Quantum chemical molecular dynamics analysis of the effect of oxygen vacancies and strain on dielectric characteristic of HfO_{2-x} films

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Abstract—The effect of strain and intrinsic defects on both electronic and structural characteristics of HfO2-x used for sub-100-nm semiconductor devices was analyzed by a quantum chemical molecular dynamics analysis. The magnitude of the band gap of HfO₂ decreases by about 10% under the applied strain of 5%. The stable crystallographic structure of the monoclinic HfO₂ changes to a cubic-like structure under the strain. The magnitude of the band gap of the HfO_{2-x} decreases drastically from 5.7 eV to about 1.0 eV due to the formation of an electronic state within the band gap when an oxygen vacancy is introduced to the perfect HfO2. In the HfO_{2-x} film, oxygen atoms near the oxygen vacancy can move drastically at temperatures higher than 800 K. Therefore, it is very important to control the chemical composition of the hafnium oxide film and to optimize the annealing condition to maintain both the high reliability and performance of the gate oxide film.

Keywords-component; Molecular Dynamics, Reliability, Band Gap, HfO₂ Film, Lattice Defect

1. Introduction

Miniaturization of the microelectronic devices in modern integrated circuits has improved their system performance drastically for the past decades. To better their high performance, the thickness of a gate dielectric film that is conventionally composed of silicon dioxide has become thinner and thinner to an atomic layer level. However, the silicon dioxide film will have to be superseded by dielectric films with higher dielectric constant, i.e., high-k materials, because leakage current through the silicon dioxide film caused by direct tunneling increases significantly and thus, deteriorates the reliability of devices seriously. But it is very difficult to form the high-k film on a silicon substrate stably because an unexpected layer such as silicon oxide forms between the film and a silicon substrate. In addition, mechanical stress or strain has been increasing in the gate oxide film because the structure of the devices has become very complicated and new gate electrode materials such as high melting point metals hold very high residual stress. High tensile strain decreases the band gap of the film and thus, increases the leaking current through the film [1-4].

When the thickness of the gate dielectric film becomes thiner and thinner, local defects in the thinned gate oxide film play a very important role on both the electronic performance and reliability of the devices. One of the most important local defect in the gate oxide film is the compositional fluctuation caused by oxygen vacancies. For example, oxygen vacancies in HfO₂ oxide, which is considered as one of the promising candidate for a gate dielectric film for sub-100-nm devices, would trap carriers easily during operation of the devices, and result in the instability of the threshold voltage. Therefore, the essential understanding of the effect of strain and defects in the hafnium oxide film on both the structural and electronic properties of the film is a key issue for improving the reliability of devices using this film. In this study, we performed a quantum chemical molecular dynamics analysis in order to make clear the effect of the strain and intrinsic defects in the film on the dielectric characteristic of hafnium dioxide (HfO_{2-x}) film.



(c) Relationship between the ideal monoclinic structure and our simulation model for HfO_2 with monoclinic phase.

Fig. 1. Analytical models of HfO2 structure

2. Analytical Model

Quantum chemical molecular dynamics simulations were performed using the colors code [5]. The formalization of this program is based on the extended Hückel approximation. This formalization accerelates the speed of calculation drasticallly comparing with other methods based on regular first principle calculations. And thus, it enables us to solve complex systems requiring large simulation models.

In this study, we calculated the structural and electronic properties of cubic and monoclinic HfO2 with oxygen vacancies. Three dimensional periodic unit cell of monoclinic HfO₂ was modeled by considering an orthogonal symmetry part from the crystal structure of HfO₂ with monoclinic phase as shown in Fig. 1. The unit cell contains 32 hafnium atoms and 64 oxygen atoms. All the parameters used for atomic potentials were determined by the basis of density functional theory (DFT) calculations to satisfy the measured properties such as geometry, binding energies, atomic charges, density of states of O2 molecules and bulk structures of Hf, and HfO₂. The magnitude of the band gap is a dominant factor that determines the dielectric properties of a gate oxide film. However, the magnitude of the band gap of HfO₂ calculated using a regular DFT method is much smaller than that of the experimental results. On the other hand, the magnitude of the band gap of HfO₂ determined by the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) calculated by our tight-binding method was 5.7 eV. This value agrees well with the reported experimental results. Therefore, we confirmed that this methodology is very powerful and reliable tool to analyze the band gap of HfO₂. Further details of our formalization are indicated in the literatures [6-8]. We modeled the structure of HfO_{2-x} that is HfO_2 with an oxygen vacancy, by eliminating one oxygen atom from the unit cell. The oxygen vacancy was coordinated by four Hf atoms. The verlet algorithm [9] was used for integrating the equations of motion, while the Ewald method [10] was applied for calculating electrostatic interactions under three-dimensional periodic boundary conditions. The molecular dynamics simulations were performed for 10,000 steps with a time step of 0.2×10^{-15} seconds at temperatures of interest.

3. Results and Discussion

3.1 monoclinic strucure with oune oxygen vacancy

To discuss the correlation between the oxygen vacancy and electrical characteristics of HfO_2 , we calculated the change of the magnitude of band gap values during the simulation. The changes of the band gap of both perfect HfO_2 and HfO_{2-x} at 300 K are plotted in Fig. 2. The calculated value of the band gap was 5.7 eV on average for HfO_2 and little fluctuation was observed during the

simulation. On the other hand, the band gap of the HfO_{2-x} was 1.0 eV on average, which was significantly smaller than that of stoichiometric HfO₂. In addition, the amplitude of the fluctuation of the band gap was bigger than that of the perfect HfO₂. Fig. 3 shows the density of states (DOS) of HfO₂ and HfO_{2-x} at the final step. The bands in the energy range -31 eV to -29 eV were mostly due to O 2s orbitals, -20 eV to -13 eV were mainly O 2p in character, and the unoccupied conduction bands mainly consist of Hf 5d orbitals. For HfO_{2-x} structure, we observed an extra peak at about -8.9 eV that was about 4 eV above the valence bands of HfO₂. Fig. 4 shows the distribution of molecular orbital corresponding to the extra peak of -8.9 eV in the HfO_{2-x}. This figure clearly indicates that this peak formed by the dangling 5d



Fig. 3. Density of states (DOS) for HfO_2 and HfO_{2-x}



Fig. 4. Distribution of molecular orbital at –8.9 eV corresponding to the extra peak in HfO_{2x}



Fig. 5 Trajectory plots of oxygen atoms. Oxygen atom labeled A is the most neighboring oxygen from the vacancy site. Oxygen atom labeled B has the same configuration as the oxygen labeled A expect for the distance from the oxygen vacancy.

orbitals of Hf atoms coordinating oxygen vacancy site and the electrons localized in the vacancy site. These results agree well with the results caluculated by ab-initio calculation [2].

Oxygen diffusion is another key factor for improving both the electronic characteristics and the reliability of the HfO₂ as a gate oxide film. It has been reported that both the trap-assisted tunneling gate leakage current and the equivalent SiO₂ thickness increase due to the oxygen transport into Si and the subsequent formation of the interfacial layer of silicon oxide. This chemical reaction varies depending on the thermal annealing condition [3]. Fig. 5 shows the trajectory plots of oxygen atoms in HfO_{2-x} during simulations at temperatures of interest. We found that the oxygen atoms near the oxygen vacancy had a large mobility and the mobility of oxygen increased remarkably with the increase of temperatures higher than 800 K. Moreover, streuctural changes from monoclinic to cubic-like structure were observed at high temperature over 800 K Therefore, it is important to optimize the annealing condition for the formation of the HfO₂ reliable gate oxide film.

3.2 cubic strucure with one oxygen vacancy

We also calculated the magnitude of the band gap of the cubic strucure similarly. The calculated value of the band gap was 5.2 eV on average and it does not fluctuate substantially during the simulation. The band gap value of the HfO_{2-x} decreased to 0.7 eV on average as shown in Fig. 2 for monoclinic HfO_{2-x}. The decrease of the band gap was also caused by the defect level at the oxygen vacancy. Moreover, the oxygen vacancy site did not move at temperatures lower than 800 K.

3.3 Inflence of strain

To analyze the strain dependence of the magnitude of the band gap of HfO_2 in monoclinic phase, the structure was

hydrostatically deformed by a certain strain and the change of the band gap was calculated. This hydrostatic tensile or compressive strain was expressed by increasing and decreasing the lattice constants of HfO2, respectively. The calculated strain dependences of the magnitude of the band gap at 300 K are summarized in Fig 6. In this figure, the positive value of the strain is tensile strain, and the negative one is compressive. The band gap values plotted in this figure are averaged in the latter half steps of the simulation, in other words, the band gap was averaged in the calculation steps from 5,000 to the final step. The effect of strain on the magnitude of the band gap varies depending on the direction of the applied uni-axial strain. The band gap value slightly increases under compressive strain and decreases under tensile strain applied along the a-axis direction. (See Fig. 1) Similar result was found in a cubic HfO₂ structure by DFT calculation [11]. However, the previously reported band gap values slightly decrease under compressive strain and little change under tensile strain in b-axis and c-axis. Fig. 7 shows the snapshots of HfO₂ at the final step under -5.0 and 5.0% strain. No drastic crystallographic deformation is observed in both -5.0 and 5.0% strain along a-axis.



Fig. 6. Strain dependence of band gap of HfO2



Fig. 7. Snapshots of HfO₂ structure at the final step of simulation under -5.0% strain.

On the other hand, the large change of the configuration is observed under the strain of -5.0% along the c-axis, which seems to change to the cubic HfO₂ structure that has higher symmetry than that in the monoclinic phase. The similar strain dependence on the structural configuration of HfO₂ was observed when the strain was applied parallel to the b-axis. Monoclinic HfO2 has two bond distances of Hf-O, short bond distance of 2.01 Å and long one of 2.27 Å, respectively as shown in Fig. 8. From the analysis of radial distribution functions of Hf-O, we found that the large change of Hf-O bond distance in HfO2 under the strain along a-axis. At the strain of -5.0% along a-axis, the long bond distance was shortened to 2.12 Å, while tensile strain of 5.0% enlarged the short bond distance to 2.19 Å. The band gap value varies depending on the atomic distance, normally it increases with decreasing the bond distance and decreases with increasing the bond distance. Therefore, the linear change of the band gap values appears in monoclinic HfO2 under the strain along a-axis. On the other hand, HfO₂ structure under -5.0% strain along the c-axis had one Hf-O bond distance of about 2.25 Å. It is known that the dielectric properties of HfO2 depend on the choice of crystalline polymorphs. For example, the variety of the crystal structure changed the band gap value of about 1 eV and the crystal in cubic phase had a small band gap comparing with the monoclinic structure [12]. Hence, the compressive strain along the b-axis and the c-axis decreased the band gap values of monoclinic HfO₂ because of the change of the unit cell from monoclinic to cubic-like structure. From these results, we confirmed that the insulating properties of HfO₂ with monoclinic phase are significantly influenced by the change of the structural configuration caused by strain.

4. Conclusion

The effect of the strain and the intrinsic defects in the HfO2-x film on both the electronic and structural characteristics of the film was analyzed using a tight-binding quantum chemical molecular dynamics method. A three dimensional periodic unit cell for monoclinic HfO₂ structure that contains 32 Hf atoms and 64 oxygen atoms was used for a model of HfO2. The application of strain changed structural characteristics of HfO2, and resulted in the change of band gap value. In addition, monoclinic HfO₂ was deformed to cubic-like structure by the applied high strain along a specific direction. We confirmed therefore, that the insulating properties of HfO2 with monoclinic phase are significantly influenced by the change of the structural configuration caused by strain. The calculated band gap value of HfO2 with one oxygen vacancy was above 1.0 eV, that was significantly smaller than that of the stoichiometric HfO2. This is because that an electronic state was generated within the band gap by oxygen vacancy. We also analyzed the temperature dependence of the mobility of oxygen

atom in HfO_{2-x} . Oxygen atoms near the oxygen vacancy moved drastically at temperatures higher than 800 K and their mobility increased further with increase of temperature. Therefore, it is important to optimize the composition of the hafnium oxide film and the annealing condition of the film to improve the reliability of the film.



References

- P. Olivo et al., IEEE Trans. Electron Devices, ED-35, 2259(1988).
- [2] E. Rosenbaum et al., IEEE Trans. Electron Devices, ED-44, 317(1997).
- [3] H. Moriya, et. al., Ext. Abs. of the 2002 Int. Conf. on Solid State Devices and Materials, 186(2002).
- [4] H. Miura and S. Ikeda, IEICE Trans. on Electronics, E82-C, No. 6, 830(1999).
- [5] A. Yamada, A. Endou, H. Takabe, K. Teraishi, S. S. C. Ammal, M. Kubo, K. G Nakamura, M. Kitajima, and A. Miyamoto, Jpn, J. Appl. Phys. 38, 2434 (1999).
- [6] K. Suzuki, Y. Kuroiwa, S. Takami, M. Kubo, A. Miyamoto, and A. Imamura, *Solid State Ionics*, **152-153**, 273 (2002).
- [7] M. Elanany, P. Selvam, T. Yokosuka, S. Takami, M. Kubo, A. Imamura, and A. Miyamoto, *J. Phys. Chem. B*, **107**, 1518 (2003).
- [8] K. Suzuki, Y. Takeda, Z. Lu, and T. Shoji, Proceeding of International Congress on Advances in Nuclear Power Plants, CD-ROM, Paper No. 4227 (2004).
- [9] L. Verlet, Phys. Rev. 159, 98 (1967).
- [10] P. P. Ewald, Ann. Phys. 64, 253 (1921).
- [11] H. Moriya, T. Iwasaki, and H. Miura, Proceeding of International Conference on Simulation of Semiconductor Process and Devices, 331 (2005).
- [12] X. Zhao and D. Vanderbilt, Proceeding of the 2002 MRS Fall Meeting, 745, p. N7.2.1.