal (Ta or Hf) ions become faster with the increase of O vacancy concentrations. The O/Ta ionic conductivity in a-TaO_x is 3~5 orders higher than that of O/Hf in a-HfO_y at the same O content. To our surprise, in the a-TaO_x with high O vacancy concentration (i.e., x = 1.5 and 1), the diffusion of Ta becomes comparable to that of O in a wide range of temperature (from 300K to 1673K). On the other hand, the diffusion of Hf in the a-HfO_y (y = 1 and 0.75) is 1 order smaller than that of O at 1673K, and the diffusion coefficients ratio between Hf and O becomes gradually larger with the decrease of temperature. Based on these results, we propose that, in the low resistance state (or high O vacancy concentration), the diffusion of metal ions is non-negligible in metal-oxide based resistive switches, especially in the a-TaO_x.

1. Introduction

O-deficient metal-oxide based resistive switching device has attracted considerable attention due to its high scalability, fast switching speed, low power consumption and potential application in next-generation resistive random access memories (RRAMs).[1] The resistive switch has a simple metal-insulator-metal (MIM) structure where an insulator (HfO_x,[2] ZrO_x,[3] TaO_x,[4] and NbO_x [5] *etc.*) layer is sandwiched between two electrically conductive electrodes. A pristine resistive switch with a high resistance state (HRS) can be switched into a low resistance state (LRS) by applying bias voltage, and the polarities of bias voltage in the SET (from HRS to LRS) and RESET (from LRS to HRS) operations of the switch are opposite to each other.

So far, amorphous TaO_x (a-TaO_x) and HfO_y (a-HfO_y) based resistive switches have been extensively reported in the literature, and show extremely high endurance, compared to RRAMs using other materials.[2,4] It is believed that the switching mechanism of resistive switches based on O-deficient materials can be ascribed to the drift/diffusion of O ions or vacancies driven by the electric field.[1] However, the role of metal ions diffusion has never been considered yet. In fact, several decades ago, Davies et al.[6] and Fehlner et al.[7] have found the diffusion of both metal and O species during the growth of oxide films such as in Al_2O_3, Nb_2O_5 and Ta_2O_5, though only O diffusion is observed in the cases of HfO_2, TiO_2 and ZrO_2 at room temperature. In addition, the diffusion of Ta has been observed in Ta/SiOCH interface, in which Ta atom is firstly oxidized into TaO_x, and then Ta ions could drift along with the applied electric field.[8] Thus, to deepen the understanding on the switching mechanism in O-deficient-materials (such as a-TaO_x and a-HfO_y) based resistive switches, it is strongly desirable to examine the switching processes more closely, especially the contribution from the diffusion of metal ions. We take this by using first-principles calculations.

2. General Instructions

Computational Methods

All calculations except those on transport properties were performed using the Vienna ab initio simulation package (VASP).[9] The model for amorphous Ta_2O_5 (a-Ta_2O_5) was generated using the melt quenching method. The a-Ta_2O_5 model consists of 32 Ta and 80 O atoms, and the lattice constants are a = b = 14.68 Å, and c = 8.19 Å. To generate the models for a-TaO_x (x = 2, 1.5 and 1), the corresponding numbers of O atoms were removed randomly from the a-$Ta_{32}O_{80}$, and melt quenching and subsequent relaxation (of both ionic position and cell volume) were performed. Similar procedure is also applied to generate amorphous HfO_y (a-HfO_y, y = 1.5, 1 and 0.75) structures, where the a-HfO_2 model consists of 36 Hf and 72 O atoms with the lattice constants a = b = 11.45 Å, and c = 10.23 Å. For all the a-TaO_x and a-HfO_y structures, $2 \times 2 \times 4$ *k*-points were used during the optimization, and $4 \times 4 \times 8$ *k*-points were adopted for examining the electronic properties. The convergence criterion for the optimization was the maximum force acting on an atom to be smaller than 0.02 eV/Å. Molecular dynamics (MD) simulation is carried out with the time step of 1fs.

Results and Discussion

To estimate the O/Ta and O/Hf diffusion in a-TaO_x (x = 2, 1.5 and 1) and a-HfO_y (y = 1.5, 1 and 0.75), we have generated time-average mean square displacement (MSD) plots at different temperatures, namely 873K, 1073K, 1273K, 1473K and 1673K. The time length (9 ps equilibration plus 30 ps MD run) employed for all temperatures considered is sufficient to observe the diffusive regime in the a-TaO_x and

a-HfO_y. MSD increases linearly with time, and the increase in MSD also occurs with increase in temperature. The diffusion coefficient and activation energy can be extracted through a simple linear fitting scheme to the Arrhenius plot in Fig.1 and 2.

Fig. 1 Computed diffusion coefficients of a-TaO_x.

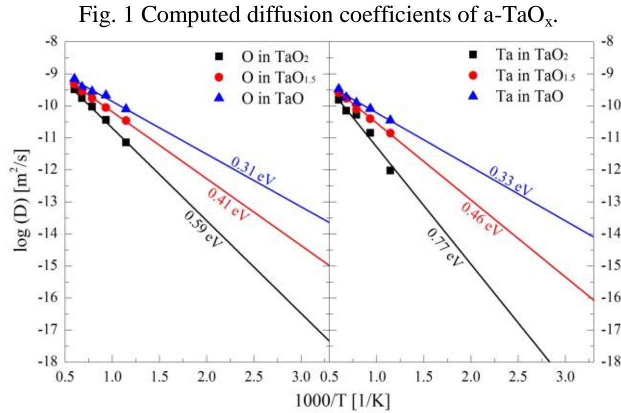
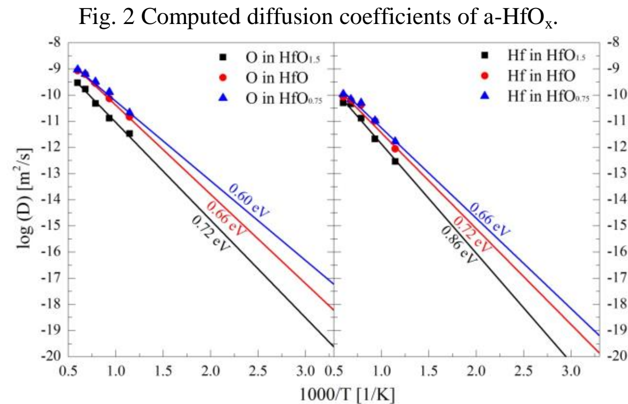


Fig. 2 Computed diffusion coefficients of a-HfO_x.



It is found that both O/Ta and O/Hf diffusions are strongly related to the O stoichiometry in the suboxide: at a given temperature, the lower the O content, the faster the O/Ta or O/Hf diffusion. The calculated activation energies for O self-diffusion in a-TaO_x (x = 2, 1.5 and 1), 0.59, 0.41 and 0.31 eV, respectively, decrease with the increase of the O vacancy concentrations. These results agree well with the experimentally estimated averaged activation energy for O atoms diffusion into Ta/Ta-suboxide, from 0.29 to 0.45 eV.[10] The estimated activation energies of O in a-HfO_y (y = 1.5, 1 and 0.75) are within the range from 0.60 to 0.72 eV, which is slightly higher than those obtained by Clima et al. using bond-boosted *ab initio* MD simulation (0.57 to 0.66 eV, with y = 1.97, 1 and 0.5).[11] Meanwhile, our calculated diffusion coefficient of O in a-HfO_y lies in the same range (from 10^{-12} to 10^{-9} m^2/s) as that of Clima et al. within the temperature from 873 to 1673K. The activation energy of O diffusion in a-HfO_y is obvious higher than that in the case of a-TaO_x, and the diffusion coefficient of O in a-HfO_x is 3~5 orders lower than that in a-TaO_x at room temperature.

Interestingly, as the increase of O vacancy concentration, the diffusions of Ta and Hf become close to that of O as shown in Fig. 1 and 2. For example, at room temperature, the diffusion coefficients of Ta in a-$TaO_{1.5}$ and a-TaO are only 1 and 0.5 orders lower than those of O, respectively, and the diffusion coefficients of Hf in a-HfO and a-$HfO_{0.75}$ are about 2 orders lower than that of O. Thus, for the a-TaO_x and a-HfO_y with high O vacancy concentration (i.e., $x \leq 1.5$, $y \leq 1$), the diffusion of metal ions is comparable to that of O, especially in a-TaO_x.

3. Conclusions

Our results reveal that the diffusion of both O and metal (Ta or Hf) ions in a-TaO_x and a-HfO_y becomes faster with the increase of O vacancy concentrations. The O/Ta ionic conductivity of a-TaO_x is obviously higher than that of O/Hf in a-HfO_y at the same O content. At the high O vacancy concentrations (i.e., x = 1, y = 0.75), the diffusion coefficients of Ta and Hf are only ~0.5 and ~2 orders lower than that of O at room temperature, respectively. Thus, our results reveal that the diffusion of metal ions should be considered in explaining the switching mechanism of oxygen-deficient-materials based resistive switches, especially in a-TaO_x.

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