The conductive path in HfO$_2$: first principles study

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Abstract: The conductive path formed by the interstitial Ag or substitutional Ag in HfO$_2$ was investigated by using the Vienna ab initio simulation package based on the DFT theory. The calculated results indicated that the ordering of interstitial Ag ions at special positions can form a conductive path, and it cannot form at other positions. The orientation dependence of this conductive path was then investigated. Various types of super cells are also built to study the rupture of the path, which corresponds to some possible “off” states.

Key words: resistance switching mechanism; DFT; conductive path; lattice orientation
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1. Introduction

Resistive random access memory (RRAM) has been widely studied, for it has many advantages such as a simple manufacturing process$^{[1,2]}$, high read and write speeds, high density storage and low power consumption$^{[3,4]}$. In addition, it is considered to be one of the most promising candidates for the next generation of nanoscale nonvolatile memory$^{[5]}$. At present, many research groups are studying RRAM based on Ag doped HfO$_2$ due to its compatibility with semiconductor fabrication processes and its ability to lower reset voltages $V_{\text{reset}}$$^{[6]}$. However, a systematic interpretation of the microscopic details of the role of Ag ions in the formation of conductive filament is still lacking. Several methods can be employed to study the mechanism, including testing the $I–V$ characteristic$^{[7,8]}$ or the transition electron microscopy (TEM)$^{[9–11]}$.

However, we use the first principles method to study the contribution of doped Ag to the electrical conduction in this paper. The energy band, projected density of states (PDOS) and the isosurface plot of partial charge density were calculated to investigate the conductive path.

2. Methods

The Vienna ab initio simulation package (VASP) is used to study the electrical structures of a HfO$_2$ cell with interstitial Ag and substitutional Ag$^{[12]}$. A plane-wave basis set with a cutoff energy of 400 eV is adopted, the projector augmented-wave (PAW) method and the generalized gradient approximation (GGA) are used to describe the electron–ion and electron–electron interaction$^{[13,14]}$. The supercell geometries are fully relaxed until atomic forces are smaller than 0.001 eV/Å. Monoclinic HfO$_2$ is used because the bases structure of amorphous HfO$_2$ is monoclinic$^{[15]}$.

3. Results and discussion

According to the geometric symmetry, the Ag ions can occupy four possible positions in one HfO$_2$ cell. The possible interstitial positions for Ag ions are marked with 1, 2, and 3, and the green ball is the possible substitutional position where a Hf ion is replaced by a Ag ion, as shown in Fig. 1.

Based on the first-principle methods, we calculate the defect formation energy of interstitial Ag and substitutional Ag. The result is shown in Table 1. The formation energy of Ag at position 3 is the lowest one. Thus, the most stable structure for one unit cell of HfO$_2$ with one doped Ag ion is found to be the Ag at position 3.

Next, we focus on a HfO$_2$ cell with one Ag ion at position 3. The energy bands are calculated, and we find that the...
interstitial Ag induces an energy sub-band just below the conduction band across the Fermi level, shown as the dotted line in Fig. 2. In order to know the components of the defect energy, the PDOS is also calculated, as shown in Fig. 3. The PDOS reveals that the defect state at the Fermi level consists of O(p), Hf(d) and Ag(p, d) states.

Also we simulate the isosurface plot of the partial charge density of the impurity energy state. Obviously, a connected path is formed via the interstitial Ag, as shown in Fig. 4. It is known that the conductive filament only appears at the conductive path.

Furthermore, in order to find the relationship between the “connected path” in a unit cell and the conductive filament in HfO₂ material with interstitial doped Ag, we build a super cell, which consists of four unit cells. Figure 5 shows this super cell from the views of [100], [010] and [001], respectively, and there is one Ag ion at position 3 in each unit cell.

Then we simulate the isosurface plot of partial charge density along three directions, and the result corresponding to the defect state for each super cell is calculated, as shown in Fig. 6. In fact, the conductive path is formed only in the [010] crystal orientation, due to the electric interactions between different ions.

Finally, the electron localization function is used to illustrate the direction of the conductive path\textsuperscript{[16]}. Figure 7 shows the electron localization function corresponding to the three orientations, in which the red region (value 1) corresponds to a perfectly localized region, illustrating a mostly covalent bonding character, the green region (value 0.5) corresponds to electron gas showing metallicity, and the values between 0 and 0.5 display the regions of low electron density, where strong ionic interactions dominate. It is seen that the electron gas is connected to form a channel in the crystal orientation. In other words, a conductive path is formed only in the [010] direction. Here, it should be noted that the calculations do not consider the oxygen vacancy because we are only interested in the effect of the doped Ag.

So, the conductive filament in HfO₂ material with interstitial Ag induces an energy sub-band just below the conduction band across the Fermi level, shown as the dotted line in Fig. 2.
4. Conclusion

We have investigated the contribution of Ag ions to the electrical conductivity in HfO$_2$ material. It was found that just one Ag ion at position 3 per unit cell can form the conductive filament, and the conductive filament is formed along the [010] crystal orientation. The connected filament will not form in the other directions. Also, some rupture states of the conductive filaments are studied.
Fig. 8. (Color online) Isosurface plot of the partial charge density corresponding to the defect states for the five models. Red balls are O, blue balls are Ag, and remaining balls are Hf. The left is coordinate system. a is the ordering Ag along [010], b is the type with one Ag missed, c missed two Ag ions, d missed 3 Ag ions, and e is the type with one Ag in other site.

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