

# Quantum Chemical Molecular Dynamics Study of Degradation Mechanism of Interface Integrity between a HfO<sub>2</sub> Thin Film and a Metal Gate Electrode

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**Abstract**— Control of the interfacial crystallographic structure between a dielectric film and a gate electrode is one of the most critical issues for assuring the high performance and the reliability of a stacked MOS structure using high-k dielectric thin films. In this study, quantum chemical molecular dynamics was applied to explicate the mechanism of degradation of interfacial integrity of the gate stack systems which is caused by point defects. We found that point defects such as oxygen and carbon interstitials deteriorate the electronic quality of a hafnium dioxide film and the W/HfO<sub>2</sub> interface structure. The estimated results were confirmed by experiments using synchrotron-radiation photoemission spectroscopy.

**Keywords**— Quantum Molecular Dynamics; synchrotron spectroscopy photoemission; Hafnium Oxide (HfO<sub>2</sub>); high-k dielectric; metal-gate electrode; composition fluctuation

## I. INTRODUCTION

Development of the electronic devices during the past decades is based on the continuous miniaturization of the microelectronic devices in integrated circuits such as metal-oxide-silicon field effect transistor (MOSFET). As the International Technology Roadmap for Semiconductors (ITRS) indicates, downsizing of the MOSFET will continue and the major dimension of MOSFET will reach about 10 nm. In this size region, constituent materials used in MOSFET such as silicon dioxide gate dielectric causes various problems around gate stack structures based on the direct tunneling current through the gate insulator [1]. To avoid this problem, the replacement of the gate oxide material from silicon dioxide to higher dielectric constant (high-k) material such as hafnium dioxide is indispensable. Moreover, in conjunction with the new dielectric stack structure, the gate electrode material has been changed from poly-silicon to metal such as tungsten because of material compatibility and the improvement of system performance [2]. It is well known, however, that the control of the interfacial crystallographic structure between the dielectric film and the gate electrode is one of the critical issues for assuring high performance and stable operation of the devices. Therefore, it is very important to make the interface

stable. This is because that a transition layer such as metal-oxide grown between them deteriorates the electronic function of the MOS structure significantly. In addition to the interfacial problem, local defects in thin gate dielectric film play a very important role on both the electronic performance and reliability of the devices [3]. One of the most important local defects in the gate dielectric is the compositional fluctuation caused by oxygen vacancies and excess oxygen. The device performance could be also affected by carbon interstitials in HfO<sub>2</sub>-based dielectric, because ALD (atomic layer deposition) or MOCVD (metal-organic chemical vapor deposition) by using an organic gas source introduces the carbon interstitials as the impurity into the film. Therefore, not only the interface control but also the defect engineering is another important issue to be discussed for the highly reliable systems. In this study, we performed a quantum chemical molecular dynamics analysis for W/HfO<sub>2±x</sub> with carbon interstitials in order to make clear the effect of point defects in the gate oxide film on the electric reliability of the device.

## II. ANALYTIAL METHOD AND RESULTS

Quantum chemical molecular dynamics simulations using the colors code was applied to the analyses of the structural and electronic properties of the W/HfO<sub>2±x</sub> interface [4]. Both the electronic and molecular structures should be solved by *ab initio* molecular dynamics method. However, *ab initio* method requires huge computational resources, and hence it can not be applied to the simulation of the complex system when the chemical reaction and atomic diffusion dynamics are discussed. On the other hand, our quantum chemical molecular dynamics method can analyze those phenomena much faster than regular first principle calculation methods because extend Hückel approximation is applied to solve the electronic state [5]. In this method, however, we have to optimize the empirical parameters used in Hamiltonian. All the 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<sub>2</sub>,

WO<sub>3</sub> bulk structures and so on. The DFT calculations were performed by using CASTEP code. The generalized gradient approximation (GGA) of Perdew et al. [6] was used for the exchange correlation functional. In this study, both the structural and electronic properties of W/HfO<sub>2</sub> with oxygen vacancies and carbon interstitials were analyzed quantitatively. The magnitude of the band gap is a dominant factor that determines the dielectric properties of the gate oxide film. Though the magnitude of the band gap of HfO<sub>2</sub> and WO<sub>3</sub> calculated by a conventional DFT method is much smaller than that of the experimental result, the magnitude of the band gap of HfO<sub>2</sub> and WO<sub>3</sub> 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 agreed well with the reported experimental results. The molecular dynamics simulations were performed for 5,000 steps with a time step of  $0.5 \times 10^{-15}$  seconds at 300 K and 700K. In our analytical model, the crystal structure of HfO<sub>2</sub> was assumed as monoclinic crystal which is stable around the room temperature [7]. Similarly, the crystal structure of tungsten was assumed as the body centered cubic structure. Total atomic number of W/HfO<sub>2</sub> system is 117 atoms in a cell (24 hafnium atoms, 48 oxygen atoms and 45 tungsten atoms).

### III. RESULTS AND DISCUSSION

#### A. Interface characteristics of W/HfO<sub>2±x</sub>

The authors have previously reported that the oxygen vacancy in HfO<sub>2</sub> crystal causes the drastic drop down of local band gap in the gate dielectric film [8]. Carbon interstitials also decreased the effective band gap of HfO<sub>2</sub> film significantly. The interstitial carbon atoms interacted with hafnium atoms and sometimes substituted into the vacant oxygen sites, subsequently form stable Hf-C bonds. Formation of Hf-C bonds gives rise to a serious shrinkage of local band gap of hafnium dioxide. Therefore, the minimization of point defects such as oxygen vacancies and carbon interstitials in hafnium dioxide film is indispensable for assuring the reliability of devices using the HfO<sub>2</sub> dielectric film. For improving the

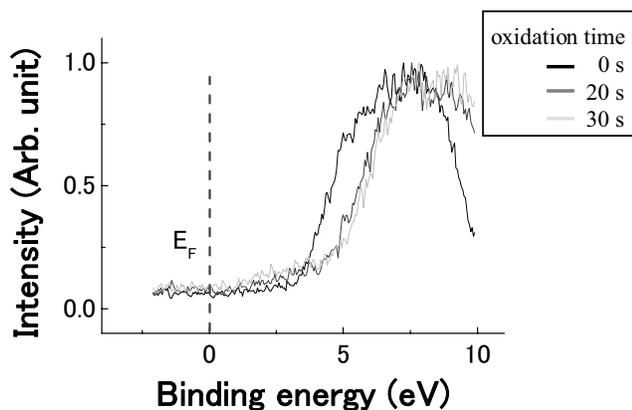


Figure 1. Shift of valence band spectra in HfO<sub>2</sub> around Fermi level dependent on the oxidation time

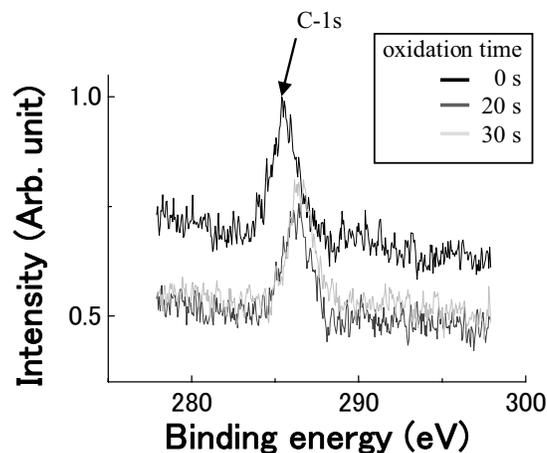


Figure 2. Shift of spectra in HfO<sub>2</sub> around C-1s peak dependent on the oxidation time

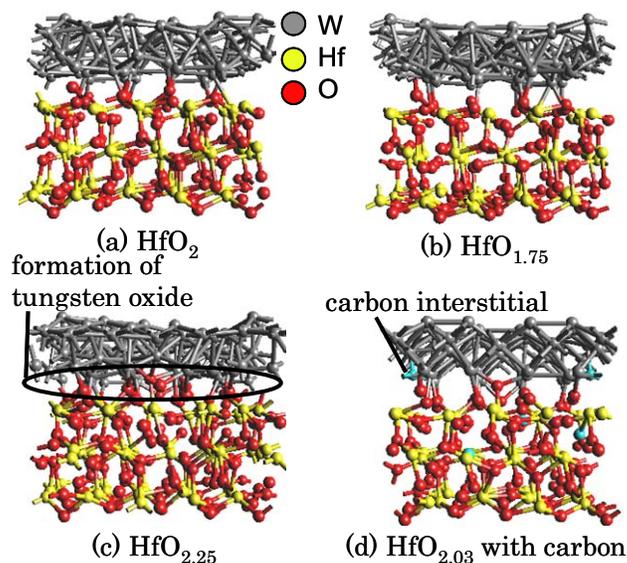


Figure 3. Final Structure of HfO<sub>2±x</sub> with carbon interstitials obtained from the simulations at 300K, (a) stoichiometric HfO<sub>2</sub>, (b) HfO<sub>1.75</sub>, (c) HfO<sub>2.25</sub>, and (d) HfO<sub>2.03</sub> with carbon interstitials

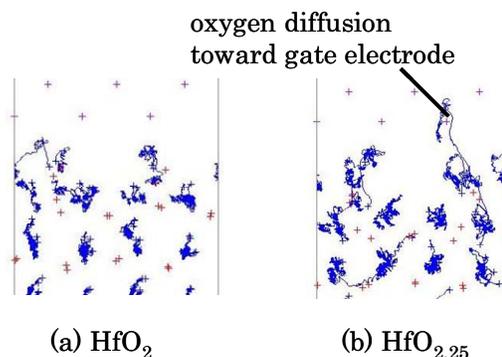


Figure 4. Trajectory of oxygen atoms obtained from the simulations at 300K, (a) stoichiometric HfO<sub>2</sub>, (b) HfO<sub>2.25</sub>

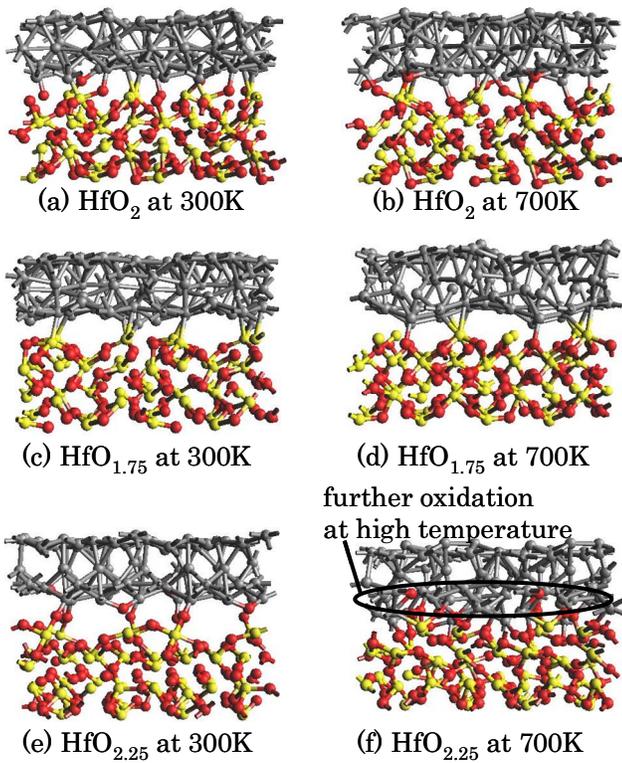


Figure 5. Final structure of  $\text{HfO}_{2+x}$  obtained from the simulations, (a) stoichiometric  $\text{HfO}_2$  at 300K, (b) stoichiometric  $\text{HfO}_2$  at 700K, (c)  $\text{HfO}_{1.75}$  at 300K, (d)  $\text{HfO}_{1.75}$  at 700K, (e)  $\text{HfO}_{2.25}$  at 300K and (f)  $\text{HfO}_{2.25}$  at 700K

electronic performance of  $\text{HfO}_2$  film, it was confirmed that post-oxidation annealing is effective to recover the drop down of local band gap caused by point defects [8]. Figure 1 shows the shift of valence band spectra of  $\text{HfO}_2$  crystal measured by using synchrotron-radiation photoemission spectroscopy. The position of the edge of valence band of hafnium oxide shifted to higher binding energy side after post-oxidation process. This result indicates the recovery of the local band gap of  $\text{HfO}_2$ . Figure 2 shows the peak shift of C-1s spectra in a  $\text{HfO}_x$  film. With the increase of the oxidation time, C-1s peak shifts to higher binding energy side. This implies that carbon interstitials is oxidized to  $\text{CO}_x$ , resulting in the reducing the Hf-C bonds. However, when the excess oxygen atoms remain in the oxide film after the post-oxidation anneal, they produce acceptor states and thus, give rise to the shrinkage of the local band gap of the oxide [8].

To discuss the effect of excess oxygen atoms in the oxidized film on electronic and structural characteristics of the interface between a metal gate and a  $\text{HfO}_2$  thin film, the structural and electronic properties of  $\text{W}/\text{HfO}_{2+x}$  with carbon interstitials were then analyzed.  $\text{HfO}_{2+x}$  structure was modeled by addition of 6 oxygen atoms in stoichiometric  $\text{HfO}_2$  to simulate the condition after post-oxidation annealing. Figure 3 shows the final configurations obtained from the simulations at 300 K. For stoichiometric  $\text{HfO}_2$ , small change in the configuration of both tungsten and  $\text{HfO}_2$  was observed. This result indicates that sharp interface structure can be formed when tungsten metal gate films are grown on stoichiometric  $\text{HfO}_2$ . On the other hand, in case of  $\text{W}/\text{HfO}_{2+x}$ , excess oxygen atoms diffused out

from  $\text{HfO}_{2+x}$  into the deposited tungsten film and form the interfacial layer of tungsten oxide as shown in Fig. 3. This diffusion phenomenon of oxygen atoms around the interface was also confirmed by trajectory analysis. Figure 4 shows the trajectory plots of oxygen atoms in  $\text{HfO}_2$  film during the simulation. This figure clearly indicates that excessive oxygen atoms notably move inside of tungsten gate electrode in  $\text{W}/\text{HfO}_{2.25}$ . Carbon interstitials also diffused into tungsten layer and formed their carbide as shown in Fig. 3 (d). From these results, it was confirmed that the formation of the interfacial transition layer is dominated by diffusion of excess oxygen and carbon interstitials near the interface. The effect of temperature on the formation of this interfacial layer was then analyzed. Figure 5 shows the final configurations obtained from the simulations at different temperature. In the cases of stoichiometric  $\text{HfO}_2$  and  $\text{HfO}_{2-x}$ , almost no difference was observed in atomic configuration of the interface between 300 K and 700 K. On the other hand, further oxidation of tungsten gate electrode was observed in  $\text{W}/\text{HfO}_{2.25}$  at 700K. This result suggests that deposition process of metal gate in high temperature activates the diffusion of excess oxygen atoms and formation of the interfacial layer. One of the most troublesome layers is tungsten oxide because it decreases the effective capacitance of the gate oxide drastically, and thus, it induces the degradation of the interface integrity and the electronic property of MOS transistor. It is very important, therefore, to minimize the concentration of local defects in the film to assure the reliability of the MOS structures.

### B. experimental validation

The estimated result of the formation of the transition layer at the interface of  $\text{W}/\text{HfO}_{2+x}$ , 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  $\text{HfO}_2$  films through the deposited tungsten gate 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 and post-oxidation conditions were analyzed. Figure 6 shows the photoemission spectra of Hf-4f in a  $\text{W}/\text{HfO}_2$  gate stack structure before and after the deposition of a tungsten film. 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 in  $\text{W}/\text{HfO}_2$ . Figure 7 shows the photoemission spectra of Hf-4f in a  $\text{W}/\text{HfO}_2$  gate stack structure with different post-oxidation times from 0 to 30 seconds. Comparing with the intensity of O-2s peak around 23 eV, it is clear that the peak intensity increases with the increasing of post-oxidation time. These changes of chemical bonding conditions in the hafnium oxide and the tungsten film indicate that the deoxidization of the  $\text{HfO}_2$  film and the formation of tungsten-oxide occurred in  $\text{W}/\text{HfO}_2$  gate stack structure. Similar change of chemical bonding condition was observed in the spectra of W-4d and W-4f. Figure 8 shows photoemission spectra of W-4f on a  $\text{W}/\text{HfO}_2$  gate stack structure. In this figure, W-4f spectrum on a tungsten oxide is also shown as a reference. The peak which is attributed to the oxidation of tungsten at about 37 eV appears in both  $\text{W}/\text{HfO}_2$  and tungsten oxide. This result clearly indicates that tungsten oxide formed at the interface of  $\text{W}/\text{HfO}_2$  gate stack. It is concluded therefore, the formation of tungsten oxide

is attributed to the excess oxygen atoms that are introduced into the film by post-oxidation after the ALD. The composition control of the hafnium dioxide film before deposition of the tungsten electrode film should be optimized for improving the quality of the gate-stack structure of hafnium dioxide.

#### IV. CONCLUSIONS

The degradation mechanism of the interface integrity between  $\text{HfO}_2$  gate dielectric film and tungsten gate electrode was analyzed using quantum chemical molecular dynamics and synchrotron-radiation photoemission spectroscopy. It was estimated that excessive oxygen atoms which are introduced into  $\text{HfO}_2$  dielectric film during post-oxidation annealing degrades the integrity of the interface due to the oxidation of the tungsten electrode. Similarly, carbon interstitials, which are automatically introduced in to the film during atomic-layer-deposition process, form tungsten carbide around the interface. These impurities deteriorate the reliability of devices seriously. The increase of the deposition temperature of tungsten accelerates the oxidation when excessive oxygen atoms remain in the oxide film before the deposition.

These results indicate that the optimization of the deposition process and the composition of the hafnium dioxide film before deposition of gate electrode is extremely important to ensure the reliability of MOS devices.

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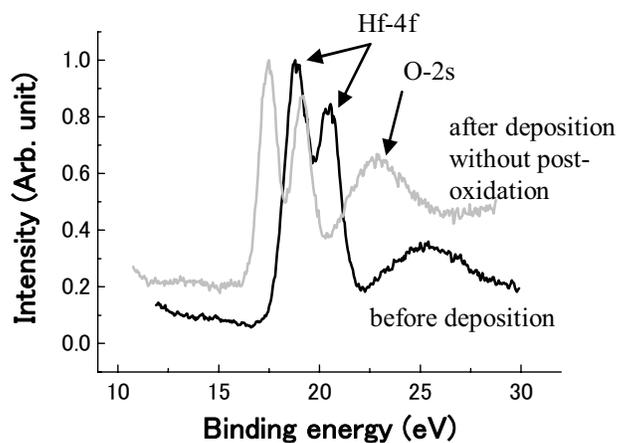


Figure 6. Peak shift of Hf-4f in the photoemission spectrum in a W/ $\text{HfO}_2$  gate stack structure after deposition of tungsten

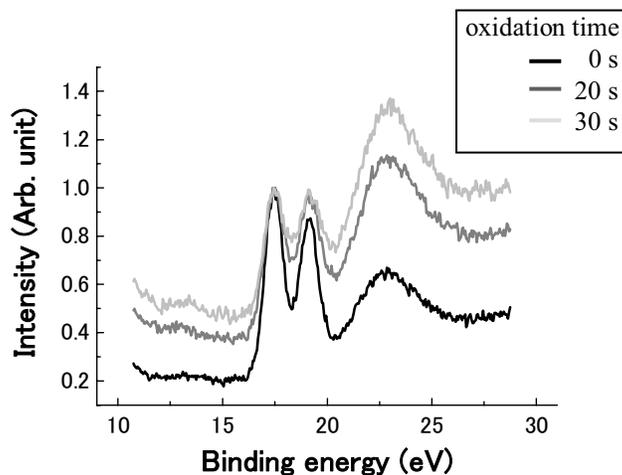


Figure 7. Photoemission spectra of Hf-4f in a W/ $\text{HfO}_2$  gate stack structure with different oxidation time

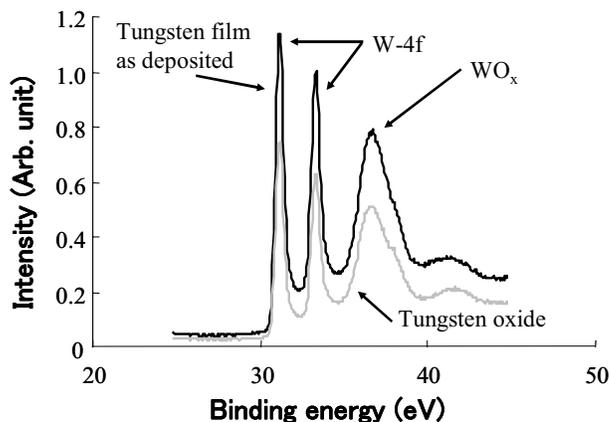


Figure 8. Photoemission spectra around W-4f peak in a W/ $\text{HfO}_2$  gate stack structure after 30 s post-oxidation and a tungsten oxide