Effect of Interface Characteristics of W/$HfO_{2\pm x}$ on Electronic Reliability: Quantum Chemical Molecular Dynamics Study

Ken Suzuki, Tatsuya Inoue and Hideo Miura
Fracture and Reliability Research Institute, Graduate School of Engineering, Tohoku University
Aramaki Aoba 6-6-11, Aoba-ku, Sendai 980-8579, Japan
Email:kn@rift.mech.tohoku.ac.jp

***Abstract*— The effect of point defects such as oxygen vacancy and carbon interstitial on structural characteristics of W/HfO_2 was analyzed by a quantum chemical molecular dynamics method. Post-oxidation annealing is effective for eliminating the oxygen deficiency of gate dielectric films. However, the excess oxygen atoms may remain in the oxide film after the post-oxidation anneal. For HfO_2, they produce acceptor states in band gap and thus, give rise to the shrinkage of the local band gap of the oxide. In addition, such excess oxygen interstitials have been found to form a tungsten oxide layer at W/HfO_2 interface during the deposition process of a tungsten gate. It is very important, therefore, to minimize the concentration of point defects in the film to assure the reliability of the MOS structures.**

Keywords- Quantum Molecular Dynamics, Reliability, Band Gap, HfO_2, Point Defect, Oxygen vacancy, Carbon interstitial

I. INTRODUCTION

Highly reliable gate stack systems using a high-k dielectric thin film such as a hafnium dioxide film and metal tungsten gate are indispensable for the development of sub-50-nm ULSI devices. It is well known, however, that the control of the interfacial crystallographic structure between the dielectric film and a Si substrate or a gate electrode material is one of the critical issues of high performance and highly reliable operation of the devices. In the new gate stack structures, it is very important to make the sharp interface between the gate oxide and the electrode for assuring the high performance of the stacked MOS structures. This is because that a transition layer between them deteriorates the electronic function of the MOS structure significantly. One of the most troublesome layers is tungsten oxide because it decreases the effective capacitance of the gate oxide drastically. Since the formation of the transition layer is dominated by diffusion of oxygen near the interface, the existence of point defects such as vacancies and interstitials should affect the diffusion of oxygen and thus, the formation of the interfacial layer. In addition to this problem, the authors have found that the local defects in the thin gate oxide play a very important role on both the electronic performance and reliability of the devices [1]. Most important local defects are oxygen vacancies and carbon interstitials. The carbon interstitials are easily introduced into HfO_2-based dielectric films because they are often deposited by ALD (atomic layer deposition) or MOCVD (metal-organic chemical vapor deposition) which applies an organic gas sources. Therefore, the defect engineering is key issue to be discussed for the highly reliable systems.

In this study, quantum chemical molecular dynamics was applied to explicate the degradation mechanism of both the dielectric properties of HfO_2 caused by point defects and the interfacial structure of the gate stack systems. In particular, the effect of oxygen vacancies and both oxygen and carbon interstitials on the formation of tungsten oxide at the interface of W/HfO_2 and the local band gap of the hafnium oxide were analyzed. The estimated results were confirmed by experiments using synchrotron-radiation photoemission spectroscopy.

II. ANALYTICAL METHOD

Quantum chemical molecular dynamics simulations were performed using the colors code [2]. Since in this program, an extend Hückel approximation is used to solve the electronic state, we have to optimize the empirical parameters used in Hamiltonian. All atomic parameters were determined on the basis of density functional theory (DFT) calculations and considering the experimental results to satisfy the measured properties such as the geometry, binding energies, atomic charges, density of states of Hf, W, HfO_2, WO_3 bulk structures and so on. DFT calculations were performed by using CASTEP code. We employed the generalized gradient approximation (GGA) of Perdew et al. [3] for the exchange correlation functional. In this study, we analyzed the structural and electronic properties of W/HfO_2 with oxygen vacancies and carbon interstitials. The magnitude of the band gap is a dominant factor that determines the dielectric properties of the gate oxide film. However, the magnitude of the band gap of HfO_2 and WO_3 calculated by a regular DFT method is much smaller than that of the experimental result. On the other hand, the magnitude of the band gap of HfO_2 and WO_3 determined by the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) calculated by our method was 5.7 eV and 2.7 eV, respectively. These values are agrees well with the reported experimental results. We modeled the structure of HfO_{2-x}, which is HfO_2 with oxygen vacancies, by eliminating oxygen atoms from the unit cell. For the unit cell of HfO_2 with

carbon interstitial model, one carbon atom was introduced in HfO_2 structure. The molecular dynamics simulations were performed for 10,000 steps with a time step of 0.5×10^{-15} seconds at several temperatures.

III. RESULTS AND DISCUSSION

A. *HfO_2 with a carbon interstitial*

In order to evaluate the effect of carbon interstitials on the insulating property of HfO_2, band gap values of HfO_2 with a carbon interstitial were calculated. We have already reported that the band gap value of the HfO_2 with a carbon interstitial decreased locally from 5.7 eV to about 1.6 eV by deoxidizing the oxide [1]. Figure 1 shows the trajectories of constituted atoms in HfO_2 with a carbon interstitial during the simulation. From this figure, we confirmed that the carbon atom had a large mobility inside of HfO_2 matrix. The magnitude of band gap of HfO_2 is strongly affected by the local structure of oxide and therefore, the large fluctuation of the band gap would appear caused by the change in the atomic configuration accompanying the migration of the carbon interstitial.

We analyzed the synergistic effect of oxygen vacancy and carbon interstitials on the magnitude of band gap. The structure of HfO_2 with both one oxygen vacancy and one carbon atom (HfO_{2-x} with a carbon interstitial) was used for the simulation. Figure 2 shows the initial and final structures obtained from the simulation at 300 K. In the initial structure, the carbon atom was at a distance of 1.3 Å from the oxygen vacancy. On the other hand, we found that the final structure of HfO_{2-x} with a carbon interstitial became $HfO_{2-x}C_x$ structure in which carbon atom can be simply considered as substitutional of oxygen atom. This is because that the carbon atom moved to oxygen vacancy and subsequently occupied the vacant site during the simulation. We have also performed DFT calculations in order to investigate the stability of the different configurations of HfO_{2-x} with carbon atom. From geometry optimization calculations, we confirmed that an oxygen vacancy is occupied by a carbon atom (see figure 3), and the configuration in which carbon atom occupies the oxygen vacancy is energetically favorable comparing with that in which a carbon atom is at interstitial positions. The magnitude of band gap obtained from our quantum chemical molecular dynamics was 0.3 eV on average, which was seriously smaller than that of HfO_{2-x} or HfO_2 with a carbon interstitial. In $HfO_{2-x}C_x$ structure, the substituting carbon atoms can form stable bonds with hafnium atoms and thus, the electronic structure around the carbon atom seems to be similar to that of the hafnium carbide. The strong interactions between carbon and hafnium atoms give rise to a serious shrinkage of local band gap oh hafnium dioxide because hafnium carbide has a good electric conductivity. We conclude therefore, coexistence of oxygen vacancy and carbon atoms in the hafnium dioxide film deteriorate the electronic reliability of the film seriously.

B. *Effect of post- oxidation annealing*

Our quantum chemical molecular dynamics analysis showed that the not only the oxygen vacancy but also the carbon interstitial induced the drastic decrease of the local band gap of hafnium dioxide. This is mainly because that new donor and acceptor levels were generated within the band gap due to the interaction between the carbon and hafnium atoms. In addition, carbon interstitials induce the deoxidization that gives rise to an oxygen vacancy in the film. In order to improve the electronic performance and reliability of the film, the minimization of point defects in hafnium dioxide film is indispensable. Since hafnium dioxide films deposited by ALD or MOCVD have oxygen deficiency, post-oxidation annealing is effective for eliminating the oxygen deficiency. In addition, the post-oxidation annealing is believed to be effective to reduce the carbon interstitials. However, the excess oxygen atoms may remain in the oxide film after the post-oxidation anneal. To simulate the influence of excess oxygen on electronic and structural characteristics of hafnium dioxide, we introduced oxygen atoms to the simulation models of HfO_{2-x} with and without carbon interstitial. Figure 4 shows the snapshots during the molecular dynamics simulation of HfO_{2-x} with both a carbon and an additional oxygen atom at 300 K. Snapshots of simulations demonstrate the major features of the

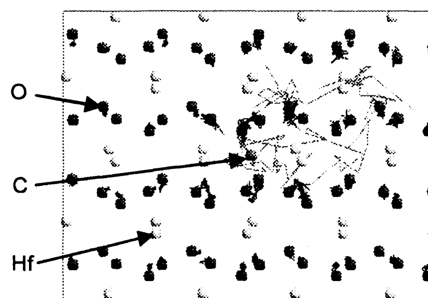

Figure 1. Trajectory plots of atoms in HfO_2 with a carbon interstitial.

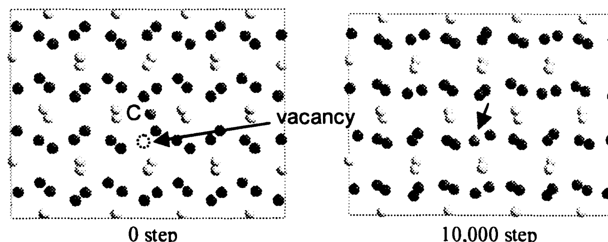

Figure 2. Initial and final structure of HfO_{2-x} with a carbon interstitial.

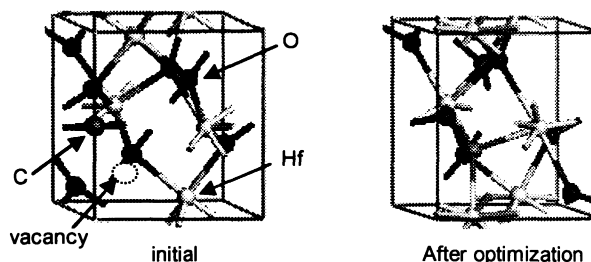

Figure 3. Initial and optimized structure of HfO_{2-x} with a carbon interstitial from DFT calculation.

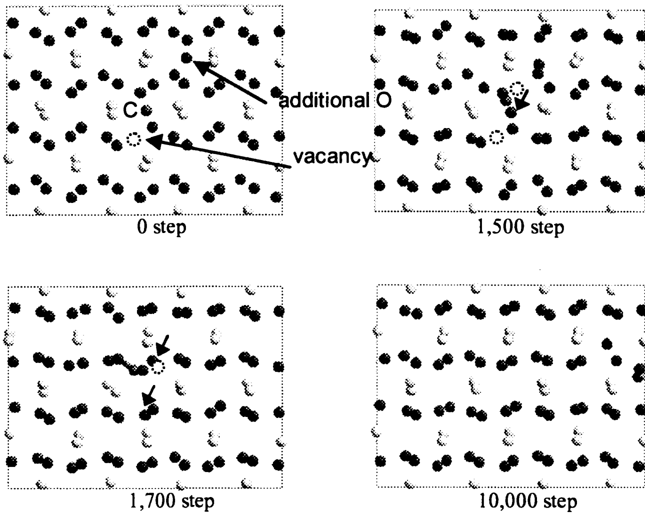

Figure 4. Change in the structure of HfO_{2-x} with both a carbon interstitial and an additional oxygen atom during the simulation.

structural rearrangement due to the addition of oxygen. The carbon atom did not occupy the oxygen vacancy site during the simulation in contrast to the case without the additional oxygen atom. On the other hand, we observed that oxygen atom neighboring the vacancy moved to the vacancy site and subsequently occupied the vacant site, which is regarded as the oxygen vacancy migration. The additional oxygen atom immediately occupied the vacant site after this migration of oxygen atom, resulting in the disappearance of oxygen vacancies in the structure. These results clearly indicate that post-oxidation annealing is effective for the reduction of oxygen deficiency in hafnium dioxide film. Figure 5 shows the change in the magnitude of band gap of HfO_2 with a carbon interstitial and an additional oxygen atom during the simulation. We can confirm that the band gap value increased to 5.8 eV in the maximum, 3.3 eV on average during the simulation and thus, the post-oxidation annealing is effective for the improvement of the electronic properties of hafnium dioxide including carbon impurity as well as the decrease of the concentration of oxygen vacancy. The calculated densities of states (DOS) around the band gap are summarized in figure 6. The band gap value of stoichiometric HfO_2 obtained from the energy gap between electron occupied and unoccupied state in this figure is 5.7 eV. This On the other hand, the band gap value of the HfO_2 with one oxygen vacancy decreased to about 1.0 eV. This is because that an extra "HOMO" peak appears in the band gap due to the oxygen vacancy. This defect state was at about 4 eV above the valence bands of the stoichiometric HfO_2 and shifted to higher energy with increase of the oxygen vacancies. Similarly, carbon interstitials also decreased the local band gap of HfO_2 film drastically by deoxidizing the oxide. As stated above, post-oxidation annealing is effective for improving the electronic properties of hafnium dioxide film. However, when the excess oxygen atoms remain in the oxide film after the post-oxidation anneal, they produce acceptor states at about 0.1 eV above the valence band and thus, give rise to the shrinkage of the local band gap of the oxide. In

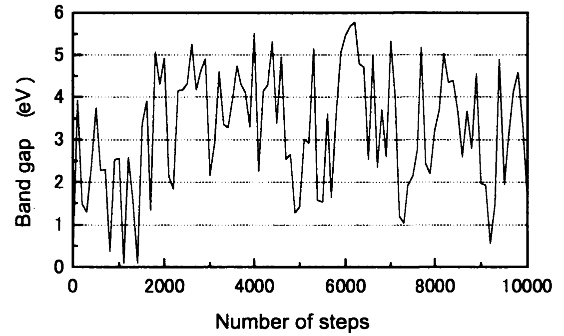

Figure 5. Change in the band gap of HfO_2 with both a carbon interstitial and an additional oxygen atom.

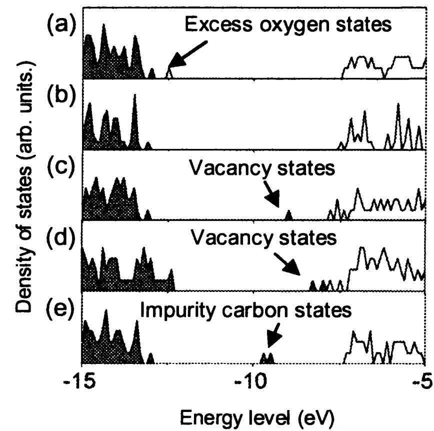

Figure 6. Density of states for (a) HfO_2 with one excess oxygen atom, (b) stoichiometric HfO_2, (c) HfO_2 with one oxygen vacancy, (d) HfO_2 with two oxygen vacancies and (e) HfO_2 with one carbon atom. In this figure, dark color of DOS indicates the electron occupied states and light one indicates the unoccupied stetes, respectively.

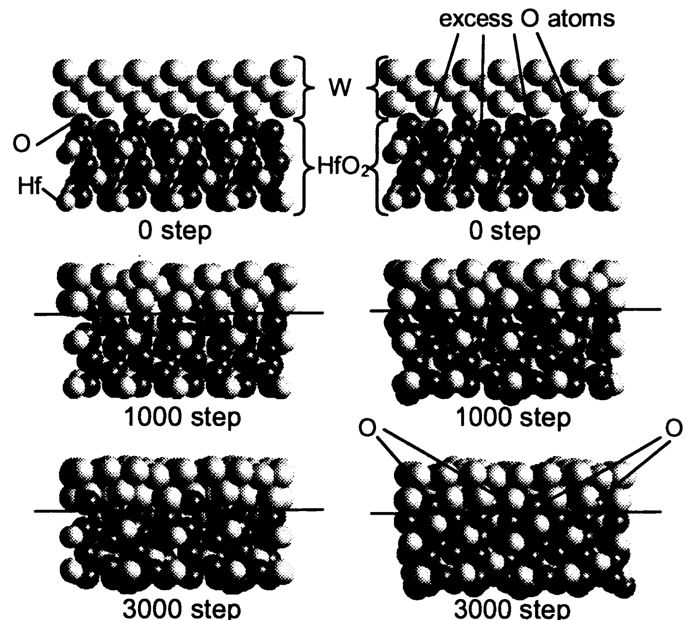

Figure 7. Estimated changes of interface structures of (a) W/HfO_2 and (b) W/HfO_{2+x} at 300 K.

addition, such excess oxygen interstitials have been found to form a tungsten oxide layer during the deposition process of a tungsten gate. Figure 7 shows example snapshots during the simulation of W/HfO_2 and W/HfO_{2+x} at 300 K. HfO_{2+x} structure was modeled by the addition of 4 oxygen atoms into stoichiometric HfO_2. It was found that sharp interface structure can be formed when tungsten metal gate films were grown on stoichiometric HfO_2. However, it was found that the excess oxygen atoms diffused out from the HfO_{2+x} into the deposited tungsten film and form the interfacial layer of tungsten oxide. It is therefore, very important to minimize the concentration of remained oxygen atoms after the post oxidation anneal.

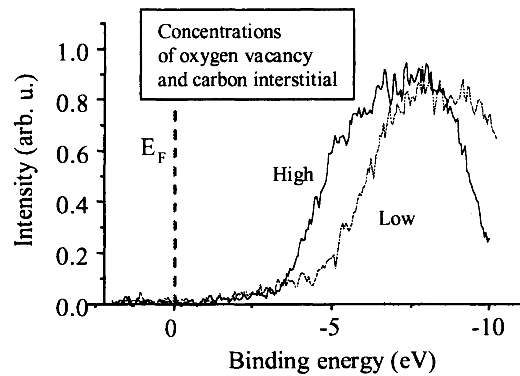

Figure 8. Examples of photoemission spectra of HfO_2 film with high and low concentration of point defects.

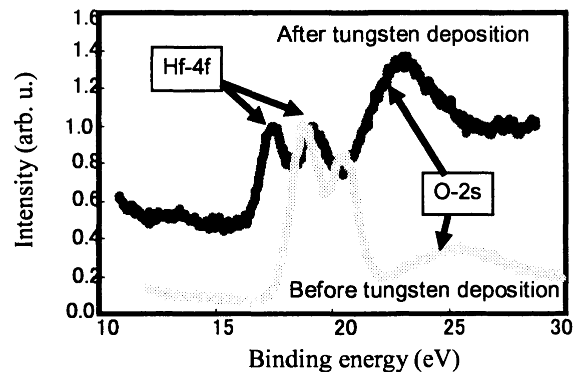

Figure 9. Photoemission spectra of Hf-4f in a W/HfO_2 gate stack structure before and after deposition of tungsten.

C. Experimental validation

The predicted point defects-induced change of the bad structure of the HfO_{2-x} films was validated by synchrotron-radiation photoemission spectroscopy. A high-energy excitation source (5947.9 eV) enabled to analyze the chemical shift of the component elements in 4-nm-thick HfO_{2-x} films through the deposited tungsten electrode. The changes of the chemical shifts of Hf 3d/4f and O 1s due to the variation of the concentration of oxygen vacancy and carbon interstitial controlled by the ALD conditions were analyzed. It was confirmed that the reduction of oxygen deficiencies and carbon interstitials in the HfO_{2-x} films increased the band gap of the films significantly as shown in figure 8. This result clearly indicates that the minimization of point defects in a hafnium dioxide film is indispensable for improving its electronic performance and reliability. The deposition of a tungsten gate electrode on the hafnium oxide film also affects the film quality as shown in figure 9. The binding energy of Hf-4f shifted to the lower energy side and a new strong peak of O-2s appeared at about 23 eV. Similar change was observed in the spectra of W-4d and W-4f. These changes of chemical bonding conditions in the hafnium oxide and tungsten films indicated the deoxidization of the $HfO_{2-x}C_y$ film and the formation of tungsten-oxide due to the excessive oxygen interstitials that were introduced into the film by post-oxidation after the ALD. The composition control of the $HfO_{2-x}C_y$ film before deposition of the tungsten electrode film, therefore, should be optimized for improving the quality of the gate-stack structure of hafnium dioxide.

IV. Conclusion

In this study, quantum chemical molecular dynamics was applied to explicate the degradation mechanism of both the dielectric properties of HfO_2 caused by point defects and the interfacial structure of the gate stack systems. We analyzed the synergistic effect of oxygen vacancy and carbon interstitials on the magnitude of band gap. We found the carbon atom moved to oxygen vacancy and subsequently occupied the vacant site during the simulation. The calculated band gap value was 0.3 eV on average, which was seriously smaller than that of stoichiometric HfO_2. In $HfO_{2-x}C_x$ structure, carbon atoms can form stable bonds with hafnium atoms. The strong interactions between carbon and hafnium atoms cause a serious shrinkage of local band gap because hafnium carbide has a good electric conductivity. We also analyzed the effects of post-oxidation annealing on the electronic and structural properties of hafnium dioxide including carbon impurity. It was found that the band gap of hafnium dioxide including the carbon impurity was increased by the addition of oxygen. However, when the excess oxygen atoms remain in the oxide film, they produce acceptor states at about 0.1 eV above the valence band and thus, give rise to the shrinkage of the local band gap of the oxide. In addition, it was found that the excess oxygen atoms diffused out from the HfO_{2+x} into the deposited tungsten film as gate electrode and form the interfacial layer of tungsten oxide. The predicted point defects-induced change of the bad structure of the HfO_{2-x} films was validated by synchrotron-radiation photoemission spectroscopy. We confirmed the reduction of oxygen deficiencies and carbon interstitials in the HfO_{2-x} films increased the band gap and the formation of tungsten-oxide due to the excessive oxygen interstitials that were introduced into the film by post-oxidation after the ALD. It is very important, therefore, to minimize the concentration of point defects in the film to assure the reliability of the MOS structures.

References

[1] K. Suzuki, et al., Proc. of SISPAD 2007, 165 (2007).
[2] A. Yamada et al., Jpn, J. Appl. Phys. 38, 2434 (1999).
[3] J. P. Perdew et al. : Phys. Rev. B 46, 6671 (1992).