The research of data retention of HfO$_2$ as trapping layer: First-principles study

Xianwei Jiang$^{1,2*}$, Feifei Wang$^{1,2}$, Haibo Wang$^{1,2}$, Jin Yang$^{1,2}$ and Shibin Lu$^{1,2}$

$^1$School of Electronic Information and Electrical Engineering, Hefei Normal University, Hefei, AnHui, 230601, China

$^2$AnHui Province Key Laboratory of simulation and design for Electronic information system, Hefei, AnHui, 230601, China

$^*$Xianwei Jiang’s e-mail: 279123127@qq.com

Abstract. The influence of the Charge Trapping Memory storage feature was researched by doping the substitutional impurity Al and introducing oxygen vacancy within HfO$_2$. Materials studio and Vienna Ab-initio Simulation Package were used to investigate the influence of doping Al on the formation of the oxygen vacancy in HfO$_2$ as trapping layer. At the same time, the interaction energy of two defects under different distances was calculated. The calculation results show that doping the substitutional impurity Al reduces the formation energy of oxygen vacancies in the HfO$_2$, and the reduced formation energy of the three-fold-coordinate O vacancy is larger than that of the four-fold-coordinated O vacancy. After having studied three different defect distances between substitutional impurity Al and three-fold-coordinated O vacancy, the results indicate that the system acquires the largest charge trapping energy, the most quantum states when the distance of the defects is 2.107Å. As a conclusion, the data retention in the trapping layer of monoclinic HfO$_2$ can be improved by doping the substitutional impurity Al. This work will provide a theoretical guidance for the performance improvement with respect to the data retention of Charge Trapping Memory.

1. Introduction

Due to the high compatible with the complementary metal-oxide semiconductor(CMOS) fabrication process, charge trapping memory (CTM)$^{[1]}$ as one promising candidate of the next generation nonvolatile semiconductor memories has been studied experimentally or theoretically for many years$^{[2-4]}$. High dielectric constant material (high-k) can effectively reduce the equivalent oxide layer thickness (EOT) under the same physical thickness, which can obtain large capacitive coupling and increase the electric field capacity, so as to achieve the requirement of reducing device size and improving device performance$^{[5]}$. In recent years, there have been many works investigating different kinds of high-k trapping layers such as HfON$^{[6]}$, HfO$_2$$^{[7,8]}$ and HfAlO$^{[9]}$ through experimental methods. The macroscopic parameters related to CTM performance mainly include data retention characteristics, program/erase endurance, window and operating voltage, etc$^{[10]}$. In order to improve performance of CTM, researchers have carried out many experimental research and theoretical calculation. Yan Ny Tan study Hafnium Aluminum Oxide as Charge Storage and Blocking-Oxide Layers in SONOS-Type Nonvolatile Memory, the results show that compared to other high-$\kappa$ charge-storage layers, HfAlO has the advantage of high-speed program/erase of HfO$_2$ as well as the good charge-retention time of Al$_2$O$_3$$^{[11]}$. So, what electrical properties does dope the substitutional impurity Al into HfO$_2$? It’s worth
studying. In the present study, the reliability of the calculating HfO$_2$ by first principle is approved and has been widely used\cite{12}.

This paper research on (TaN-Al$_2$O$_3$-HfO$_2$-SiO$_2$-Si) TAHOS structure affect the performance of memory macro defect in the distance. The interaction energy and formation energy of substitutional impurity Al with three-fold-coordinated O vacancy (V$_{O3}$) composite defects and substitutional impurity Al with four-fold-coordinated O vacancy (V$_{O4}$) composite defects with different defect spacing were calculated based on the first principle. The results show that the system is relatively easy to form and stable when the distance between substitutional impurity Al and V$_{O3}$ is 1.973Å, 2.107Å and 2.195Å. The influence of different distance on CTM performance was studied by calculating the defect charge trapping energy, quantum states in the above three systems.

2. Computational details

2.1 Methods

Our calculations were carried out via employing the density functional theory (DFT) plane wave basis set and Projector Augmented Wave (PAW) seudopotential\cite{13} as implemented in the Vienna \textit{ab initio} simulation package (VASP). Electron exchange and correlation are described using the Perdew, Burke, and Ernzerhof (PBE) version of the generalized gradient approximation (GGA). After convergence test, a plane wave basis set with cutoff energy of 500 eV and 3×3×3 grids for Brillouin zone are adopted. Atomistic geometries are fully relaxed until the force on each atom is less than 0.015eV/Å.

2.2 Model

While m-HfO$_2$ is stable at ambient conditions, the monoclinic phase HfO$_2$ (m-HfO$_2$) is taken as the research object. We choose m-HfO$_2$ with group space P121/C1 as the primitive cell. The bulk lattice parameters have been optimized: a=5.118Å, b=5.185Å, c=5.284Å. Isolated defects are modeled by using a 96-atom supercell. The supercell is obtained by a 2×2×5 translation from the primitive cell. V$_O$ defect model is obtained by removing the corresponding oxygen atoms in the complete m-HfO$_2$ crystal cell. In this model, on the basis of V$_O$ defect crystal cell, trivalent substituent Al atoms are added, where Al atoms are substituent Hf atoms.

3. Calculation results and analysis

The formula for the formation of neutral V$_O$ in the composite system is as follows:

\[ E_f = E_{HfO_2-AlO_{K4}} - E_{HfO_2-AlO_{K4}} + \mu_O \]

Where, $E_f$ is the formation energy of system contain O vacancy(V$_O$), $E_{HfO_2-AlO_{K4}}$ is the total energy of the optimized composite defective body formed by adding substitutional impurity Al in the presence of V$_O$ in the supercell, $E_{HfO_2-AlO_{K4}}$ is the energy of the optimized by adding substitutional impurity Al in the supercell. $\mu_O$ is the chemical potential of O atom. The smaller the formation energy is, the easier the defect to form.

Because of Coulomb force, the interaction between defects should not be ignored. We use the following formula to quantify the interaction between Al$_{Hf}$ and V$_O$:

\[ E_{int} = E \left( Al_{Hf} + V_O \right) + E_{bulk} - E \left( Al_{Hf} \right) - E \left( V_O \right) \]

$E_{int}$ is interaction energy, $E \left( Al_{Hf} + V_O \right)$ is the total energy of the optimized composite defective body formed by adding substitutional impurity Al in the presence of V$_O$ in the supercell. $E_{bulk}$ is the total energy of m-HfO$_2$ supercell, $E \left( Al_{Hf} \right)$ and $E \left( V_O \right)$ are the total energy of supercell containing substitutional impurity Al and one oxygen vacancy, respectively. If $E_{int}$ is negative, then the interaction is attractive. Otherwise, it is repulsive. The more negative the interaction energy is, the
stronger the attractive interaction is, and the more likely to form defect clusters, indicating that the structure is more stable.

There are two kinds of oxygen atoms in \( m\)-HfO\(_2\), respectively three-fold-coordination oxygen atom(O\(_3\)) and four-fold-coordination oxygen atom(O\(_4\)). Therefore, Vo can be formed in two forms, three-fold-coordinated O vacancy (Vo\(_3\)) and four-fold-coordinated O vacancy (Vo\(_4\)). We calculate the formation energy of Vo and the interaction energy when Al\(_{HF}\) and Vo exist at the same time respectively. The x-axis represents the distance between the defects, the result as shown in figure 1.

Figure 1 shows that compared with the formation energy of Vo\(_3\) and Vo\(_4\), the formation energy of Vo after doping the substitutional impurity Al can be significantly reduced, and the formation energy of Vo\(_3\) is lower than that of Vo\(_4\), which indicating that Vo\(_3\) is easier to form than Vo\(_4\). Therefore, doping the substitutional impurity Al is more conducive to the formation of oxygen vacancies. Due to the charge transfer between Al\(_{HF}\) and Vo, Vo changes from neutral state to +1 state and \( V_{o3}^{+1} \) is more stable than \( V_{o4}^{+1} \), so the formation energy of Al\(_{HF}\)+Vo\(_3\) system is smaller than that of Al\(_{HF}\)+Vo\(_4\) system. The interaction energy of Al\(_{HF}\)+Vo\(_3\) is smaller than that of Al\(_{HF}\)+Vo\(_4\), indicating that Vo\(_3\) is more likely to form defect clusters and the structure is more stable. Based on the above situation, the minimum formation energy and interaction energy of 3+ Al\(_{HF}\)+Vo\(_3\) will be selected in the following study, namely, the three cases with the closest distance (the distance is 1.973Å, 2.107Å and 2.195Å, respectively) will be analyzed and discussed to study the influence of different distance between defects spacing on the properties of m- HfO\(_2\) materials.

3.1 Charge trapping energy
Electrons or holes are the charge carriers to program and erase CTM. We simulate the injection (program) and removal (erase) of charge carriers by altering the number of electrons in the supercell. In this paper, we calculate the trap energy of m-HfO\(_2\) with three defects, and the equations are shown as follows:

\[
\Delta E_e = \chi_{bulk}^e - \chi_{defect}^e \\
\Delta E_h = \chi_{bulk}^h - \chi_{defect}^h
\]

The subscript (bulk and defect) implies whether or not the supercell contains defect. \( \chi = E^{eq} - E^0 \) (q=e or h) represents the trap energy of electrons or holes, n is the number of the charge, and q represents electrons or holes. The ability of the defect system to trap electrons and holes are show as in equation (3), respectively; bulk represents the intrinsic supercell and defect represents the supercell with defect. If trap energy is positive, then trapping corresponding charge carriers will result in energy
release. Otherwise, the trapping process is accompanied by energy absorption. The larger the charge trap energy is, the stronger the trap energy of the defect system is to the carrier. We calculate the trap energy at three different distances of the defect, as shown in figure 2.

![Figure 2. The charge trapping energy](image)

The results show that the charge trapping energies of electron at the three distances are 0.958 eV, 1.331 eV and 1.062 eV respectively, and the trapping energies of hole are 3.482 eV, 3.653 eV and 3.543 eV respectively, indicating that the system is of dual capture, which can capture both electrons and holes. Compare three cases, it is concluded that the defects distance is 2.107 Å, whether capture electrons or holes, the charge trapping energy of system is the biggest. So, the bound energy of carrier is the largest energy carrier bound, also means that the carrier to be erased from the system need the maximum energy, indicating that the carrier is not easy to be erased. So, the data retention of carrier is the strongest at this time.

3.2 Quantum states

Density of states can show numbers of electron that in the unit energy, which means the distribution of electron energy in a certain range. In order to further understand the status of composite system, we studied the density of states about the defect level that from the composite system. Density of states function \( g(E) \) is quantum states that in the bandgap near energy \( E \) per unit energy of interval number, is between \( E \) and \( E+dE \) the quantum states can be expressed as

\[
dZ = g(E)dE
\]

(4)

![Figure 3. Quantum states](image)

Quantum states can be used to describe the probability that the defect energy level caused by the introduction of defects may be occupied by carriers. The larger the quantum states, the larger the number of trapped carriers. Quantum states number at the defect energy level is calculated by integrating the density of states with equation (4) and results show in figure 3. The total quantum
states at the defect energy level in the three cases is 215.663, 217.042 and 215.296, respectively. The results show that the total number of quantum states at the defect level is the largest when the distance of the defects is 2.107 Å. Consequently, this indicated that the data retention capacity of carriers is the strongest at this case.

4. Conclusion
This paper studied the data retention characteristics of trapping layer charge in CTM based on the first principle of density functional theory and MS software. The results show that when the distance of defects is 2.107 Å the charge trapping energy of system is the biggest and can capture both free electrons and holes. The data retention in the trapping layer of monoclinic HfO₂ can be improved by doping the substitutional impurity Al. This work will provide a theoretical guidance for the performance improvement with respect to the data retention of Charge Trapping Memory.

Acknowledgments
This work is supported by the Natural Science Foundation of the Higher Education Institutions of Anhui Province (Grant No. KJ2016A574). Besides, all the numerical calculations in this paper have been done with the help of the Supercomputing Center of Anhui University of China.

References
[1] Tiwari, S., Rana, F., Hanafi, H., et al. (1996) A silicon nanocrystals based memory. Appl. Phys. Lett., 68:1377.
[2] Shi, R. P., Huang, X. D., Sin, J. K. O., et al. (2015) Nb-doped Gd₂O₃ as charge-trapping layer for nonvolatile memory applications. Appl. Phys. Lett., 107:163501.
[3] Gong, C. G., Yin, Q.N., Ou, X., et al. (2014) The dominant factors affecting the memory characteristics of (Ta₂O₅)ₓ(Al₂O₃)₁₋ₓ high-k charge-trapping devices. Appl. Phys. Lett., 105:123504.
[4] Tsai, C.Y., Chin, A., (2012) High-performance charge-trapping flash memory device with an ultrathin 2.5-nm equivalent-thickness trapping layer. IEEE Trans. Electr. Dev., 59:252-254.
[5] Choi, C., (2012) Thickness and material dependence of capping layers on flatband voltage (VFB) and equivalent oxide thickness (EOT) with high-k gate dielectric/metal gate stack for gate-first process applications. Microelectron. Eng., 89:34-36.
[6] Wu, J.Y., Chen, Y.T., Lin, M.H., et al. (2010) Ultrathin HfON Trapping Layer for Charge-Trap Memory Made by Atomic Layer Deposition. IEEE Electron Dev. Lett., 31:993-995.
[7] Bi, J.S., Xu, Y.N., Xu G B , et al. (2018) Total Ionization Dose Effects on Charge Trapping Memory (CTM) with Al₂O₃/HfO₂/Al₂O₃ Trilayer Structure. IEEE Trans. Nucl. Sci., 65:200-205.
[8] Lu, W.J., Dai, Y.H., Wang, F.F., et al. (2017) Research on c-HfO₂ (0 0 1)/α-Al₂O₃ (1 -1 0 2) interface in CTM devices based on first principle theory. AIP Advances, 7:125001.
[9] Tan, Y. N., Chim, W. K., Choi, W.K., et al. (2004) High-K HfAlO charge trapping layer in SONOS-type nonvolatile memory device for high speed operation. In: International Electron Devices Meeting. San Francisco. pp.889.
[10] Tan, Y. N., Chim, W.K., Cho, B. J.,et al. (2004) Over-erase phenomenon in SONOS-type flash memory and its minimization using a hafnium oxide charge storage Layer. IEEE Trans. Electr. Dev., 51:1143-1147.
[11] Tan, Y. N., Chim, W. K., Choi, W.K., et al. (2006) Hafnium Aluminum Oxide as Charge Storage and Blocking-Oxide Layers in SONOS-Type Nonvolatile Memory for High-Speed Operation. IEEE Trans. Electr. Dev., 53: 654-662.
[12] Zhang, W., Hou, Z.F., (2014) Interplay between gadolinium dopants and oxygen vacancies in HfO₂: A density functional theory plus Hubbard U investigation. J. Appl. Phys., 115:124104.
[13] Kresse, G., and Joubert, D., (1999) From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B, 59:1758-1775.