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_{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 interactivity[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

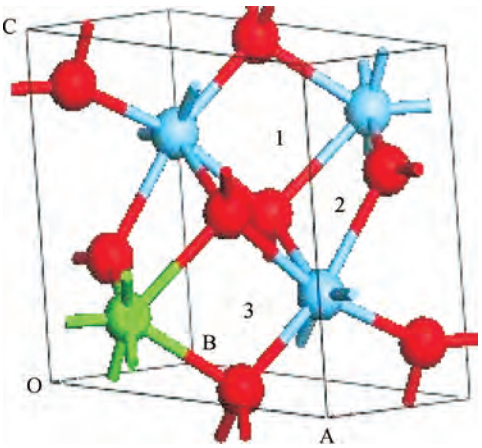

Fig. 1. (Color online) Unit cell of HfO_2. 1, 2, and 3 are the possible interstitial sites, and the green one is the possible substitutional site. The red balls are O ions, the green ball and the other three balls are Hf ions.

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Table 1. Formation energy.

Sites	Position 1	Position 2	Position 3	Substitutional site
Formation energy (eV)	6.53	6.6	5.90	12.72

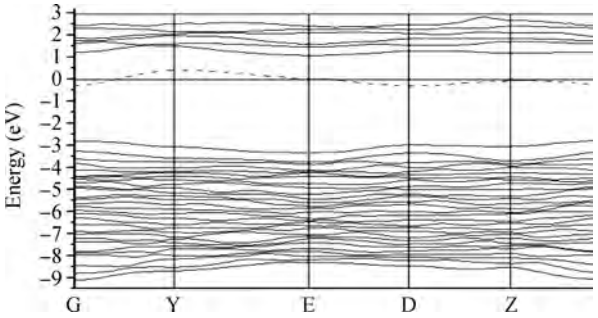

Fig. 2. Energy band structure of HfO_2 with an interstitial Ag at site 3. The dark line near 0 eV is the Fermi level.

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 HfO_2 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[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 HfO_2 material with intersti-

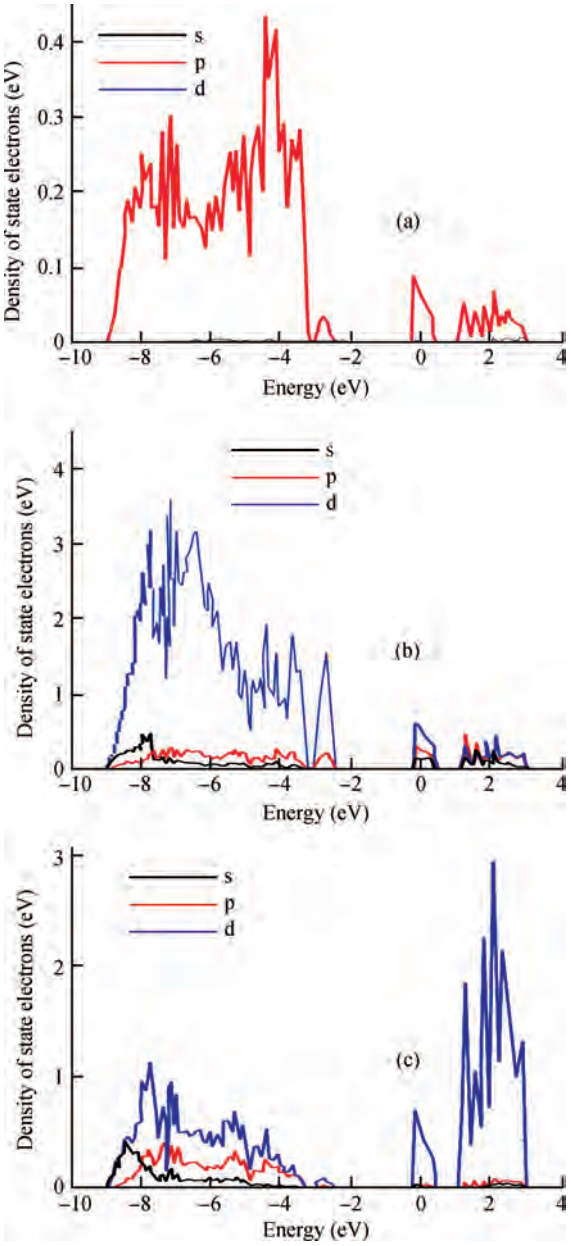

Fig. 3. (Color online) Projected density of state. (a) The PDOS of O. (b) The PDOS of Ag. (c) The PDOS of Hf. The dark line is s state, red line is p state, and the blue line is d state.

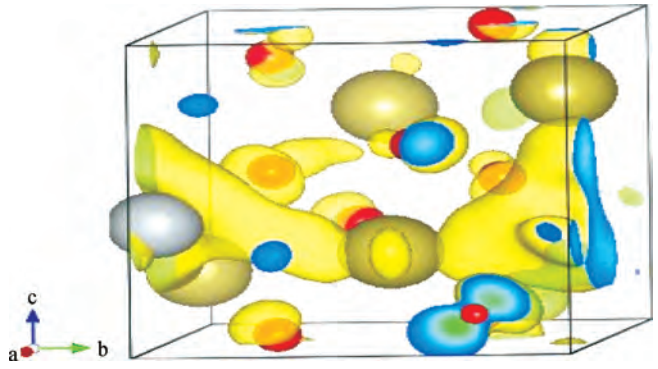

Fig. 4. (Color online) Isosurface plot of partial charge density caused by the defect state. Red balls are O, silver gray ball are Ag, and the rest are Hf.

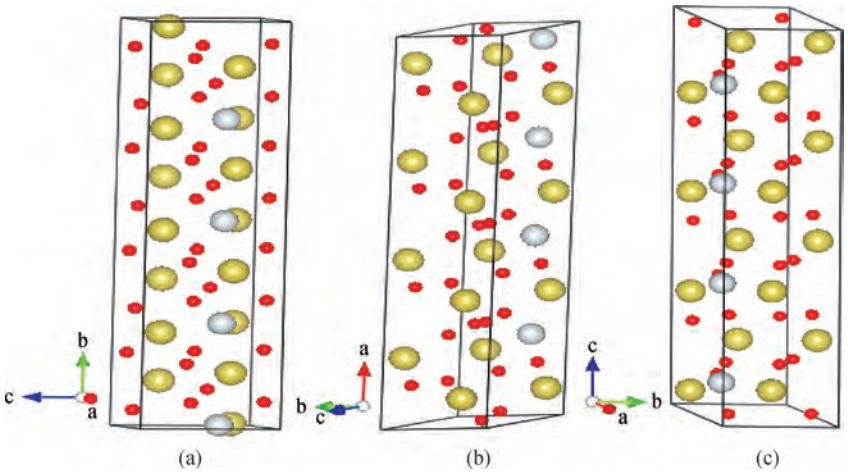

Fig. 5. (Color online) (a) Viewed from [010] lattice orientation. (b) Viewed from [100] lattice orientation. (c) Viewed from [001] lattice orientation. The red balls are O, blue balls are Ag, and the rest balls are Hf.

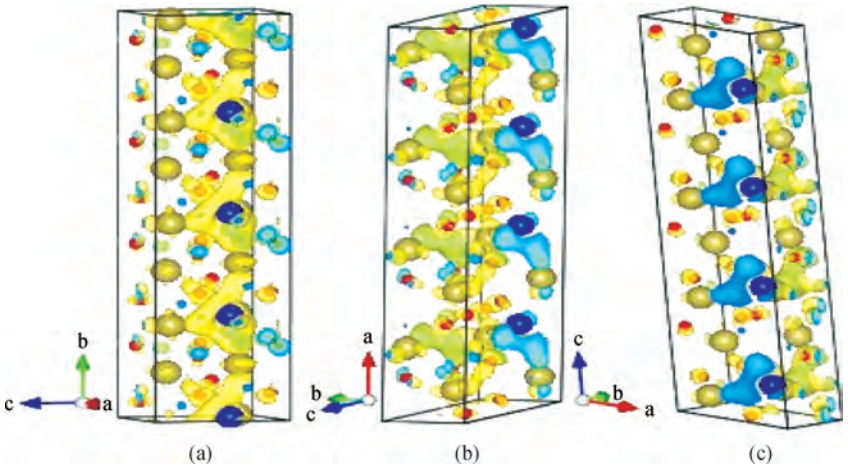

Fig. 6. (Color online) Isosurface plot of partial charge density corresponding to the defect state for the super cells of HfO_2 along the [010] lattice orientation and [100] lattice orientation and [001] lattice orientation (c) show in figures a, b, c. And the coordinate system is given in Fig. 5.

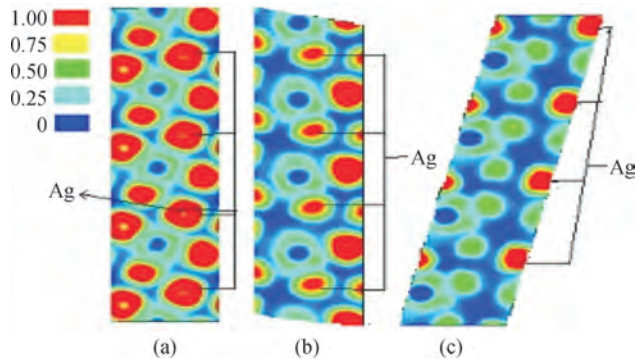

Fig. 7. Electron localization function corresponding to the three types of super cells. 0–0.5 is low electron density, 0.5 is electron gas, 1 is perfect localization.

tial doped Ag is orientation dependent; once the HfO_2-based RRAM is set, the conductive filaments are formed in the [010] direction. But what states do the conductive filaments become? Here, we use five models to investigate the RRAM at the "on" state and "off" state, corresponding to the conductive path conduction or rupture, as shown in Fig. 8. All five models contain four unit cells stacked along the [010] direction. In the first model, four Ag ions are the same at each unit cell, corresponding to position 3. There are three Ag ions, two Ag ions and one Ag ion in the second, third and fourth models respectively. In the last one, there are four Ag ions in the super cell, but one Ag ion is not at the interstitial position of 3. The first type of super cell forms a connected path. In other words, it is in the "on" state. The remaining models are the possible "off" states.

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.

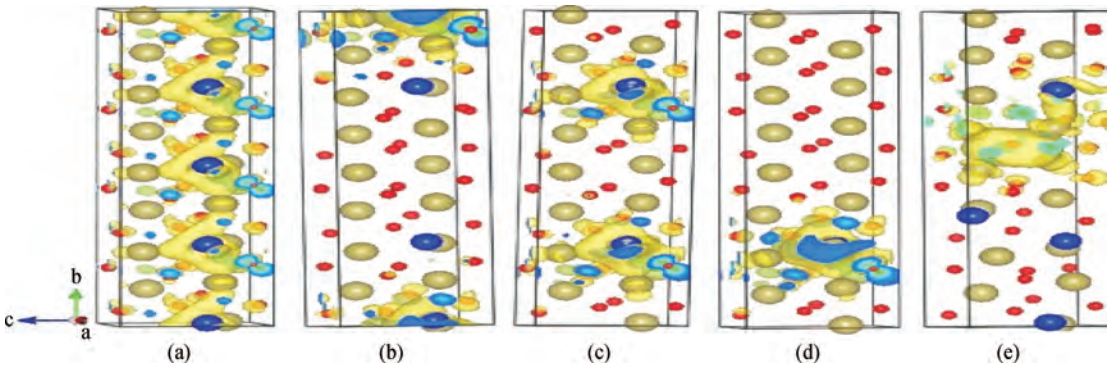

Fig. 8. (Color online) Isosurface plot of the partial charge density corresponding to the defect states for the five models. Red balls are O, blue balls are Ag, and remaining balls are Hf. The left is coordinate system. a is the ordering Ag along [010], b is the type with one Ag missed, c missed two Ag ions, d missed 3 Ag ions, and e is the type with one Ag in other site.

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