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Influence of Oxygen Composition and Carbon Impurity on Electronic Reliability of HfO_2

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Abstract

The effect of point defects such as oxygen vacancy and carbon interstitial on both electronic and structural characteristics of hafnium dioxide was analyzed by a quantum chemical molecular dynamics method. When a carbon atom as the impurity is introduced in hafnium dioxide, carbon impurity states (donor and acceptor) are formed in the band gap of hafnium dioxide. The band gap calculated from the energy difference between the donor and acceptor decreases to 1.6 eV. We conclude therefore, it is very important to control the composition of HfO_2 films in order to assure the electronic performance and reliability of hafnium dioxide film.

1 Introduction

Highly reliable gate stack systems using a high-k dielectric thin film such as a hafnium dioxide film are indispensable for the development of the sub-50-nm ULSI devices. It is well known, however, that the control of the interfacial crystallographic structure between the film and a Si substrate or a gate electrode film is one of the critical issues of high performance and stable operation of the devices. In addition, point defects such as oxygen vacancies and interstitials were found to make impurity-induced donor or acceptor sites in the band gap of the hafnium dioxide. 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, quantum chemical molecular dynamics was applied to explicate the degradation mechanism of dielectric properties of hafnium dioxide caused by point defects. Effect of oxygen vacancies and carbon interstitials on the local band gap of the oxide were analyzed.

2 Analytical Model

Quantum chemical molecular dynamics simulations were performed using the colors code [1]. 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 the atomic parameters were determined on the basis of density functional theory (DFT) calculations and considering the experimental results. In this study, we calculated the structural and electronic properties of monoclinic HfO_2 with

oxygen vacancies and carbon interstitial. The magnitude of the band gap is a dominant factor that determines the dielectric properties of the gate oxide film. We calculated the band gap value of HfO_2 from the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). 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 300 K.

3 Results and Discussion

One of the most important local defects in the gate oxide film is the compositional fluctuation caused by oxygen vacancies. Previously, we have reported the effect of oxygen vacancies on dielectric characteristics of hafnium oxide [1]. We found the drastic decrease of local band gap of hafnium oxide due to the oxygen vacancies. In addition to the oxygen vacancies, the insulating properties of hafnium dioxide could be affected by carbon interstitials, because ALD (atomic layer deposition) or MOCVD (metalorganic chemical vapor deposition) by using an organic carbon source gives the carbon interstitials as the impurity into the film. Therefore, in this study, we analyzed the effect of carbon interstitials on both the electronic and structural characteristics of hafnium dioxide. To evaluate the effect of carbon interstitials on the insulating property of HfO_2, the band gap value of HfO_2 with a carbon interstitial was calculated. The changes in the band gap of both stoichiometric HfO_2 and HfO_2 with a carbon interstitial at 300 K are plotted in figure 1. We calculated the average value of band gap in the latter half of the simulation, from 5,000 to the final step. The average value of band gap was 5.7 eV for stoichiometric HfO_2 and little fluctuation due to the thermal vibration of lattice atoms was observed during the simulation. For HfO_2 with a carbon interstitial, the band gap was quite small value of about 1.6 eV on average. This result reveals that the band gap structure of hafnium dioxide films is strongly affected by carbon interstitials. It is very important, therefore, to minimize the carbon concentration to assure the reliability of the films. This figure also clearly indicates that the amplitude of the

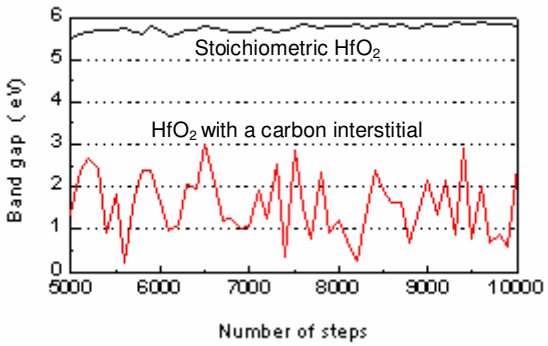

Figure 1: Change in the band gap of HfO_2 and HfO_2 with a carbon interstitial.

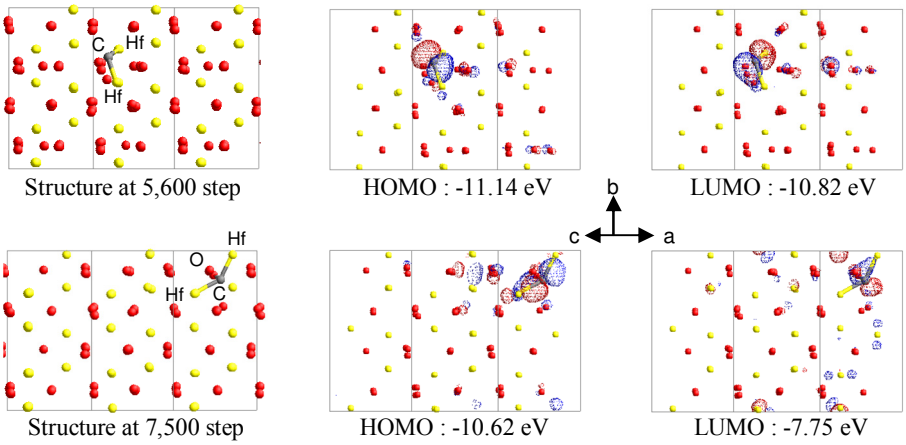

Figure 2: Distribution of HOMO and LUMO in HfO_2 with a carbon interstitial and their energy levels.

fluctuation of the band gap in HfO_2 with a carbon interstitial is considerably bigger than that of the stoichiometric HfO_2. To discuss the details of large fluctuation of the band gap, we analyzed the correlation between the atomic configuration and the characteristics of HOMO and LUMO. Figure 2 shows the spatial distributions of HOMO and LUMO in HfO_2 with a carbon interstitial at 5,600 step (band gap value: 0.3 eV) and 7,500 step (band gap value: 2.9 eV). From this figure, it is found that both HOMO and LUMO mainly distribute around the interstitial carbon atom at both simulation steps. This result, in which the carbon atom makes a major contribution to both HOMO and LUMO, indicates that HOMO and LUMO correspond to the impurity states (donor and acceptor) of carbon interstitial in the hafnium dioxide film. For 5,600 step, both HOMO and LUMO are seen to be a bonding orbital between the carbon atom and hafnium atoms. The distances between the carbon and the bonding hafnium atoms were about 1.9Å, which are shorter than the Hf-C bond distance in the hafnium carbide (HfC) crystal. On the other hand, the distance between the carbon and the nearest oxygen atom was 1.8 Å, which is longer than the typical bond distance between carbon and oxygen atom. For 7,500 step, the HOMO exhibits a similar character to that at 5,600 step, whereas the LUMO is localized on the carbon atom. We found that although little difference of Hf-C bond distances between at 5,600 step and 7,500 step, the carbon atom bonded to an adjacent oxygen atom of the matrix with the bond distance of 1.1 Å at 7,500 step. When HfO_2 with a carbon interstitial had a very small value of band gap, the relatively long distance between the carbon and the nearest oxygen atom was observed. We conclude therefore, that the strong interaction between carbon and hafnium would cause a drastic decrease of local band gap.

Since hafnium dioxide films deposited by ALD or MOCVD have oxygen deficiency, the reoxidation annealing is believed to be effective for improving the oxygen content of the film. We consider that the reoxidation is also effective to reduce the carbon intersitials and thus, the effects of reoxidation on the electronic and structural properties of hafnium dioxide including carbon impurity were studied. Figure 3 shows the snapshots during the molecular dynamics simulation of HfO_2 with both a carbon atom and an additional oxygen atom. The carbon atom moved toward the additional

oxygen atom and bonded to it at 2,400 step After that, the carbon atom diffused together with the additional oxygen atom as CO molecule for a while. As seen in figure 3, we observed that the carbon atom bonded to one of the oxygen atoms in the structure during almost all the simulation time. These results imply that the interaction with oxygen dominates the arrangement of the carbon atom unlike the case without the additional oxygen atom. In addition, it was found that band gap value increased to 5.8 eV in the maximum, 3.3 eV on average during the simulation and thus, the additional oxygen atoms into the film could eliminate the impurity states caused by carbon interstitial in the band gap. Therefore, we confirmed that the addition of oxygen is effective for improving the electronic performance of hafnium dioxide.

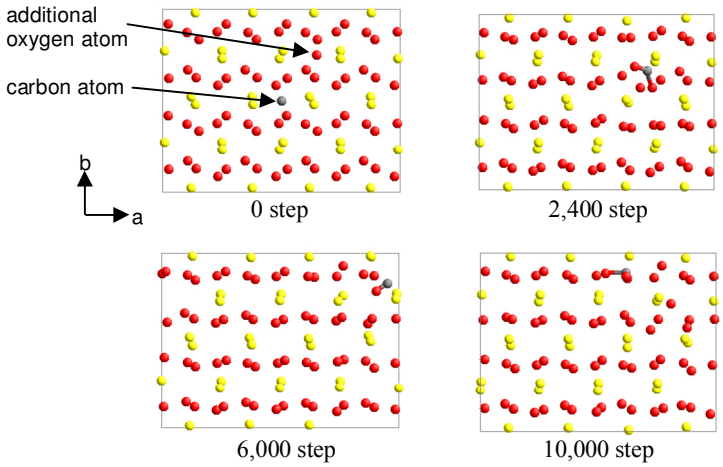

Figure 3: Change in the structure of HfO_2 with both a carbon interstitial and an additional oxygen atom during the simulation.

4 Conclusion

When a carbon atom as the impurity was introduced in HfO_2 film, the impurity states (donor and acceptor) were formed in the band gap of hafnium dioxide. The magnitude of the band gap of the HfO_2 with a carbon interstitial decreased locally from 5.7 eV to about 1.6 eV. On the other hand, we found that the introduction of the additional oxygen into the HfO_2 with a carbon interstitial eliminated the carbon impurity states in the band gap. It is very important, therefore, to control the composition of hafnium dioxide films in order to assure the electronic performance and reliability.

Reference

[1] Y. Ito et al., Proc. of the 2006 Int. Conf. on Simulation of Semiconductor Processes and Devices, 150 (2006).