

Research Article

Nature of the Interstitials in Titanium Dioxide and Their Impact on Transmission Coefficient: *Ab Initio* Calculations

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The *ab initio* calculations about the properties of the interstitials doping in the rutile TiO₂ and their impact on the transport coefficients are reported. As the doping of the Zr or Ti interstitials in the TiO₂, the lattice Ti⁴⁺ ions acquire the excess electrons so reduced to the Ti³⁺ or Ti²⁺ ions. However, the Cu interstitials could not lose enough electrons to reduce the lattice Ti⁴⁺ ions. Furthermore, the Ti or Cu interstitials in the ZrO₂ also are unable to promote the lattice Zr⁴⁺ ions to form the lattice Zr³⁺ or Zr²⁺ ions. The high transport coefficients are observed in the defected TiO₂ with the Ti or Zr interstitials as the high concentration of the Ti³⁺ or Ti²⁺ ions. So, the Zr interstitials are the favorable choice for the extra-doping to improve the transport properties in the TiO₂-based resistive random access memory.

1. Introduction

In the recent years, the resistive random access memory (ReRAM) has been extensively studied due to its high operation speed, the long retention time, and the low power consumption. It always uses the metal-insulator-metal as the basic structure. Various transition metal oxides, such as TiO₂, CuO, HfO₂, and ZrO₂, are applied as the insulator of the ReRAM cells [1, 2]. For the preeminent resistive switching characteristic, TiO₂ is one of the most promising materials for the insulator in ReRAM. Up to now, one of the major challenges is the large variation of the switching parameters induced by the random formation of the conduction path under the external electrical fields. It needs to clarify the resistive switching mechanisms to solve this problem and finally improve the reliability of these devices. For the insulator of the rutile TiO₂, the leakage currents are often explained with the gap states originating from the point defects, such as the oxygen vacancies and Ti interstitials [3–8]. In contrast, these defects could improve the resistive switching characteristics. When doping in the rutile TiO₂,

it is necessary to investigate the role of the interstitials in the conduction path for the resistive switching, such as Cu interstitials and Zr interstitials. Many novel systems, such as Pt/ZrO₂/TiO₂/Pt, Pt/Ti/TiO₂/Pt, Cu/ZrO₂:Cu/Pt, and Cu/ZrO₂:Ti/Pt, have been proposed to explain the resistive switching mechanism [9–11]. In this work, we would address the impact of the Cu/Ti/Zr interstitials on the fine structure of the defected TiO₂.

2. Method

The structural model of the perfect rutile TiO₂ is presented with a primitive cell (lattice parameters $a = b = 4.594 \text{ \AA}$, $c = 2.959 \text{ \AA}$). We construct $1 \times 1 \times 6$ supercells ($a = b = 4.594 \text{ \AA}$, $c = 17.754 \text{ \AA}$) as the initial structural model. The Ti interstitials are doped in the $1 \times 1 \times 6$ supercells at (2.297, 2.297, 2.959), (2.297, 2.297, 8.877), and (2.297, 2.297, 14.795). The Cu interstitials or the Zr interstitials are doped in the defected TiO₂ at the same coordinates as Ti interstitials as shown in Figure 1(a). We build the $1 \times 1 \times 3$ supercells of the defected ZrO₂ ($a = b = 5.070 \text{ \AA}$, $c = 15.210 \text{ \AA}$) with the Ti interstitials

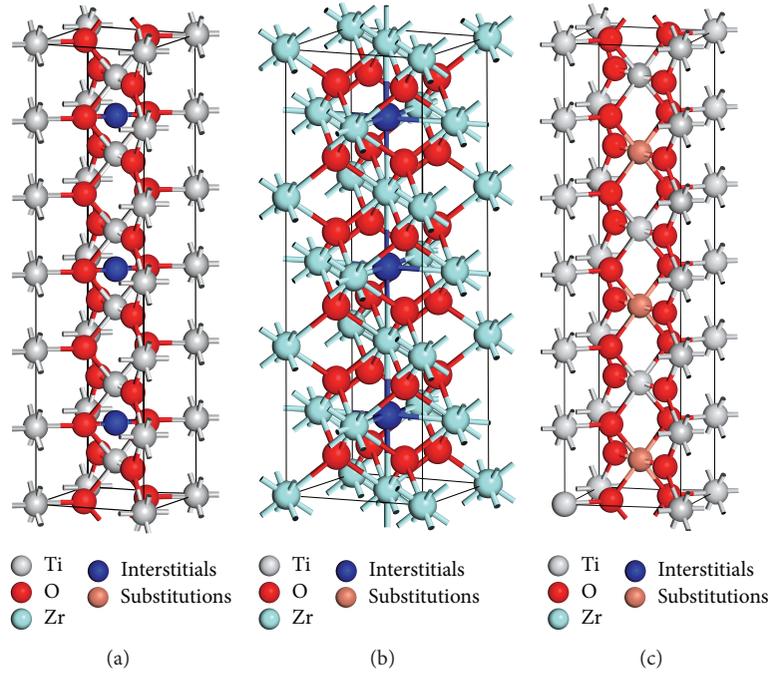


FIGURE 1: Configuration of the defected TiO_2 with the interstitials (a), the defected ZrO_2 with the interstitials (b), and the defected TiO_2 with the substitutions (c).

or the Cu interstitials at (2.535, 2.535, 2.630), (2.535, 2.535, 7.690), and (2.535, 2.535, 12.716) as shown in Figure 1(b). For the comparison, we use the $1 \times 1 \times 6$ supercells of the defected TiO_2 with the Cu substitutions or the Zr substitutions for the Ti atoms at (2.535, 2.535, 1.480), (2.535, 2.535, 7.398), and (2.535, 2.535, 13.316) as shown in Figure 1(c). All the structures are relaxed under the electric field of 10.4 MV/cm.

We explore the DMol³ program to carry out the spin polarized density functional calculations. These geometries are optimized using the double-numeric quality basis set (DNP) equal to 3.5, together with the PBE (Perdew, Burke, and Ernzerhof) gradient-corrected functional to describe the exchange and correlation effects [12]. Special sampling points in the Brillouin zone are used with the Monkhorst-Pack schemes of $3 \times 3 \times 1$ k-point meshes [13]. A thermal smearing of 0.01 Ha (1 Ha = 27.2114 eV) and a global orbital cutoff of 5.2 Å are employed to improve computational performance. The wave basis set with a cutoff energy of 400.0 eV is adopted. The tolerances of energy, gradient, and displacement convergence for the geometric optimization and energy calculation are set to 1×10^{-5} Ha, 2×10^{-3} Ha/Å, and 5×10^{-3} Å, respectively. We further use Virtual NanoLab program to calculate the transmission coefficient with the DFT-PBE function at 300 K. The cutoff of the grid mesh is set to 40 hartree. The basis sets of double zetas and polarization orbitals (DZP) are performed in the transport simulations.

3. Results and Discussions

Figure 2 depicts the slices of the deformation electron density in [110] for the defected TiO_2 with the Cu interstitials (a), Ti interstitials (b), Zr interstitials (c), and the corresponding

white-black views (d–f). The gray balls and the red balls indicate Ti-atoms and O-atoms, respectively. The brown balls, the blue balls, and the green balls separately stand for the Cu interstitials, Ti interstitials, and Zr interstitials. We set the spectrum of the deformation electron density to the blue-green-red from -0.1 to 0.1 electrons/Å³. The deficiencies for the electrons are indicated in blue color, while the enrichment is in red color. In Figure 2(a), it would be seen that some regions with blue color lie around the Cu interstitials. They are also correspondingly found in the dark round in Figure 2(d). It means that the Cu interstitials lose the electrons to form the ionic bonds with the nearby O-ions. The weak electron-clouds with light red locate among the Ti(2) atom and the Ti(3) atom, the Ti(4) atom and the Ti(5) atom. The light gray in the corresponding regions is found in Figure 2(d). It means the formation of the weak Ti-Ti bonds as the doping of the Cu interstitials. In Figure 2(b), the aggregated electron-clouds with the dark red color would be seen among the lattice Ti-ions and the Ti interstitials. These red electron-clouds seat at the bonds of the Ti-Ti bonds. They are corresponding to the belt-like dark regions in Figure 2(e). In Figure 2(c), the aggregated electron-clouds between the Ti-ions and the Zr interstitials show the weaker than those in Figure 2(b). The more irregular belt-like dark regions are shown in Figure 2(f). The introduction of the Ti interstitials and the Zr interstitials could not induce the formation of the ionic bonds with the lattice O-ions. We would employ the Mulliken charges to explain the difference of the deformation electron density [14].

Figure 3 shows the Mulliken charge of the three types of the defected TiO_2 with the interstitials. Ti(1)–Ti(6) indicate the lattice Ti-ions, and i(7)–i(9) mean the interstitials

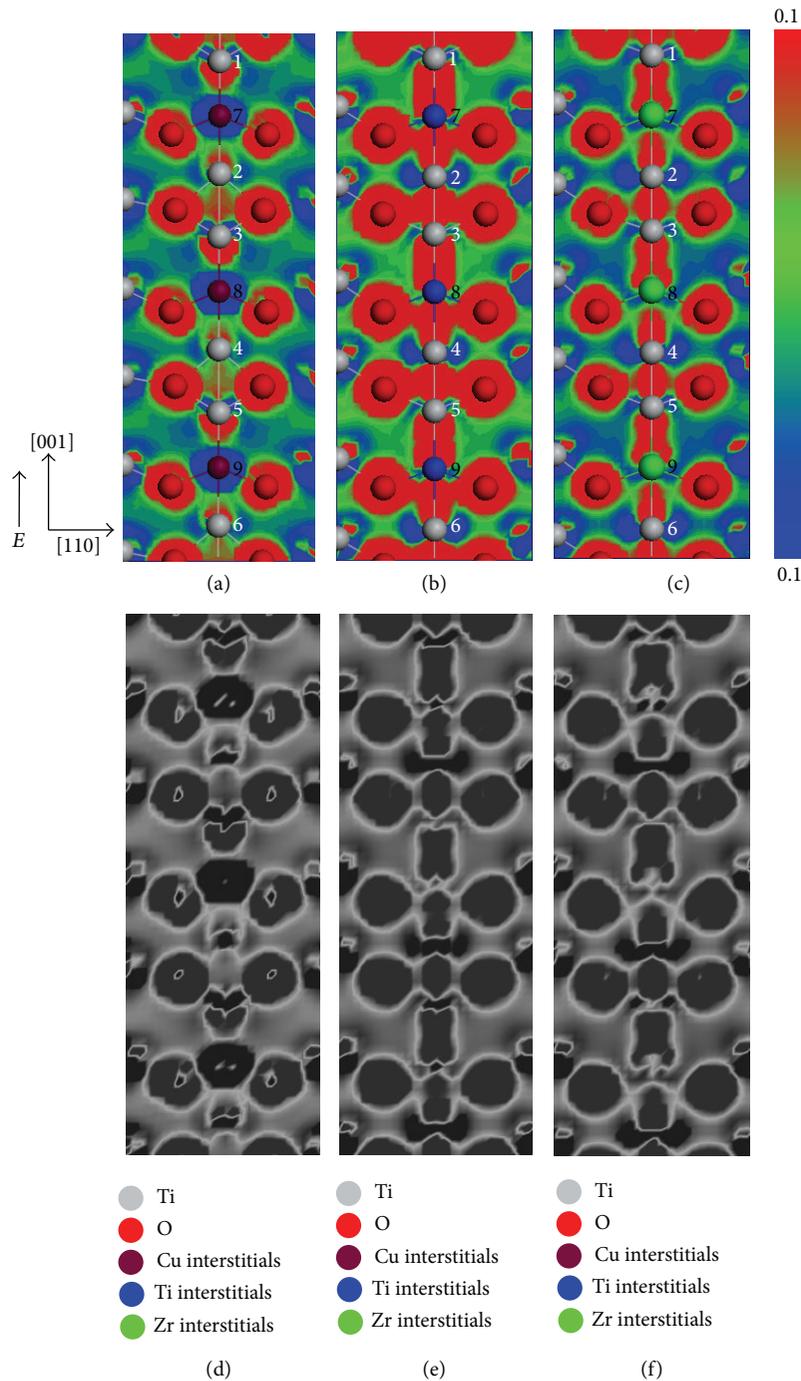


FIGURE 2: Deformation electron density in [110] for the defected TiO_2 with the Cu interstitials (a), Ti interstitials (b), Zr interstitials (c), and the corresponding white-black views (d–f).

with Number 7–Number 9 as shown in Figure 2. We use the $\text{Ti}_{12}\text{Cu}_3\text{O}_{24}$, $\text{Ti}_{15}\text{O}_{24}$, and $\text{Ti}_{12}\text{Zr}_3\text{O}_{24}$ to stand for the structures in Figure 2. The Mulliken charges of the Ti-ions in perfect TiO_2 are 1.721 eV. The Mulliken charges of the lattice Ti-ions in $\text{Ti}_{12}\text{Zr}_3\text{O}_{24}$ (49.9% of 1.721 eV) are smaller than those in $\text{Ti}_{15}\text{O}_{24}$ (66.8%) and $\text{Ti}_{12}\text{Cu}_3\text{O}_{24}$ (80.4%). The Mulliken charges for the Zr interstitials in $\text{Ti}_{12}\text{Zr}_3\text{O}_{24}$ are larger than those for the Ti interstitials in $\text{Ti}_{15}\text{O}_{24}$ and Cu

interstitials in $\text{Ti}_{12}\text{Cu}_3\text{O}_{24}$. The Mulliken charges for the lattice Zr ions in the perfect ZrO_2 are 2.292 eV. So the Zr interstitials in $\text{Ti}_{12}\text{Zr}_3\text{O}_{24}$ lose more electrons and the corresponding Ti atoms are reduced to the Ti^{3+} or Ti^{2+} ions with the smallest Mulliken charges. The electric field of 10.4 MV/cm redistributes the electrons which transfer between the lattice Ti atoms and the interstitials. It would explain the difference of Mulliken charges among the Ti(1)–Ti(6) atoms.

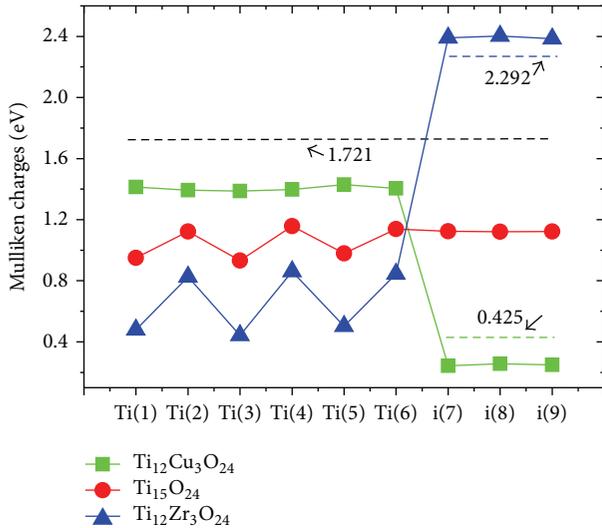


FIGURE 3: Mulliken charges in the defected TiO_2 with the interstitials.

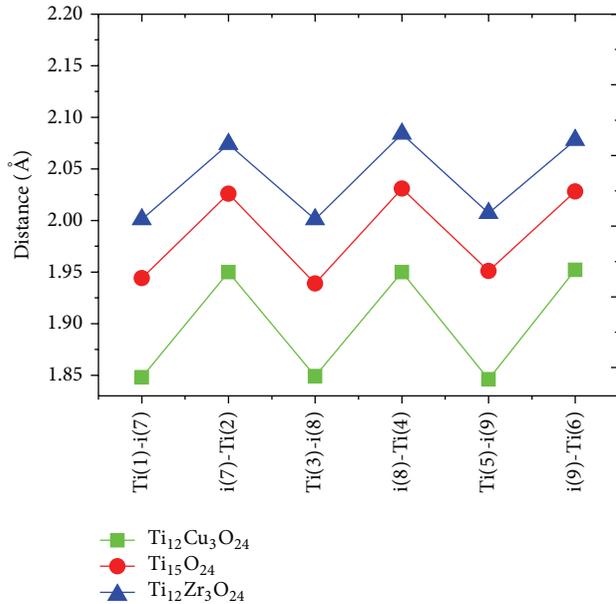


FIGURE 4: Distances among the lattice Ti-ions and the interstitials in the defected TiO_2 with the interstitials.

Figure 4 shows the distances among the lattice Ti-ions and the interstitials. The Ti(1)-i(7) means the distance between the lattice Ti(1) atom and the interstitial of Number 7. The distances between the interstitials and the lattice Ti-ions in the $\text{Ti}_{12}\text{Cu}_3\text{O}_{24}$ are shorter than those in $\text{Ti}_{15}\text{O}_{24}$ and $\text{Ti}_{12}\text{Zr}_3\text{O}_{24}$.

Figure 5 shows the partial density of states for the defected TiO_2 with the Cu interstitials (a), Ti interstitials (b), and Zr interstitials (c). The curves with the light green color, the red color, the blue color, the dark green color, and the pink color separately indicate the p states, the d states, the sum states, the DOS induced by the Ti-ions (Ti(1)-Ti(6)), and the DOS

induced by the interstitials. In Figure 5, all the conduction bands are split into two parts, t_{2g} and e_g orbitals of the Ti-ions. The t_{2g} states have a lower energy than the e_g states. They originate from the antibonding interactions of the Ti-3d states and the O-2p states due to the doping of the interstitials. The Fermi energy level lies in the defect energy level near the valence band maximum in Figure 5(a) and in the valence bands in Figures 5(b) and 5(c). It is corresponding to the two types of the conduction mechanisms, the hole-dominated and the electron-dominated, respectively. The defect energy levels lie on the top of the valence band maximum (VBM) in Figure 5(b), much deeper states than the others in Figures 5(a) and 5(c). They are largely composed of the lattice Ti-3d states rather than the Cu-3d states or the Zr-3d states. It also shows the strong hybridization between the O-2p and the Ti-3d orbitals. So it induces the electrons strongly localized at the Ti^{3+} or Ti^{2+} trap centers.

In Figures 2–5, it could be clearly seen that the interstitials in the defected TiO_2 can induce the lattice Ti atoms to Ti-ions with the lower valence. Next, we continue to consider the defected ZrO_2 with the Ti interstitials and the Cu interstitials.

Figure 6 depicts the deformation electron densities in [110] and the partial density of states for the defected ZrO_2 with the Ti interstitials (a, c) or Cu interstitials (b, d). Figure 6(e) shows the partial density of states for the perfect ZrO_2 . In Figure 6(a), less electron-cloud with red color locates around the lattice Zr-ions and the Ti interstitials. The Mulliken charges of the Ti interstitials are equal to 0.061 eV, 0.058 eV, and 0.063 eV. It means that these Ti interstitials lose little electrons and keep the metallic characteristics. The Mulliken charges of the lattice Zr-ions are about 2.076 eV (90.5% of 2.292 eV), which show the less reduction by Ti interstitials. In Figure 6(b), some regions with weak blue color lie around the Cu interstitials. The Mulliken charges of the Cu interstitials are equal to about -0.058 eV, -0.145 eV, and -0.031 eV. It means that these Cu interstitials even gain little electrons. The Mulliken charges of the lattice Zr interstitials are about 2.105 eV (91.8% of 2.292 eV), which also show the less reduction by Cu interstitials.

In Figure 6(c), the Fermi energy level locates in the defect energy levels on the bottom of the conduction band minimum, which means the n -type semiconductor characteristics. The defect energy levels mainly originate from the contribution of Ti-3d atom orbital of the Ti interstitials. The band gap is 0 eV. In Figure 6(d), the defect energy levels on the top of the valence band maximum mainly originate from the cocontribution of the Cu-3d atom orbital of the Cu interstitials and the O-2p atom orbital of the lattice O-ions. They shift the valence bands edge to the higher energy to narrow the band gap to 2.176 eV, which appears to be smaller than the band gap of 2.573 eV in the perfect ZrO_2 in Figure 6(e). The Fermi energy level locates on the bottom of the conduction band minimum, which also means the n -type semiconductor characteristics.

We have addressed the defected TiO_2 and the defected ZrO_2 with the interstitials. The Zr interstitials in the defected TiO_2 reduce the lattice Ti-ions to the Ti^{3+} or Ti^{2+} ions. However, the Ti interstitials in the defected ZrO_2 do not

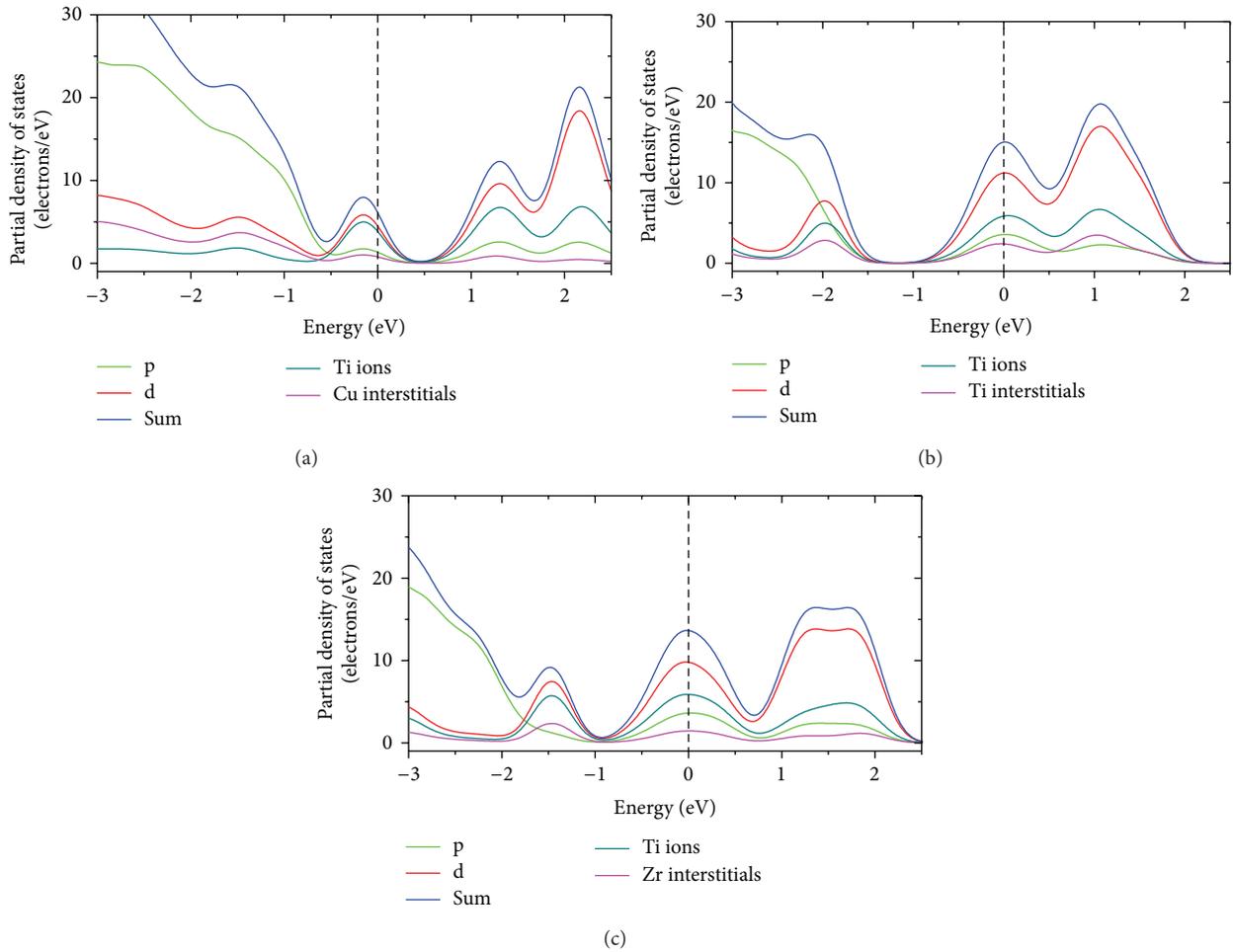


FIGURE 5: Partial density of states for the defected TiO_2 with the Cu interstitials (a), Ti interstitials (b), and Zr interstitials (c).

reduce the lattice Zr-ions. Next, the Cu substitutions or the Zr substitutions for the lattice Ti atoms in the defected TiO_2 would be considered.

Figure 7 shows the partial sectional view of the structures in [110] for the defected TiO_2 with Cu substitutions (a) and Zr substitutions (b). The gray balls, the red ball, the pink balls, and the green ball indicate the Ti atoms, the O atoms, the Cu substitutions, and the Zr substitutions, respectively. The data with green color means the Mulliken charges. The Mulliken charges of the Cu substitutions and Zr substitutions in the defected TiO_2 are larger than those in the perfect CuO (0.735 eV) and in the perfect ZrO_2 (2.292 eV). The Mulliken charges of the Ti-ions are larger than 1.59 eV, which appear to be distinct to those in Figure 3. So the Cu substitutions or Zr substitutions in the defected TiO_2 always induce the formation of the Ti^{4+} ions.

Figure 8 shows the partial density of states for the defected TiO_2 with Cu substitutions (a) and Zr substitutions (b). The curves with the light green color, the red color, the blue color, and the dark green color separately indicate the p states, the d states, the sum states, and the DOS induced by the substitutions. The Fermi energy levels locate on the top of the valence band maximum but with the lower energy in

Figure 8(a) than that in Figure 8(b). The defect energy levels in Figure 8(a) lie on the top of the valence bands maximum. So they shift the valence bands edge to the higher energy to narrow the band gap to 1.360 eV. The band gap in Figure 8(b) is 1.632 eV, larger than that in Figure 8(a). These band gaps are still larger than those in Figure 5 in the defected TiO_2 with the interstitials.

Figure 9 shows the transmission coefficients for the defected ZrO_2 with the Cu interstitials (a), the Ti interstitials (b), the defected TiO_2 with the Zr interstitials (c), the Ti interstitials (d), and the Cu interstitials (e). In Figures 9(c) and 9(d), no transmission gap would be found for the defected TiO_2 with the interstitials, while a transmission gap of 0.8 eV in Figure 9(b) in the defected ZrO_2 with the Ti interstitials was found. In Figure 9(a), the transmission coefficient is equal to zero at $-2.1 \text{ eV} \sim -0.6 \text{ eV}$ which is consistent with the density of states as shown in Figure 6(d). In Figures 9(a)–9(d), the transport coefficients appear oscillated above 0 eV. In comparison to Figure 2 and Figure 6, we find that the oscillations originate from the coupling of the electrons and the holes. In Figure 2(b), the large blocks of the electrons enrichment with red color are observed between the O-ions and the Ti-ions, while the relatively small blocks of the

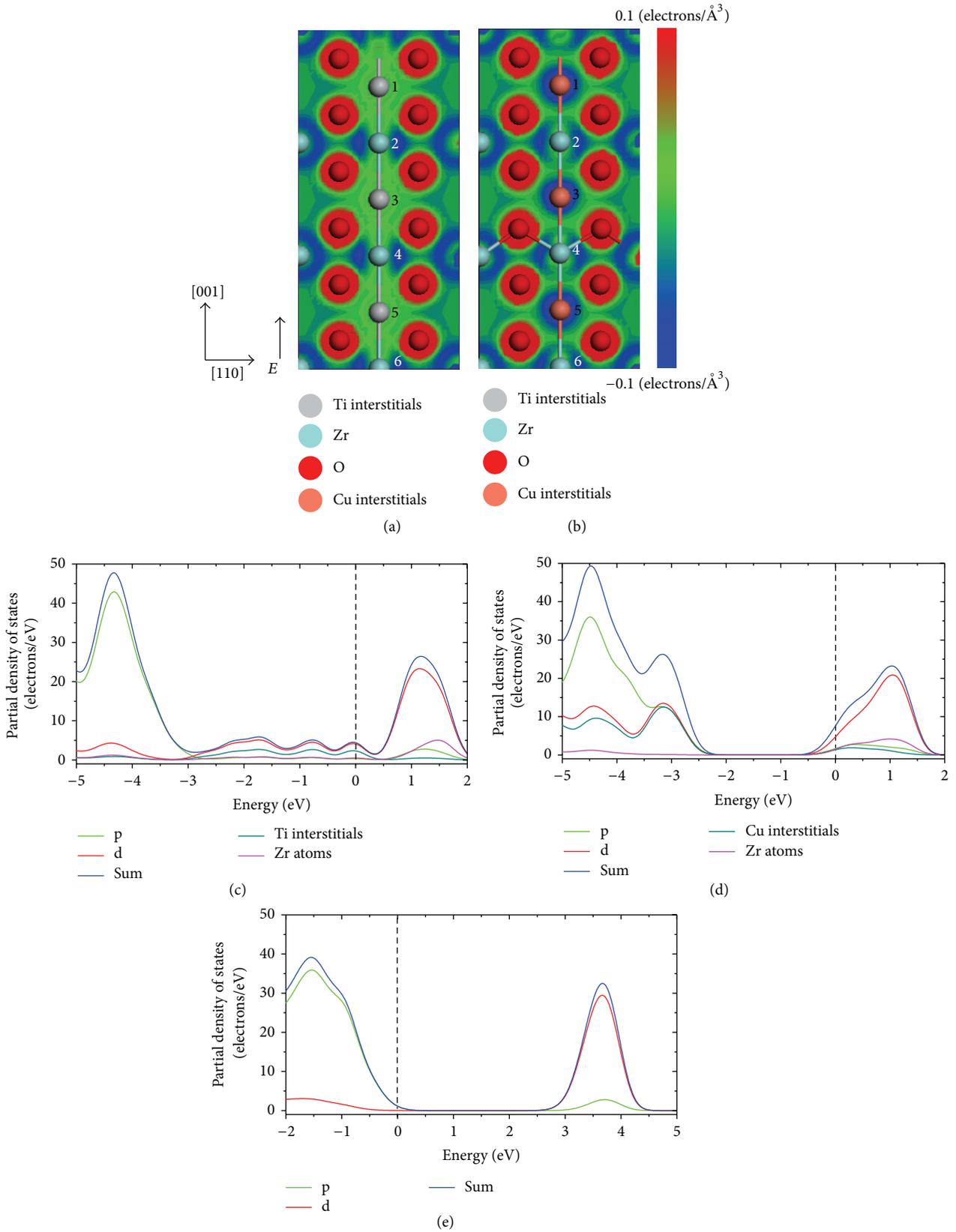


FIGURE 6: Deformation electron density in $[110]$ for the defected ZrO_2 with the Ti interstitials (a) and Cu interstitials (b); partial density of states for the defected ZrO_2 with the Ti interstitials (c) and Cu interstitials (d); (e) density of states for the perfect ZrO_2 .

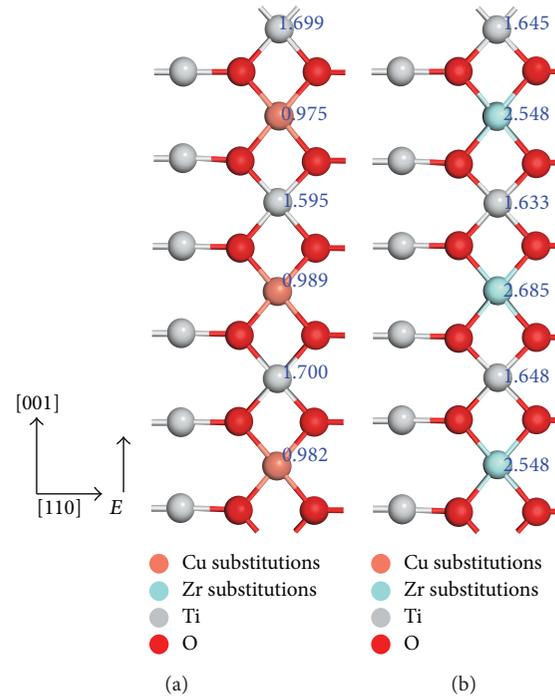


FIGURE 7: Partial sectional view in [110] for the defected TiO_2 with the Cu substitutions (a) and Zr substitutions (b).

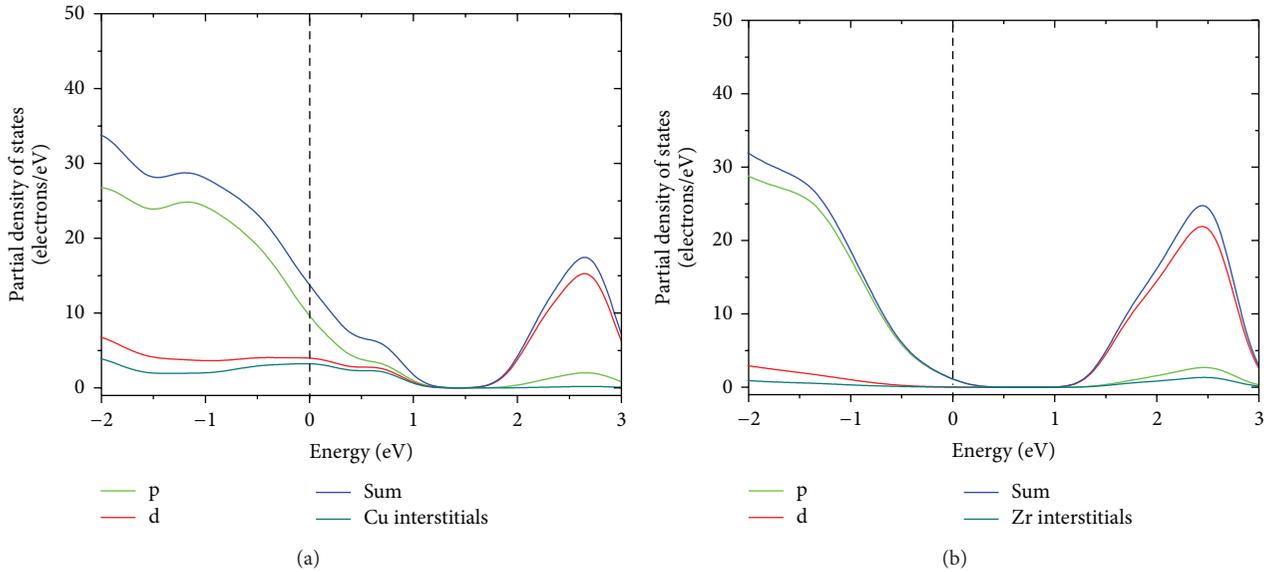


FIGURE 8: Partial density of states for the defected TiO_2 with the Cu substitutions (a) and Zr substitutions (b).

electrons deficiency with blue color or light green color are also found between them. It induces the weak coupling of the electrons and the holes. So the weaker oscillations are found in Figure 9(d) in the defected TiO_2 with the Ti interstitials. In contrast, the large blocks of the electrons deficiency in Figure 6(a) locate around the Ti-ions and the Zr-ions. It shows the severe oscillations in Figure 9(b) as the strong coupling of the electrons and holes in the defected ZrO_2 with the Ti interstitials. The relative Fermi energy levels also could explain these phenomena. The strong hybridization between

O-2p and Ti-3d orbitals decreases the transport coefficients from -1.5 eV to -0.5 eV in Figure 9(c) and from -1.3 eV to -0.7 eV in Figure 9(d). The transport coefficients at -2.0 eV \sim -1.5 eV in Figure 9(c) are lower than those in Figure 9(d) as the lower DOS of the defect energy levels in Figure 5(c) in the defected TiO_2 with the Zr interstitials. So the advanced transport coefficients are found in the defected TiO_2 with the Ti interstitials and then in the defected TiO_2 with the Zr interstitials and the worst in the defected TiO_2 with the Cu interstitials.

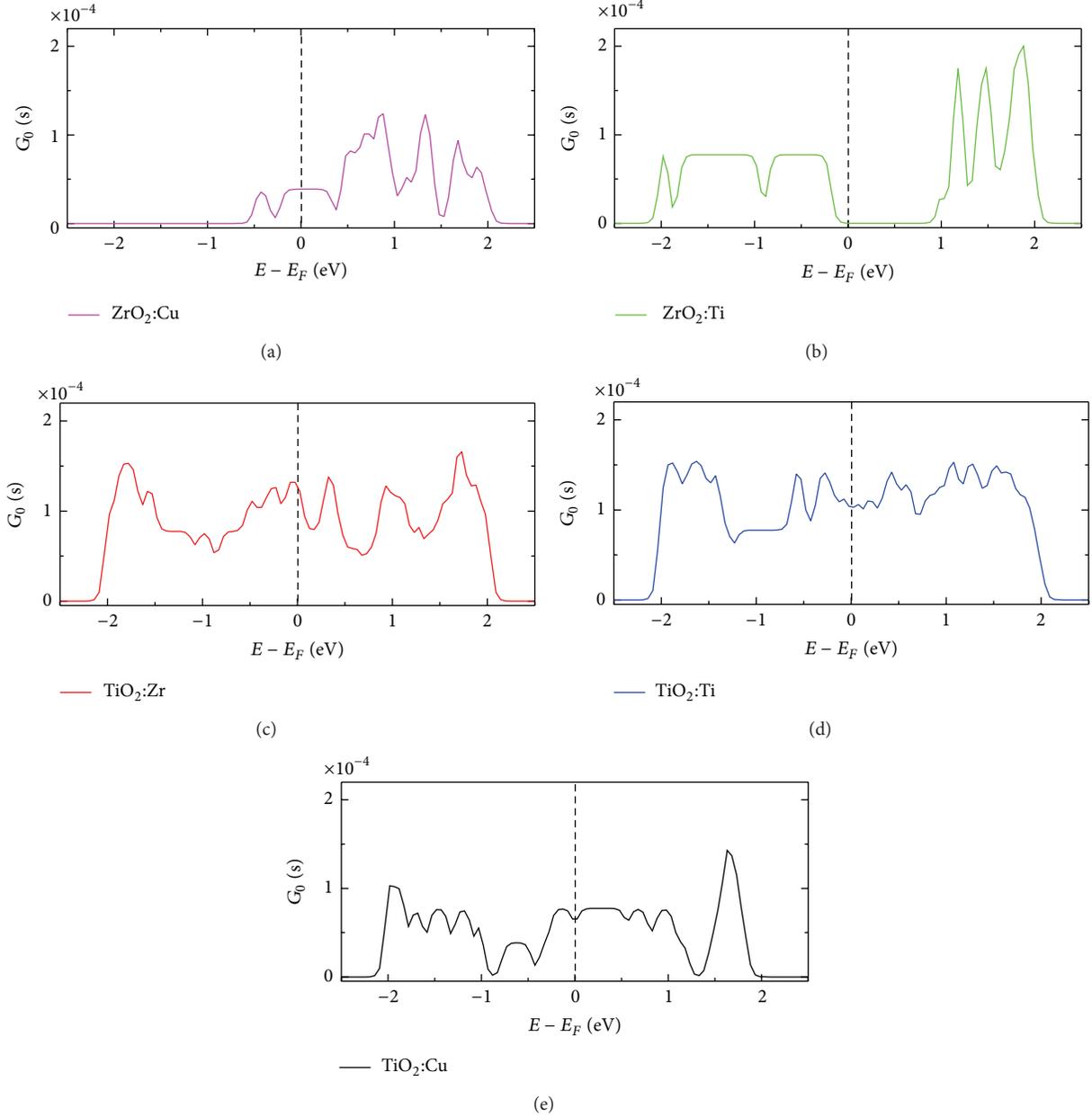


FIGURE 9: Transmission coefficients for the defected ZrO_2 with the Cu interstitials (a), Ti interstitials (b), the defected TiO_2 with the Zr interstitials (c), Ti interstitials (d), and Cu interstitials (e).

The formation energies of the Ti interstitials, the Zr interstitials, and the Cu interstitials are 5.95 eV, 8.86 eV, and 10.24 eV. The better stability of the Ti interstitials self-doping in the TiO_2 improves the transport properties. For the Cu atoms or Zr atoms, their steady coordination valences with O atoms are +2 in CuO or +4 in ZrO_2 . In the above discussions, the doping of the Zr interstitials in TiO_2 reduces the lattice Ti^{4+} ions to the Ti^{3+} or Ti^{2+} ions and leads to the higher transport coefficients than the Cu interstitials do. So, for the metal atoms with the valences of +4 or more in their binary oxides, their interstitials doping in TiO_2 could further reduce the Ti^{4+} ions to the Ti^{3+} or Ti^{2+} ions rather than those with the lower valences in the binary oxides, such as +3 or +2. We

use the Fe interstitials (+3) and Hf interstitials (+4) to verify the conclusion [15, 16]. The results of the Mulliken charges of the interstitials and the lattice Ti atoms would be seen in Figure 10. It is clearly seen that the Mulliken charges of the Ti-ions in $\text{Ti}_{12}\text{Hf}_3\text{O}_{24}$ are much smaller than those in $\text{Ti}_{12}\text{Fe}_3\text{O}_{24}$.

4. Conclusions

We focus on *ab initio* calculations about the role of the interstitials doping in the rutile TiO_2 and their impact on the transport coefficients. We find that the Zr or Ti interstitials in the TiO_2 lose the electrons and induce the formation

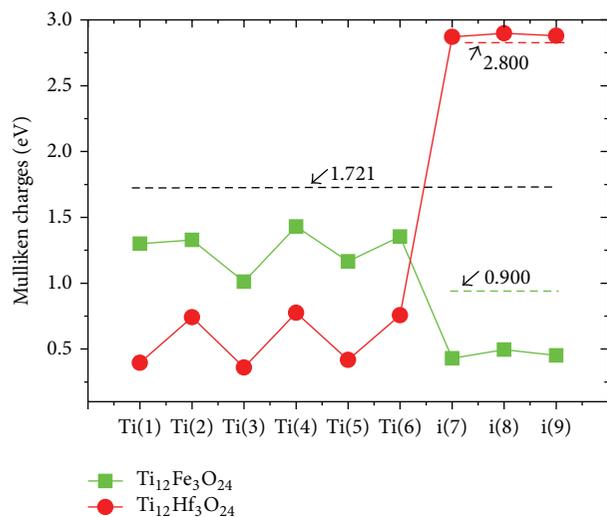


FIGURE 10: Mulliken charges in the defected TiO_2 with the Fe or Hf interstitials.

of the Ti^{3+} ions with the low Mulliken charges. The Cu interstitials also reduce the lattice Ti^{4+} ion but with less extent. By contrast, the Ti or Cu interstitials in the ZrO_2 do not induce the formation of the lattice Zr^{3+} ions. Furthermore, the Cu or Zr substitutions for the Ti atoms in the TiO_2 also keep the lattice Ti-ions in the +4 valence. As the formation of the Ti^{3+} trap centers, the Ti or Zr interstitials in TiO_2 lead to the higher transport coefficients than the Cu interstitials do. Finally, we propose that the doping of the metal atoms with the valences of +4 or more in their oxides may be beneficial for the formation of the Ti^{3+} ions in TiO_2 and so improves the transport properties. This work may be helpful to guide the doping principle in the metal/ TiO_2 /metal structure of the resistive random access memory [17].

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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