Strain Dependence of Dielectric Properties and Reliability of High-k Thin Films

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***Abstract*— The effect of strain on both electronic and structural characteristics of HfO_2 used for sub-50-nm semiconductor devices was analyzed by a quantum chemical molecular dynamics analysis. The band structure of HfO_2 is strongly affected by strain in the film. Based on the change rate of band gap obtained from our simulations, the strain sensitivity of the relative permittivity of HfO_2 film is predicted to about 2.4%/1%-strain. The predicted strain sensitivity was validated quantitatively by measuring the change of the capacitance of MOS capacitors using a HfO_2 gate dielectric film. It is very important, therefore, to minimize the mechanical strain in the dielectric film to assure the reliability of MOS transistor.**

Keywords- *Quantum Chemical Molecular Dynamics; Reliability; Band Gap; HfO_2 Film; Strain*

I. INTRODUCTION

Electronic products such as mobile phones and PCs have been miniaturized continuously and their functions have been improved drastically. To keep their high performance, the thickness of the gate dielectric film has become thinner and thinner to an atomic layer level. 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. In conjunction with the new dielectric stack, metal gates are replacing polysilicon gate electrodes for material compatibility and system performance. Since the new gate stack structure has become very complicated and new metal gate materials with high melting point hold very high residual stress, mechanical stress or strain has been increasing in the gate dielectric film. Since high stress and strain deform the crystallographic structure of thin films in gate stack, the electronic functions and reliability of LSI devices may be deteriorated due to the change of band gap of semiconductor or dielectric materials. Actually, it is well known that tensile strain increases the leaking current though the dielectric film [1-4], which would be resulted from decreasing in band gap of gate dielectric materials by the strain. Therefore, the detailed understanding of the influence of strain on both the structural and electronic properties of a high-k dielectric film and control of the residual stress are key issues for improving the reliability of devices using the film. In this study, we performed a quantum chemical molecular dynamics analysis for HfO_2 film under strain in order to make clear the effect of strain on the dielectric characteristic of hafnium dioxide film. In addition, the change of the capacitance of MOS capacitors using HfO_2 gate dielectric film by the mechanical strain was measured applying the four-point bending method for the validation of simulation results.

II. ANALYTICAL METOD

Quantum chemical molecular dynamics simulations were applied to the analysis of the monoclinic HfO_2 crystal structure using the colors code [5]. Three dimensional periodic unit cell of monoclinic HfO_2 was modeled by select an orthogonal symmetry part from the crystal structure of HfO_2 with monoclinic phase. Figure 1 shows the relationship between the calculating model and ideal monoclinic structure of HfO_2. Since an extend Hückel approximation is used in this program to solve the electronic state, we have to optimize the empirical parameters in Hamiltonian. In this study, all the atomic parameters were determined on the basis of density functional theory (DFT) calculations and the experimental results. Details regarding the parameterization are indicated in the literature [6].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). For analysis of the strain dependence of band gap value of HfO_2 monoclinic phase, the equilibrium HfO_2 structure was hydrostatically deformed by the applied strain and the change of the band gap was calculated. In order to obtain the equilibrium lattice constants of monoclinic HfO_2

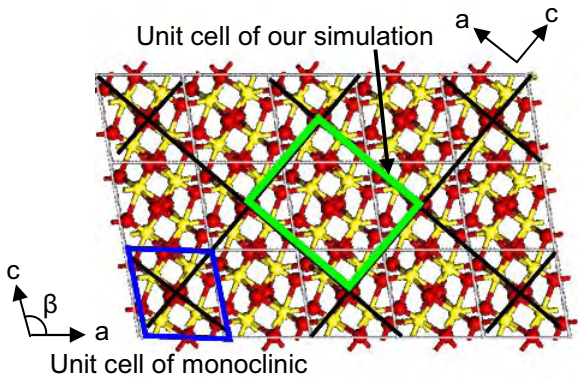

Figure 1. Relationship between the ideal monoclinic structure and our simulation model for HfO_2 with monoclinic phase.

structure, the structural relaxation calculation was performed by changing the volume at 300 K. After the relaxation calculation, it was assumed that this monoclinic HfO_2 structure was under strain-free condition. Then, the structure was deformed by uni-axial tensile or compressive strain to investigate the strain dependence of band gap values. The uni-axial tensile strain and compressive one were applied to the equilibrium structure by increasing and decreasing the length of the unit cell from equilibrium values, respectively. In order to calculate the band gap value of stained structure, molecular dynamics simulations were performed for 20,000 steps with a time step of 0.2×10^{-15} seconds under the fixed volume condition (no fluctuation of lattice constants during the simulation) at 300 K.

III. Results and Discussion

A. *Strain dependece of band gap*

The calculated strain dependences of the magnitude of the band gap at 300 K are summarized in Fig. 2. In this figure, the positive value of the strain is tensile strain, the negative one is compressive strain and the axis indicates the uni-axial strain direction. Previously, we have reported that the atomic configuration of monoclinic HfO_2 changed to cubic-like configuration when the compressive strain increased to 5% in b- and c-axis [6]. In this study, the uni-axial strain ranged from -2% to 2% in all directions to avoid large structural change such as phase transition, and we confirmed that no drastic crystallographic deformation occurred in this strain range. 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 10,000 to the final step. As a general tendency, the band gap values increase under compressive strain and decrease under tensile strain, although the band gap values at -2% and 2% strain along a-axis differ from this tendency. Similar tendency was found in a cubic HfO_2 structure by DFT calculation [7]. Change rate of magnitude of band gap obtained from our simulation in strain range from -1% to 1% is 0.8%/1%-strain. The change in the values of HOMO and LUMO of HfO_2 with 1% and -1% strain along b-axis are shown in Fig. 3. Comparing with the HfO_2 without strain, the energy level of LUMO shifted to lower and HOMO shifted to higher in 1% strain, on the other hand, LUMO shifted to higher and HOMO shifted to lower in -1% strain. The magnitude of the energy shift of LUMO due to the strain is found to be larger than that of HOMO. This result clearly indicates that energy of LUMO, which corresponds to the bottom of conduction band, is mainly changed by the uni-axial strain.

It is known that the dielectric properties of HfO_2 depend on the choice of crystalline polymorphs. For example, it is known that the variety of crystal structure changed the band gap value of about 1 eV and cubic phase had a small band gap comparing with the monoclinic structure [8]. We have considered, therefore, that strain induced structural change in HfO_2 thin film is an important factor that dominate degradation of reliability and performance of the gate dielectric film under mechanical strain. In order to discuss the structural change of monoclinic HfO_2 structure under uni-axial strain, the change of

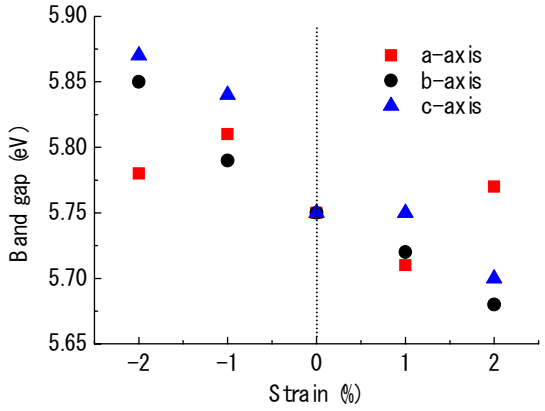

Figure 2. Strain dependence of band gap of monoclinic HfO_2.

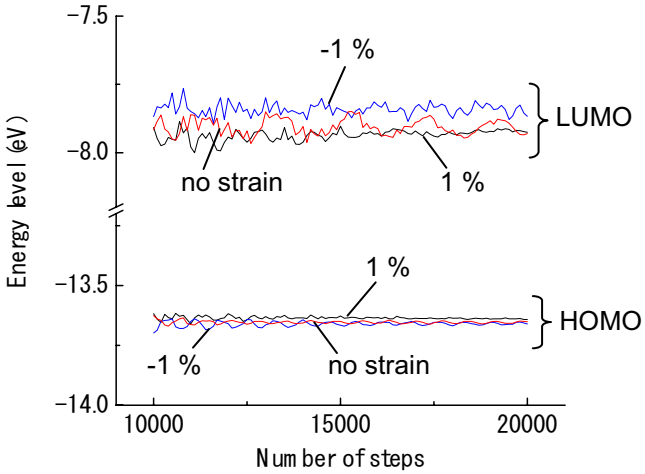

Figure 3. Change in the energy level of HOMO and LUMO in HfO_2 with 1% and -1 % strain along b-axis during simulation.

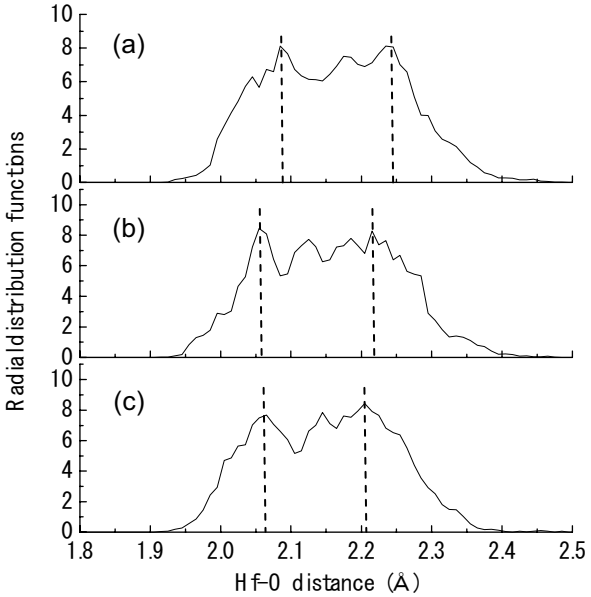

Figure 4. Radial distribution functions of Hf-O in HfO2.with (a) 1 % stain, (b) no strain and (c) -1 % strain along b-axis.

atomic configurations during the simulation was analyzed using radial distribution functions. Figure 4 shows radial distribution functions between hafnium and oxygen atoms during the simulation. In monoclinic HfO_2 without strain, there are two different bond lengths of Hf-O, short bond length of 2.06 Å and long one of 2.22 Å respectively as shown in Fig. 4 (b). From the analysis of radial distribution functions of Hf-O in strained HfO_2, we found that Hf-O bond lengths varied depending on the strain. At strain of -1% in b-axis, the long bond length was slightly shortened to 2.21 Å, while tensile strain of 1% elongated both short and long bond length to 2.09 and 2.24 Å, respectively. Normally the magnitude of band gap increases with decreasing the bond length and decreases with increasing the bond length. Therefore, the linear change of the band gap value is considered to be due to the linear change of Hf-O bond lengths by applied strain. From these results, we confirmed that the band structure of monoclinic HfO_2 is strongly affected by the change of Hf-O bond lengths caused by the applied strain.

B. Experimental validation

The change of the capacitance of MOS capacitors using HfO_2 gate dielectric film by the mechanical strain was measured by applying the four-point bending test for the validation of simulation results. The thickness of HfO_2 gate dielectric film was about 5 nm in MOS capacitor. The mounted sample was bended by applying a four-point bending method as shown in Fig. 5. The applied surface strain was monitored by strain gauges attached on the bending jig. The applied strain was monitored by three strain gauges adhered to the back surface of the bending beam. The beam was bended by screws fixed at the both edges of the beam. The symmetry of the loading condition was controlled by balancing the output of the adhered gauges. The change of the resistance of each gauge was measured by contacting proves as shown in the figure. The resistance change of each gauge was measured under uni-axial tensile stress loading condition. During the strain measurement, the ambient temperature was controlled at 30 ± 0.1 °C.

The relationship between relative permittivity (k) and band gap (E_g) is expressed by the following equation (1).

$$k = 1 + \frac{\alpha}{E_g^{\,2}} \qquad :\alpha = 4\pi^2 n e^2 h^2 / k_0 m^* \tag{1}$$

Here, n is the electron concentration. m* is the effective mass of electron. h is the Planck's constant. e is the electron's charge. The band gap is varied caused by the change of the distance between atoms due to mechanical strain. The relationship between relative permittivity (k) and strain (ε) can be expressed by the following equation (2) by differentiating the statement of equation (1) with respect to strain.

$$\frac{\partial k}{\partial \varepsilon} \cong 4\pi e^2 h^2 / k_0 \cdot \frac{\partial}{\partial \varepsilon}\left(\frac{n}{m^* E_g^{\,2}}\right) \tag{2}$$

Generally, the electron effective mass is proportional to the

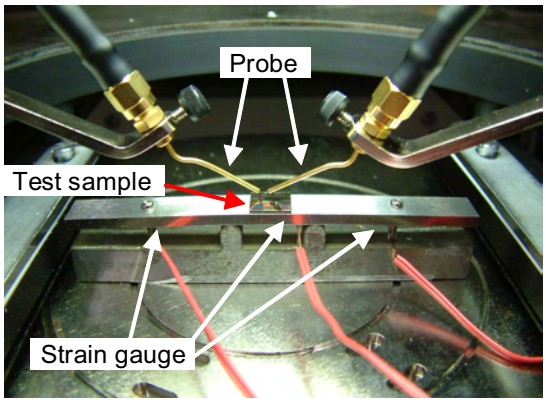

Figure 5. Outlook of fout-point bending method.

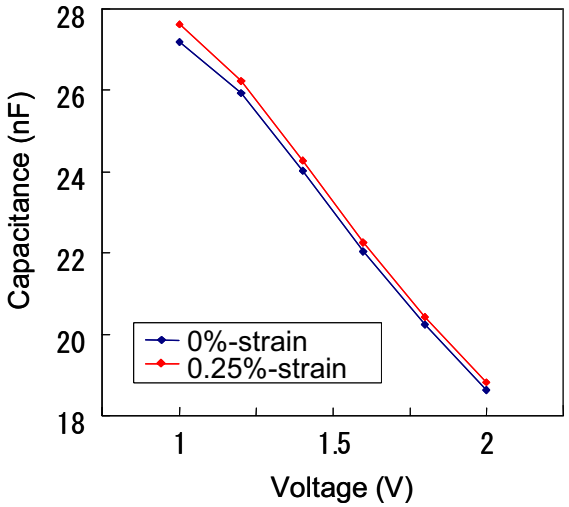

Figure 6. Effect of tensile strain on a capacitance of MOS capacitor using a HfO_2 gate dielectric.

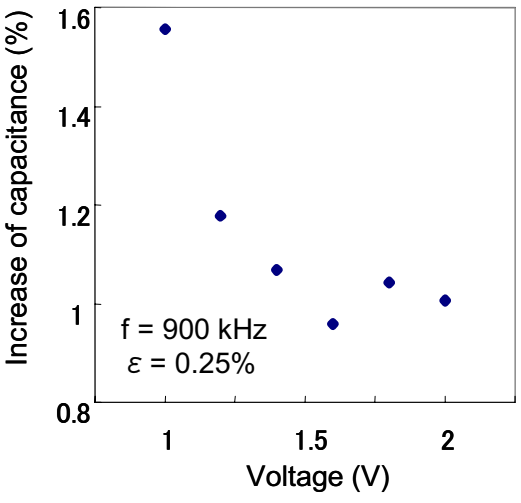

Figure 7. Change of capacitance in MOS capacitor using a HfO_2 gate dielectric by tensile strain.

energy band gap. This simple relation m* = βEg (β is constant) is applied to equation (2) and relationship between relative permittivity and strain is given by the following equation (3).

$$\frac{\partial k}{\partial \varepsilon} \cong 4\pi e^2 h^2 / \beta k_0 \cdot \frac{\partial}{\partial \varepsilon}\left(\frac{n}{E_g{}^3}\right) \quad (3)$$

According to equation (3), the change of the relative permittivity caused by strain is inversely proportional to the cube of band gap. Based on the change rate of band gap obtained from our simulation (0.8%/1%-strain), the strain sensitivity of the relative permittivity of HfO_2 film is predicted to about 2.4%/1%-strain. Figure 6 shows an example of the effect of tensile strain on C-V characteristic of MOS capacitor. The applied strain was about 0.25%. The frequency was 900 kHz. This figure clearly shows the capacitance of MOS capacitor is increased by tensile strain. The increase rate of capacitance at several voltage levels is summarized in Fig. 7. From the measurement of the change of C-V characteristic caused by mechanical strain, the change rate of the capacitance was estimated to be about 4%/1%-strain. This measured sensitivity of the relative permittivity of HfO_2 caused by the mechanical strain was in good agreement with the predicted strain sensitivity of the relative permittivity based on our simulation. Therefore, it is very important to minimize the residual stress and strain for decreasing the change of electronic functions of capacitors, leading to assure the reliability of devices using the HfO_2 dielectric film. In addition, the strain (stress) sensitivity of devices should be evaluated quantitatively before the structural design and the allowable limit of stress should be determined for assuring the reliability of the products.

IV. CONCLUSION

In this study, quantum chemical molecular dynamics simulations were applied to explicate the effect of strain on the dielectric characteristic of hafnium dioxide film. In order to analyze the strain dependence of the magnitude of the band gap of HfO_2 monoclinic phase, the structure was deformed by the applied uni-axial strain and the change of the band gap was evaluated. From the simulations, we found that the band gap value increased under compressive strain and decreased under tensile strain as a general tendency. The magnitude of band gap increased with decrease of Hf-O bond lengths and decreased with increase of Hf-O bond lengths. The relationship between band gap value and Hf-O bond lengths indicates that band gap values changes predominantly by the change of Hf-O bond lengths due to the strain. Change rate of magnitude of band gap obtained from our simulations in strain range from -1% to 1% is 0.8%/1%-strain. In order to validate the strain dependence of band gap obtained from the simulation, the change of the capacitance of MOS capacitors using a HfO_2 gate dielectric film by the mechanical strain was measured by applying the four-point bending method. Based on the change rate of band gap estimad from simulations, the strain sensitivity of the relative permittivity of HfO_2 film is predicted to about 2.4%/1%-strain. From the measurement of the change of C-V characteristic caused by mechanical strain, the change rate of the capacitance was about 4%/1%-strain. This measured sensitivity of the relative permittivity of HfO_2 caused by the mechanical strain was in good agreement with the predicted strain sensitivity of the relative permittivity based on our simulation. We conclude, therfore, that the dielectric properties of HfO_2 thin film are significantly influenced by the structural change caused by the applied strain. Thus, it is very important to minimize the residual stress and strain for decreasing the change of electronic functions of capacitors for assuring the reliability of devices using the HfO_2 dielectric film.

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