First-principles study of carbon impurity effects in the pseudo-hexagonal Ta₂O₅

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Abstract

Carbon-impurity effects on electronic structures and oxygen-vacancy formation stability of Ta₂O₅ resistive memories are investigated using the density-functional theory. Generalized gradient approximation with on-site Coulomb corrections is employed for the investigation. The unintentionally incorporated carbon can cause unwanted increase in the resistive off-state leakage current by extending the defect state region in the bandgap. The carbon impurities are found to be preferentially located in the neighborhood of the oxygen vacancies, and they reduce the oxygen-vacancy formation energy, which is predicted to have an influence on lowering the forming voltage.

KEYWORDS: Density-functional theory, Resistance random access memory, Ta₂O₅,

Carbon impurity, Oxygen vacancy

1. Introduction

Resistance random access memory (ReRAM) is one of the most promising candidates for future non-volatile memory devices owing to its simple structure, high speed of operation, low power consumption, and high-density integration [1-6]. Among the various candidates for resistive materials, conventional binary transition metal oxides (TMOs) such as TiO_2 , ZrO_2 , HfO_2 , and Ta_2O_5 are particularly attractive because they can be mass-produced easily. In particular, Ta_2O_5 -based ReRAM devices showed superior endurance properties and switching performances (i.e., high switching speed, large on/off resistance ratio, low operating voltage, and low reset current) [7-9]. The structural properties and electronic structures of Ta_2O_5 have been previously investigated by several research groups, and various polymorphs have been reported for Ta_2O_5 [10-15]. Recently, Nashed *et al.* [13] used the Perdew–Burke–Ernzerhof hybrid functional (PBE0) [16], and their calculated bandgap energies were 2.92 and 2.45 eV for δ - and β - Ta_2O_5 , respectively. The structures and electronic properties of Ta_2O_5 polymorphs were calculated in our previous paper [17] using the density-functional theory (DFT), employing the generalized gradient approximation (GGA) with on-site Coulomb corrections applied on the $5d$ orbital electrons of Ta atoms (U^d) and $2p$ orbital electrons of O atoms (U^p). Using this approach, a pseudo-hexagonal structure was found to be a more stable polymorph of Ta_2O_5 over δ - and β - Ta_2O_5 structures and metastable relative to other recently proposed structure [18], and its diffraction spectrum and bandgap energy and in good agreement with experimental data. Therefore it was proposed as a new candidate structure that might be formed during the resistive switching process in a ReRAM.

Meanwhile, the metal organic precursors comprising hydrogen and carbon atoms, which were usually used for metal-oxide deposition, could be incompletely dissociated during the reaction. These atoms could be incorporated into the films as impurities during the deposition processes such as atomic layer deposition and chemical vapor deposition; it is believed to affect insulating properties such as leakage current density [19, 20]. It could have an influence on the resistive off-state leakage current in the ReRAM as well. It is known that hydrogen can affect the chemical and electronic properties of TMOs [21, 22]; in ZnO, it has been theoretically reported that hydrogen forms a complex with oxygen vacancy, where it takes the place of the missing oxygen atom, and binds covalently to the surrounding Zn atoms [23]. The formation of such a vacancy-impurity complex has an important consequence because it can change the deep donor character of the oxygen vacancy. Thus, the resistive switching characteristics of the TMOs can be affected by impurities. Therefore, in this paper, we address the carbon-impurity effects on the electronic structures and the oxygen-vacancy formation stability of the pseudo-hexagonal Ta₂O₅ using DFT calculations for an in-depth understanding of the effects of impurity on the resistive switching characteristics.

2. Computational methods

Density-functional calculations using the Vienna *ab initio* simulation package were carried out for the study of Ta₂O₅ [23-25]. We used GGA+*U* method for the description of the exchange and correlation energies of the electrons. On-site Coulomb corrections were applied to both the *d* orbital electrons of the metal and the *p* orbital electrons of oxygen ($U^d = 6$ eV and $U^p = 9$ eV) to reproduce accurate structural parameters and bandgap energies [17], which is vital for the adequate evaluation of defect states in the bandgap. An energy cutoff of 250 eV was employed for the plane-wave expansion of electron wave functions. The ionic potentials were described by projector augmented-wave pseudopotentials [23]. For *k*-point integration within the first Brillouin zone, a $2 \times 2 \times 2$ Gamma centered grid was selected. The O $2s^2 2p^4$ and Ta $5p^6 5d^3 6s^2$ were considered as valence electrons. All atoms were allowed to relax with an energy-convergence tolerance of 10^{-6} eV/atom, and the ground state was obtained by minimizing the force on each atom to be less than 0.001 eV/Å. The simulation cell was a $2 \times 2 \times 4$ pseudo-hexagonal Ta₂O₅ supercell with 224 atoms (64 Ta and 160 O atoms), in which carbon impurities and oxygen vacancies were introduced.

3. Results and discussion

Figures 1(a) and 1(b) show the supercell structure ($2 \times 2 \times 4$) of the pseudo-hexagonal Ta_2O_5 , and the electron localization function (ELF) of the perfect supercell, respectively. The ELF gives an account of the type of bonding preferred and has a value between 0 (low electron density) and 1 (perfectly localized regions), with 0.5 corresponding to an electron-gas indicating metallic nature [26]. Six O atoms, forming a distorted octahedral structure, surround the Ta atoms. On the other hand, O atoms are surrounded by three Ta atoms in a planar geometry.

First, the effect of carbon impurities in Ta_2O_5 was investigated. We considered the carbon-impurity effect on the atomic bonding in Ta_2O_5 using ELF to access the degree of electron localization. Figures 2(a) and 2(e) show the ELF and the corresponding iso-surfaces ($0.05 \text{ e}/\text{\AA}^3$) of the partial charge density distribution of defect states in the bandgap for the interstitial carbon (C_i) in Ta_2O_5 without oxygen vacancy (V_O), which indicates that one carbon is inserted in the empty site in the perfect Ta_2O_5 supercell. In this case, C_i binds to oxygen ($O10$) and the bond length between $O10$ and C_i is $1.22 \text{ \AA}$, as indicated in Table 1. Figures 2(b), 2(c), and 2(d) show the ELF for one carbon impurity located in, near, and far, from the oxygen vacancy site in Ta_2O_5 with one oxygen vacancy (V_O), respectively [designated by the “C-Condition A”, “C-Condition B”, and “C-Condition C”]. Figures 2(f)–(h) show the corresponding iso-surfaces ($0.05 \text{ e}/\text{\AA}^3$) of the partial charge density distribution of defect states in the bandgap for each condition. The carbon impurity located in the oxygen vacancy (C_A) makes a complex with oxygen vacancy; whereas, similar to the interstitial carbon without oxygen vacancy, the carbon impurity located near the oxygen vacancy (C_B) binds to oxygen ($O4$) and the

bond length between $O4$ and C_B is 1.24 Å. There is no interaction between the oxygen vacancy and carbon in the C-Condition C. In addition, it is observed that there is more charge transfer when an oxygen-carbon complex is formed, compared to a vacancy-carbon complex. It is also observed that carbon prefers to form an O-C complex in the immediate vicinity of the oxygen vacancy, inducing charge delocalization around the oxygen vacancy and affecting the local electronic structure (Figures 2(f) and 2(g))

In order to find the carbon-impurity induced defect states, we calculated the total density of states. Figure 3 shows the total density of states (DOS) of the (a) interstitial C in Ta_2O_5 without V_O and (b) C-Condition A, (c) C-Condition B, and (d) C-Condition C in Ta_2O_5 with single V_O . The corresponding number of electrons for all defect states in the bandgap calculated in Ta_2O_5 without/with V_O and with one carbon is shown in Table 2. In case of the interstitial C, as shown in Figure 3(a), one carbon atom causes seven occupied defect states in the bandgap, which are composed of four spin-up and three spin-down states. The interstitial carbon atoms may cause an increase in the resistive off-state leakage current. In C-Condition A, C-Condition B, and C-Condition C, six defect states are presented in the bandgap because there are two defects— one each for oxygen vacancy and carbon. Although there is a difference in the energy levels of defect states, the shape of DOS and defect states are very similar for the different cases of carbon impurity with oxygen vacancy. Irrespective of the distance between an oxygen vacancy and a carbon, the carbon atoms can apparently cause an increase in the resistive off-state leakage current, because the defect states in the bandgap could act as the current path [27, 28].

Figure 4 shows the partial density of states of the (a) interstitial C in Ta_2O_5 without V_O and (b) C-Condition A, (c) C-Condition B, and (d) C-Condition C in Ta_2O_5 with a

single V_O . The occupied defect states are formed not only by the nearby Ta atoms around the oxygen vacancy and carbon, but also by carbon itself. On the other hand, the unoccupied defect states are mainly formed by carbon.

Figure 5(a) shows the relative energy of Ta_2O_5 with one oxygen vacancy and one carbon. The relative energy of the case X is defined as $E_{total}(X) - E_{total}(C-Condition B)$, where $E_{total}(X)$ and $E_{total}(C-Condition B)$ are the total energies of the case X, and the C-Condition B, respectively. The C-Condition A and C-Condition B are more stable than the C-Condition C. The C-Condition B is the lowest in energy and the energy difference between C-Condition A and C-Condition B is 0.03 eV per formula unit. This indicates that the carbon atom is preferentially located in the neighborhood of the oxygen vacancy. Furthermore, the carbon-impurity effect on oxygen-vacancy formation is investigated by calculating the oxygen-vacancy formation energy in the presence of carbon. Because all simulations were carried out in the neutral charge state, the oxygen-vacancy formation energy is defined as [29]

$$E_{form} = E_{tot,impurity,V_O} - E_{tot,impurity} + \mu_0. \quad (1)$$

in which, $E_{tot,impurity}$ and $E_{tot,impurity,V_O}$ are the relaxed total energies of the impurity-incorporated supercell before and after an oxygen vacancy is created, respectively. μ_0 is the oxygen chemical potential at room temperature based on analytical quantum formulations [30]. Figure 5(b) shows oxygen-vacancy formation energy in Ta_2O_5 with one oxygen vacancy and one carbon. The carbon atom reduces the oxygen-vacancy formation energy by 9.62 eV, which is predicted to have an influence on lowering the forming voltage.

4. Conclusion

We performed first-principles calculations employing GGA with U^d and U^p on-site corrections to study carbon-impurity effects on the electronic structures and oxygen-vacancy formation stability of the pseudo-hexagonal Ta_2O_5 . Carbon atoms extend the defect state region in the bandgap and can cause an increase in the resistive off-state leakage current, regardless of the distance between the oxygen vacancy and carbon. The carbon impurities are found to be preferentially located in the neighborhood of oxygen vacancies and they reduce the oxygen-vacancy formation energy, which is predicted to have an influence on lowering the forming voltage.

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Table 1. Comparison of bond lengths calculated in Ta₂O₅ without/with V_O and with one carbon to those of the perfect supercell.

	Perfect supercell	Interstitial C (C _i) in Ta ₂ O ₅ without V _O	C-Condition A (X=A, C _A)	C-Condition B (X=B, C _B) in Ta ₂ O ₅ with single V _O	C-Condition C (X=C, C _C)
Ta1-Ta2	3.25	2.91	3.34	4.29	3.28
Ta1-Ta3	3.80	>5	4.18	3.56	3.72
Ta2-Ta3	3.43	3.48	3.63	3.66	3.31
Ta1-O1	2.07	4.09	-	-	-
Ta2-O1	2.07	1.83	-	-	-
Ta3-O1	1.98	1.87	-	-	-
Ta1-O2	2.06	>5	2.01	1.95	2.05
Ta1-O3	1.98	4.45	2.07	4.11	2.00
Ta1-O4	1.99	2.11	1.98	2.84	1.95
Ta2-O4	2.01	2.05	2.05	2.17	2.02
Ta2-O5	1.85	2.04	1.87	1.97	1.89
Ta2-O6	1.84	1.87	1.85	1.95	1.83
Ta3-O7	2.02	1.93	1.96	2.01	2.03
Ta3-O8	1.97	1.97	1.96	1.92	2.01
Ta3-O9	1.87	1.96	1.96	1.94	1.87
Ta1-C _i	-	>5	-	-	-
O10-C _i	-	1.22	-	-	-
Ta1-C _X	-	-	2.16	2.13	>5
Ta2-C _X	-	-	2.33	2.16	>5
Ta3-C _X	-	-	2.12	3.00	>5
O4-C _X	-	-	2.62	1.24	>5

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Table 2. Number of electrons for all defect states in the band gap calculated in Ta₂O₅ without/with V_O and with one carbon.

	Interstitial C in Ta ₂ O ₅ without V _O	C-Condition A	C-Condition B in Ta ₂ O ₅ with single V _O	C-Condition C
Spin-up	4	3	3	3
Spin-down	3	3	3	3

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Figure captions

Figure 1. (Color online) (a) Structure of the pseudo-hexagonal Ta_2O_5 . Small yellow ball and big red one denote the Ta atom and the O atom, respectively, (b) ELF of the perfect supercell. ELF showing the missing electrons in the blue region and the highly localized ones in the red region.

Figure 2. (Color online) (a)–(d) ELF and (e)–(h) iso-surface ($0.05 \text{ e}/\text{\AA}^3$) of partial charge density distribution of all defect states in the bandgap. [(a) and (e): Interstitial C in Ta_2O_5 without V_O , (b) and (f): C-Condition A, (c) and (g): C-Condition B, (e) and (h): C-Condition C]

Figure 3. Total density of states of the (a) interstitial C in Ta_2O_5 without V_O , (b) C-Condition A, (c) C-Condition B, and (d) C-Condition C in Ta_2O_5 with single V_O .

Figure 4. Partial density of states of the (a) interstitial C in Ta_2O_5 without V_O , (b) C-Condition A, (c) C-Condition B, and (d) C-Condition C in Ta_2O_5 with single V_O .

Figure 5. (a) Relative energy and (b) oxygen-vacancy formation energy in Ta_2O_5 with one oxygen vacancy and one carbon.

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