Improvement of the Interface Integrity between a High-k Dielectric Film and a Metal Gate Electrode by Controlling Point Defects and Residual Stress

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Abstract— **In this study, the influence of composition of thin films on the interface integrity between a hafnium dioxide thin film and a gate electrode was investigated by using a quantum chemical molecular dynamics method. Effect of the fluctuation of the composition around the $HfO_{2\pm x}$/metal interface on the formation of the interfacial layer was analyzed quantitatively. Post-oxidation annealing after deposition of the hafnium oxide film restored oxygen vacancies and removed carbon interstitials from the film and thus, improved the quality of the oxide. However, when the excessive interstitial oxygen atoms remained in the film, the quality of the interface was deteriorated by forming a new interfacial oxide layer between the hafnium oxide and the deposited metal such as tungsten. No interfacial layer was observed, however, when a gold thin film was deposited on the hafnium oxide film with the various defects. Therefore, it is very important to control the composition around the interface, i.e., to minimize those point defects in the hafnium dioxide films and/or to introduce a diffusion barrier layer onto the oxide for improving the electronic performance and reliability of the stacked structure.**

I. INTRODUCTION

Highly reliable gate stack systems using a high-k dielectric thin film such as a hafnium dioxide (HfO_2) 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 novel 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 decreases the effective capacitance of the gate oxide and consequently deteriorates the electronic function of the MOS devices significantly. In addition to the interfacial problem, local defects in thin gate dielectric films play a very important role on both the electronic performance and reliability of the devices. One of the most important local defects in the gate dielectric is the compositional fluctuation caused by oxygen vacancies, oxygen and carbon interstitials. Quantum chemical molecular dynamics analysis showed that the quality of the high-k oxide film was deteriorated seriously by such point defects in the film because of the formation of the impurity states in the band gap of the film [1-3]. In particular, unexpected drastic decrease of the effective band gap of a hafnium dioxide thin film was caused by interstitial carbon atoms which remain in the film in large quantities after the film deposition process using organic gas sources. In addition, since the formation of the transition layer is dominated by diffusion of oxygen atoms near the interface, the existence of vacancies and interstitials should affect the diffusion and thus, the formation of the interfacial transition layer. Therefore, not only the interface control but also the defect engineering is other important issue to be discussed for the highly reliable systems. In this study, influences of the compositional fluctuation and residual stress of the oxide film on the interface integrity between a $HfO_{2\pm x}$ thin film and a metal gate electrode thin film was investigated by using quantum chemical molecular dynamics. The estimated changes of the interface structure were confirmed by experiments using synchrotron radiation photoemission spectroscopy.

II. ANALYTICAL METHOD

Computational chemistry approach is very effective in obtaining detailed information on the atomic bonding structure of materials for understanding the chemical and physical phenomena. *Ab initio* methods such as density functional theory (DFT) are widely used to study the material properties because it can provide accurate descriptions of electronic states. However, *ab initio* methods require 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. Tight binding molecular dynamics is another approach which can analyze large complex model faster than *ab initio* simulations. In this study, quantum chemical molecular dynamics (QCMD) simulations based on extended Hückel approximation were applied to the

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analysis of monoclinic $HfO_{2\pm x}$ with carbon and oxygen interstitials, and metal (tungsten or gold)/$HfO_{2\pm x}$ stacked structure using the colors code [4]. We modeled the structure of HfO_{2-x}, which is HfO_2 with oxygen vacancies, by eliminating oxygen atoms randomly from stoichiometric HfO_2 monoclinic structure. For the analytical model of HfO_2 with carbon or oxygen interstitials, a few carbon or oxygen atoms were introduced in interstitial sites of HfO_2 monoclinic structure. We used the two-dimensional slab models for the analysis of metal/$HfO_{2\pm x}$ interface. In order to investigate the effect of lattice strain on the interface integrity, three different orientation relationships between tungsten and $HfO_{2.12}$ were considered. The initial atomic configurations of interface models are shown in Fig. 1. In the interface models, the tungsten layer was stacked on the HfO_2 layer to fit the lattice constants of HfO_2. Surface lattice mismatch between W(001) and $HfO_{2.12}$(001), $HfO_{2.12}$(101) and $HfO_{2.12}$(111) in the simulation models are 8 %, 4% and 0.6 %, respectively.

Since extend Hückel approximation is used in our quantum chemical molecular dynamics simulations to solve the electronic state, we have to optimize the empirical parameters used in Hamiltonian. All the atomic parameters, therefore, were determined quantitatively based on the density functional theory (DFT) calculations and the experimental database. The parameters were determined by minimizing the differences between the analyzed results and the measured properties such as the geometry, binding energies, atomic charges, density of states of Hf, W, Au, 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. [5] for the exchange correlation functional. Though the magnitude of the band gap is a dominant factor that determines the dielectric properties of the gate oxide film, it is well known that the magnitude of the band gap of HfO_2 and WO_3 calculated by a conventional 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, and these values agreed well with the reported experimental results. Thus, our method should be effective for evaluating the integrity of the interfaces. The molecular dynamics simulations were performed for 10,000 steps with a time step of 0.5×10^{-15} seconds at 300 K.

III. Analytical Results

The authors have previously reported that point defects such as oxygen vacancies and oxygen interstitials in a HfO_2 crystal cause the drastic drop down of local band gap of the HfO_2 because point defects create donor or acceptor states in the band gap [1]. Carbon interstitials also decreased the effective band gap of a HfO_2 film significantly [2]. This is because that the interstitial carbon atoms interact with lattice hafnium atoms and create impurity states due to the formation of Hf-C bonds in the band gap of HfO_2. In addition, we found that some interstitial carbons substitute the debonded site of a HfO_2 crystal and consequently $HfO_{2-x}C_x$ structure was formed. Magnitude of the local band gap of $HfO_{2-x}C_x$ structure obtained from our quantum chemical molecular dynamics was 0.3 eV. 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 substituting carbon atoms 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 of hafnium dioxide because hafnium carbide has a good electric conductivity. Carbon interstitials are easily introduced into HfO_2-based dielectric films because dielectric films are deposited by ALD (atomic layer deposition) or MOCVD (metal-organic chemical vapor deposition) process using an organic gas source. Therefore, the minimization of the number of carbon interstitials in the hafnium dioxide film is indispensable for assuring the reliability of devices using HfO_2-based dielectric films. For improving electronic performance of the gate stack structures, we confirmed that post-oxidation annealing is effective for recovering the drop down of the local band gap caused by oxygen vacancies [3]. To simulate the effect of post-oxidation annealing on the removal of carbon interstitials, interstitial oxygen atoms were introduced to the HfO_2 thin film with carbon interstitials. Figure 2 shows the change of the structure of the HfO_2 thin film including carbon and oxygen interstitials at 300 K. Both the formation of CO molecules by interstitial oxygen atoms and subsequent evacuation of these CO molecules from the film were observed. Thus, the post-oxidation annealing is very effective for removing carbon interstitials from the HfO_2 film.

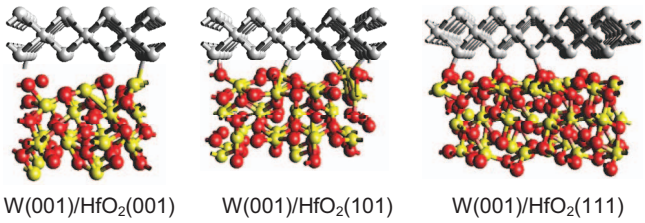

Figure 1. Basic QCMD simulation models of the W/HfO_2 interface. Oxygen and carbon interstitials are introduced into the models to analyze effects of these point defects on the electronic stractures of hafnium oxide and the stability of the interface between the the oxide and tungsten gate electrode.

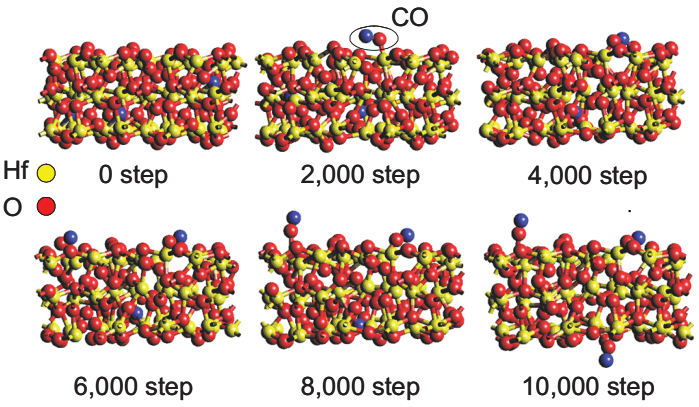

Figure 2. Change of atomic configuration of the HfO_2 thin film including 3 carbon interstitials and 6 oxygen interstitials. CO molecules formed by the reaction between oxygen abd carbon interstitials were evacuated from the film at final step.

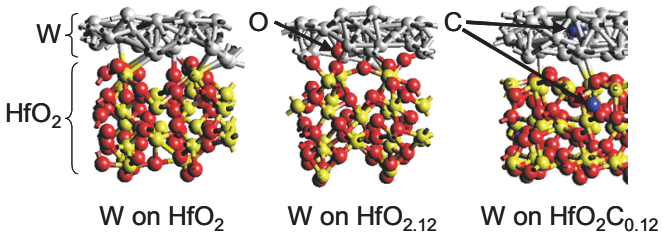

Figure 3. Examples of estimated changes of the interfacial structure between the HfO_2 (001) layer and tungsten (001) layer depending on the oxide composition. Tungsten oxide or tungsten carbide was grown partially due to the diffusion of the interstitials into the tungsten gate.

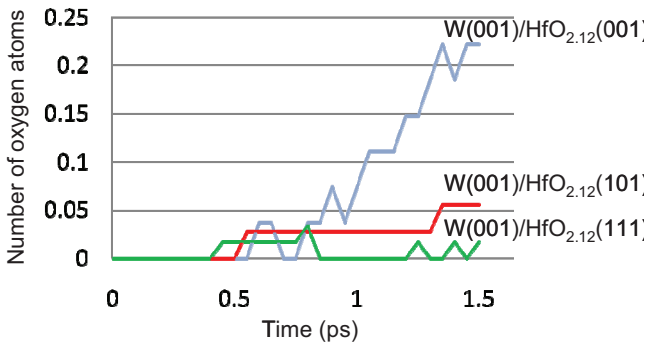

Figure 4. Change in the number of oxygen atoms diffusing into the tungsten film of the W/$HfO_{2.12}$ interfaces during the simulation.

Next, the influence of remained point defects such as oxygen and carbon interstitials in the hafnium oxide after the post oxidation annealing on the integrity of the interface between the oxide film and the deposited metal was analyzed. Figure 3 shows an example of the estimated result of the influence of the remained oxygen and carbon interstitials on the interfacial structure. When there were no interstitials in the oxide, the configuration of both the tungsten and HfO_2 layers were stable and the sharp interface structure was observed. Thus, an ideal interface structure can be achieved if the perfect hafnium dioxide is prepared before deposition of the gate metal. On the other hand, some oxygen atoms diffused into the tungsten film and thus, tungsten oxide was grown partially around the interface, when the excess oxygen interstitials remained in the hafnium oxide film ($HfO_{2.12}$) before the deposition of the tungsten film. This result indicates that although post oxidation annealing is effective for improving the electronic quality of the hafnium oxide with oxygen vacancies and carbon interstitials, heavy oxidation should deteriorate the interfacial integrity of MOS structures. In order to investigate the influence of lattice strain of the deposited metal layer on the interfacial structure, we compared the diffusion of oxygen atoms around W/$HfO_{2.12}$ interface with different orientation relationships. As in the case of W(001)/$HfO_{2.12}$(001) interface, diffusion of oxygen atoms into the tungsten film and formation of interfacial layer of tungsten oxide were observed in the W(001)/$HfO_{2.12}$(101) and W(001)/$HfO_{2.12}$(111) interfaces. Figure 4 shows the change in the number of oxygen atoms diffusing into tungsten film per one tungsten atom during the simulation. The number of

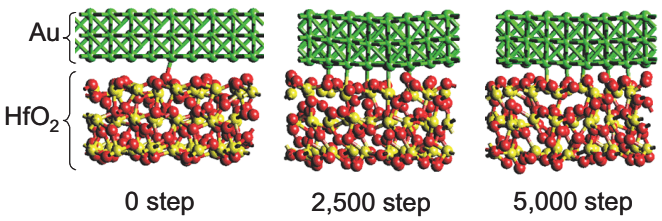

Figure 5. Estimated changes of the interfacial structures between $HfO_{2.12}$ and gold gate. No transition layer was grown and the interface structure was stable.

oxygen atoms in tungsten film of the W(001)/$HfO_{2.12}$(001) interface is much larger than that of the W(001)/$HfO_{2.12}$(101) and W(001)/$HfO_{2.12}$(111) interfaces. This result indicates that the tungsten film was oxidized easily by the diffusion of excess oxygen in the W(001)/$HfO_{2.12}$(001) interface. In terms of energetic stability of HfO_2 surface structure, HfO_2(111) is the most stable surface structure, and HfO_2(001) surface structure is more stable than the HfO_2(101) surface. However, tensile strain in the tungsten film of the W(001)/$HfO_{2.12}$(001) interface was larger than that of other interface models. Therefore, the diffusion rate of oxygen atoms into the tungsten film varied depending on the crystal orientation of HfO_2 due to the intrinsic strain around the W/HfO_2 interface. The remained carbon interstitials also diffused into the tungsten film and formed tungsten carbide near the interface ($HfO_2C_{0.12}$ in Fig.3). This formation of carbide also changes the electronic structures of the stacked structure. Therefore, the control of the composition of the HfO_2 film before the deposition of gate metal is very important to assure the electronic integrity of the stacked structure.

In order to protect the oxidation of the gate electrode material, the introduction of a diffusion barrier layer between the hafnium oxide and the gate electrode material is indispensable for assuring the high quality of the stacked structure. To discuss the efficiency of the diffusion barrier layer, we changed the material of the metal electrode from tungsten to gold. Figure 5 shows an example of the estimated results of the effects of gold on the interfacial structure. When the material of the metal electrode was changed from tungsten to gold, the interface structure was found to become stable regardless of the composition of the hafnium oxide. No change of the electronic structure appeared by the introduction of this layer. Therefore, gold is one of the effective candidates for the diffusion barrier material

IV. PHOTOEMISSION SPECTROSCOPY RESULTS

The estimated point defects-induced change of the interfacial structure between the $HfO_{2+x}C_y$ film and the metal gate electrode was validated by synchrotron-radiation photoemission spectroscopy. A high-energy excitation source (5947.3 eV) enabled to analyze the chemical shift of the component elements in the 4-nm thick $HfO_{2+x}C_y$ films with metal gate of 4-nm thick tungsten, aluminum and gold. The HfO_2 thin films of 4-nm thick were deposited by ALD. These films contained large density of carbon interstitials and oxygen vacancies. Post oxidation annealing was performed

after the film deposition. Detection angle of the photoemission spectroscopy was 88 and 30 deg. Figure 6 shows the photoemission spectra of Hf-4f in a W/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. Detection angle of the photoemission spectroscopy was changed from 88 deg to 30 deg to confirm that the O-2s peak appeared only around the interface. The intensity of the O-2s peak increased drastically after the change of this detection angle. This result suggests that the there is a strong gradient of oxygen and the concentration of oxygen around the interface was higher than that in the surface area. Thus, it can be concluded that interstitial oxygen atoms diffused out from the oxide and they diffused into the gate metal and thus, oxidized the gate metal partially. Figure 7 shows the measured change of the spectrum of Hf-4f caused by the change of material of the gate electrode deposited on $HfO_{2+x}C_y$. It was found that the peak of O-2s appeared clearly when the gate electrode material was tungsten or aluminum. On the other hand, no clear peak of the O-2s was observed when the gate electrode material was gold. This result indicated that both aluminum and tungsten gates were oxidized partially. This oxidation can be attributed to the excess oxygen in the hafnium oxide before the deposition of the metal electrodes. In addition, the peak positions of Hf-4f varied substantially depending on the gate electrode material. This peak shift indicates that the quality of the hafnium dioxide changed significantly depending on the gate electrode material.

Therefore, it is very important to minimize the concentration of both the remained oxygen and carbon interstitials in the hafnium oxide before the deposition of a gate electrode because both oxygen interstitials and carbon interstitials diffuse out from the oxide and thus, oxidize the gate electrode material. In order to protect the oxidation of the gate electrode material, the introduction of a diffusion barrier layer between the hafnium oxide and the gate electrode material is indispensable for assuring the high quality of the stacked structure. Gold is one of the effective candidates for the diffusion barrier material.

V. CONCLUSIONS

The influence of the composition of the HfO_2 film on the interface integrity between the film and a gate electrode was investigated by using a quantum chemical molecular dynamics method. Though post oxidation annealing of the HfO_2 film is effective for improving the oxide quality, excessive interstitial oxygen atoms remained in the film after the annealing deteriorate again the interface integrity because of the formation of a new interfacial oxide layer at the bottom of the deposited metal such as tungsten. No interfacial layer was observed, however, when a gold thin film was deposited on the hafnium oxide. Therefore, it is very important to control the composition of the HfO_2 film strictly, i.e., to minimize the point defects in the HfO_2 film for improving the electronic performance and reliability of the stacked structure. Introduction of a diffusion barrier layer onto the oxide is another effective method.

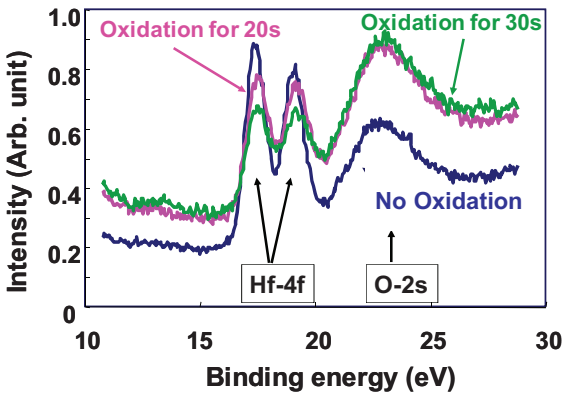

Figure 6. Photoemission spectra of Hf-4f in a W/HfO_2 gate stack atructure with different oxidation time.

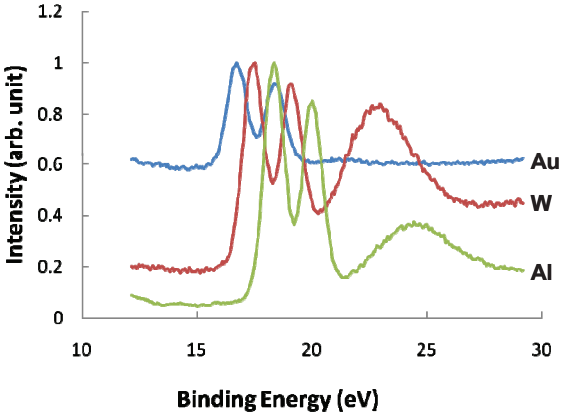

Figure 7. Change of the Hf-4f spectrum due to the change of the material of gate electrode. Clear peak of O-2s appeared when the gate material was tungsten or aluminum, while no O-2s peak appeared when the gate material was gold.

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