

Quantum Chemical Molecular Dynamics Analysis of the Effect of Intrinsic Defects and Strain on Dielectric Characteristic of Gate Oxide Films

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Abstract - In order to make clear the effect of strain and intrinsic defects in SiO₂ on both its electronic and structural characteristics, we performed a quantum chemical molecular dynamics analysis for SiO_{2-x} structure under strain. The band gap of SiO₂ changes significantly by the deformation of the Si-O-Si bond angle due to the applied strain. The crystallographic structure of the SiO_{2-x} deforms drastically because the Si-O bonds neighboring an oxygen vacancy are broken and a free silicon monoxide molecule is generated in the SiO_{2-x} structure. The magnitude of the band gap of the SiO_{2-x} decreases from 8.9 eV to 6.3 eV due to the change in the atomic configuration accompanying the diffusion of the free monoxide. In addition, the band gap decreases further under large tensile strain. We can conclude, therefore, that both the existence of oxygen vacancies and tensile strain in SiO_{2-x} films deteriorate the electronic reliability of the oxide film seriously.

I. INTRODUCTION

Electronic products such as mobile phones and PCs have been miniaturized continuously and their functions have been improved drastically. With miniaturization of semiconductor devices, the structure of devices has become very complicated. Since multi-layered structures of thin films are used for electronic devices, the constituent materials have large mechanical stress, strain and atomic defects caused by the lattice mismatch between the adjacent layers. Mechanical stress or strain in a gate oxide film of a MOS transistor decreases its band gap and thus, increases the leakage current through the film [1-4]. Local defects in the thin gate oxide film are also an important factor that determines both the electronic performance and reliability of the devices because localized states formed within the mid position of the band gap of the gate oxide film with intrinsic defects results in the leakage current and the degradation of the insulating property of the film. One of the most important local defects in the gate oxide film is the compositional fluctuation caused by oxygen or silicon vacancies introduced near the interface between the thermally oxidized Si-dioxide and the remained Si. Therefore, the detailed understanding of structural and electronic properties of non-stoichiometry SiO₂ under mechanical strain is a key issue for improving both the electronic characteristics and the reliability of the device. In this study, we performed a quantum chemical molecular dynamics analysis for SiO_{2-x} structure under strain in order to make clear the effect of the strain and intrinsic defects on dielectric characteristics of the oxide.

II. METHOD

The crystallographic structure and distribution of electron density are described well by *ab initio* molecular dynamics method and this method succeeds to provide us the useful information on the atomic bonding structure of materials. However, this method requires huge computational resources, and hence it can not be applied to the simulation of the complex system where the reaction dynamics should be considered. On the other hand, the tight-binding quantum chemical molecular dynamics method used in this study enables us much faster simulation than those based on regular first principle calculations because the formalization of this method is based on the extended Hückel approximation. We performed quantum chemical molecular dynamics simulation by using the colors code developed in Tohoku University [5].

The equations to be solved in this program are shown in equation (1) and (2):

$$HC = SC\varepsilon \quad (1)$$

$$C^T SC = I \quad (2)$$

where H is the Hamiltonian matrix, S is the overlap matrix, C is the eigen vector, ε is the eigen value, and C^T is the transformation matrix of C . The total energy between any pair of atoms, designated as A and B , is given by the following expression:

$$E = \sum_{A=1}^M \frac{1}{2} m_A v_A^2 + \sum_{i=1}^{OCC} n_i \varepsilon_i + \sum_{A=1}^M \sum_{A<B}^M \frac{Z_A Z_B e^2}{r_{AB}} + \sum_{A=1}^M \sum_{A<B}^M E_{repuls}(r_{AB}) \quad (3)$$

where the first, second, third, and fourth terms represent the kinetic energy, the summation of the eigenvalues of all occupied orbitals (orbital energy of valence electron calculated by extended Hückel approximation), the Coulombic interaction energy, and the short-range exchange-repulsion interaction energy, respectively. Here, m and v are mass and velocity of atoms, Z_A and Z_B are the charge of atoms, e is the elementary electric charge, and r_{AB} is the internuclear distance. The short-range exchange-repulsion term, $E_{repuls}(r_{AB})$ is given by

$$E_{repuls}(r_{AB}) = b_{AB} \exp\left(\frac{a_{AB} - r_{AB}}{b_{AB}}\right) \quad (4)$$

where the parameters a and b represent the sum of the size and stiffness of the atoms, A and B, respectively. Equation (5) is used for calculation of the force acting on the atom.

$$F_A = \sum_{A \neq B} \sum_{i=1}^M C_i^T \frac{\partial H}{\partial r_{AB}} C_i + \sum_{A \neq B} \sum_{i=1}^M \epsilon_i C_i^T \frac{\partial S}{\partial r_{AB}} C_i - \sum_{A \neq B} \frac{Z_A Z_B e^2}{r_{AB}^2} + \sum_{A \neq B_i} \frac{\partial E_{repuls}(r_{AB})}{\partial r_{AB}} \quad (5)$$

The parameters used in Hamiltonian were determined to satisfy the properties such as the geometry, binding energies, atomic charges and density of states of O_2 molecules, Si, and SiO_2 bulk structures obtained from the density functional theory (DFT) calculations or experiments. Three dimensional periodic unit cell for α -cristobalite that contains 32 silicon atoms and 64 oxygen atoms was used as SiO_2 for gate oxide. We modeled the non-stoichiometry SiO_2 (SiO_{2-x}) by eliminating oxygen atoms from the α -cristobalite unit cell to characterize the defect structure due to the oxygen vacancy. Calculation models used in this study are shown in Figure 1. The band gap value is a dominant factor of the insulating properties of the gate oxide film. However, the band gap of SiO_2 calculated by regular DFT method is known to be much smaller than the experimental value. In contrast, the band gap of SiO_2 determined from the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) calculated by our tight-binding method was 8.9 eV, which was in good agreement with the reported experimental values. Hence, we can confirm that this methodology is very powerful tool to analyze the strain dependence of the band gap. Further details regarding the parameterization can be seen in the literature [6-8]. The verlet algorithm [9] was used for integrating the equations of motion, while the Ewald method [10] was applied for calculating electrostatic interactions under three-dimensional periodic boundary conditions. The molecular dynamics simulations were performed for 20,000 steps with a time step of 0.2×10^{-15} second at 300 K.

III. RESULTS AND DISCUSSION

To analyze the strain dependence of the magnitude of the band gap of SiO_2 , the α -cristobalite structure was hydrostatically deformed and the change of the band gap was calculated. This hydrostatic tensile or compressive strain was expressed by increasing and decreasing the lattice constants of α -cristobalite. The calculated strain dependences of the magnitude of the band gaps are summarized in Figure 2. In this figure, the positive value is tensile strain, the negative one is compressive strain. The band gap values plotted in this figure are averaged in the latter half of the simulation, from 10,000 to the final step. The magnitude of the band gap slightly increases under compressive strain along both the a -, and the c -axis strain. This strain dependence is in good agreement with previous results by DFT calculation [4]. On the other hand, the band gap values decrease drastically under the tensile strain along the a -axis.

When the strain of 7.5 % is applied along the a -axis, the band gap value shrinks from 8.9 eV to 7.8 eV. When the tensile strain is applied along the c -axis, the band gap value

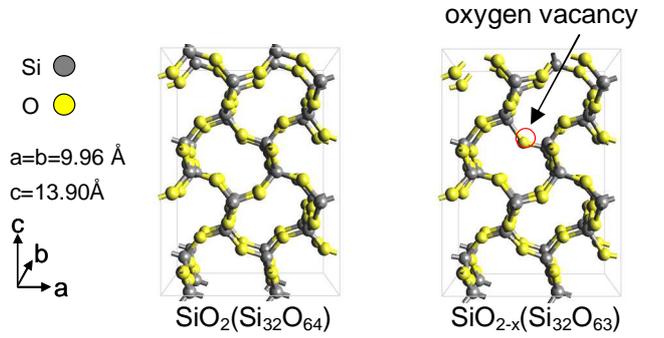


Figure 1: Model of SiO_2 and SiO_{2-x} crystal (α -cristobalite).

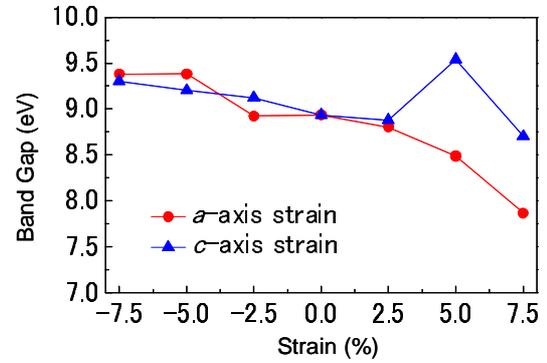


Figure 2: Strain dependence of band gap for SiO_2 . The positive value of strain is tensile, and the negative one is compressive.

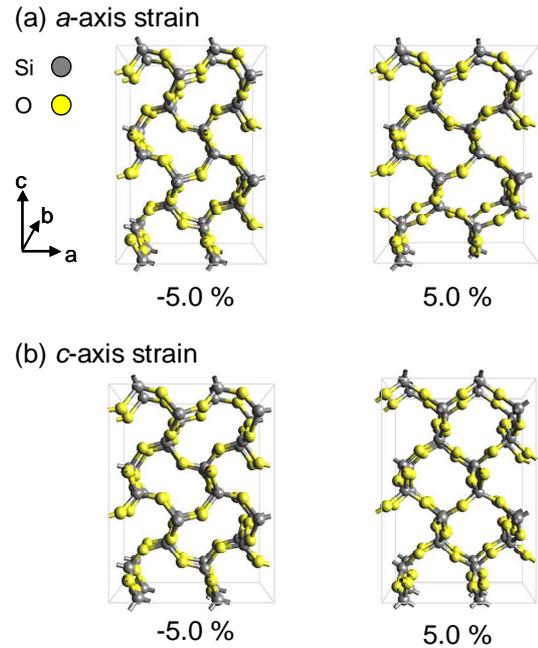


Figure 3: Snapshots of α -cristobalite structure with -5.0 and 5.0 % strain at the final step of simulation.

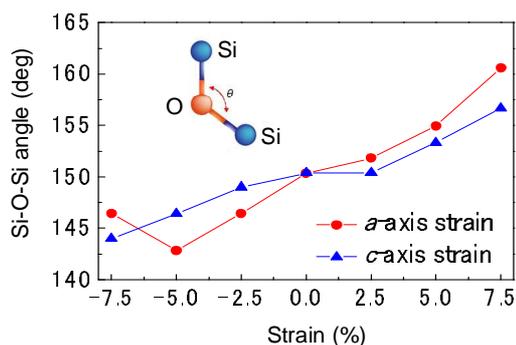


Figure 4: Correlation between average bond angles of Si-O-Si and strain.

reaches a maximum at 5.0 %. Figure 3 shows the final configuration of SiO_2 with -5.0 and 5.0 % strain. The large deformation of the α -cristobalite structure is observed under the tensile strain. In particular, the structure under 5.0 % strain along the c -axis seems to be close to the structure of β -cristobalite, which would be one of the reasons why the 5.0 % c -axis strain produced the maximum band gap in this simulation. From the analysis of radial distribution functions of Si-O, the bond lengths of Si-O in strained α -cristobalite did not change significantly from the average distance in the structure without strain. On the contrary, the large change occurred in the Si-O-Si bond angle in the strained structure. The correlation between the average Si-O-Si bond angle and the applied strain are shown in Figure 4. The bond angles become larger with the increase of the tensile strain. From these results, the band gap of α -cristobalite is significantly influenced by the deformation of the bond angles caused by strain.

The crystallographic structure of SiO_{2-x} that was expressed as the α -cristobalite structure with an oxygen vacancy changed drastically during the simulation. The Si-O bonds facing the oxygen vacancy were broken and a free silicon monoxide molecule (SiO) was generated and diffused into the lattice. It has also been reported that SiO molecule generated and diffused into SiO_2 [12]. Hence, the generation of SiO molecule in SiO_{2-x} is considered to be the potential process for the deformation of the non-stoichiometry SiO_2 structure. We also found that two kinds of defects, Si(O3) and O(Si1) sites, in the SiO_{2-x} structure during the simulation. At the Si(O3) site, a silicon atom bonds with three oxygen atoms. At the O(Si1) site, an oxygen atom bonds with only one silicon atom. Figure 5 shows the changes in the band gap of SiO_{2-x} . The distance between the liberated SiO molecule and the nearest atom in the lattice is also plotted in this figure. Calculated value of the band gap was 7.8 eV on average for the SiO_{2-x} , implying that the insulating property decreases in the SiO_{2-x} film. The figure also clearly indicates that SiO_{2-x} structure has large fluctuation of the magnitude of the band gap and the band gap value decreases when the distance between SiO molecule and the matrix becomes shorter during the simulation. To discuss the correlation between the atomic configuration and the band gap value, we analyzed the distribution of molecular orbitals and their energy levels.

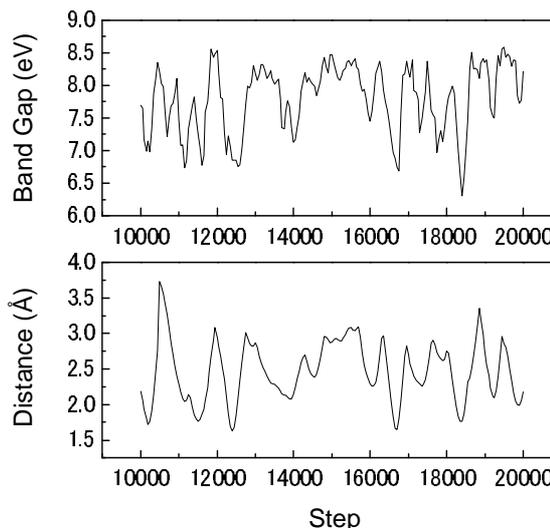


Figure 5: Change in the band gap of SiO_{2-x} (one oxygen vacancy) and distance between free SiO molecule and the matrix.

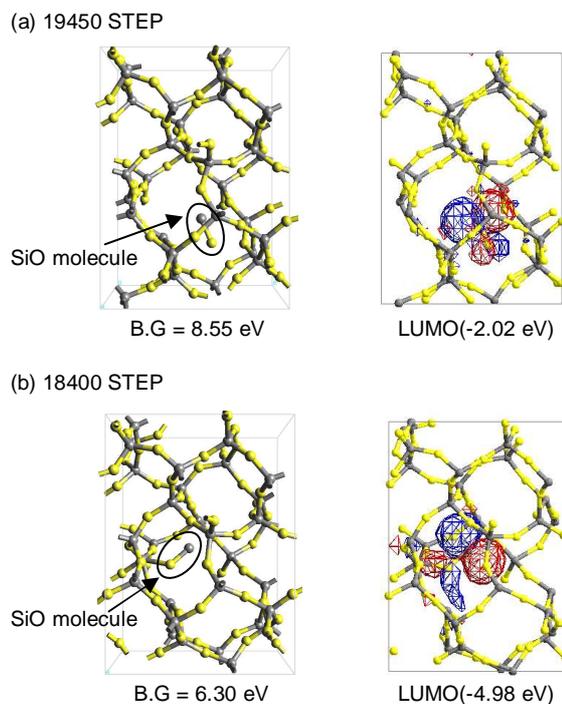


Figure 6: Defect structure and LUMO distribution of SiO_{2-x} (one oxygen vacancy).

Figure 6 shows the SiO_{2-x} structure and LUMO distribution at 19,450 and 18,400 step. For the structure at 19,450 step where the liberated SiO molecule was free in the lattice, the band gap value was 8.6 eV, which was almost the same value of the perfect SiO_2 crystal. On the other hand, the SiO molecule bonded to an adjacent silicon atom of the matrix at 18,400 step and its band gap was quite a small value of 6.3 eV. We observed that the energy of LUMO that mainly distributed around the liberated SiO molecule shifted to the low energy level at the atomic configuration in which the

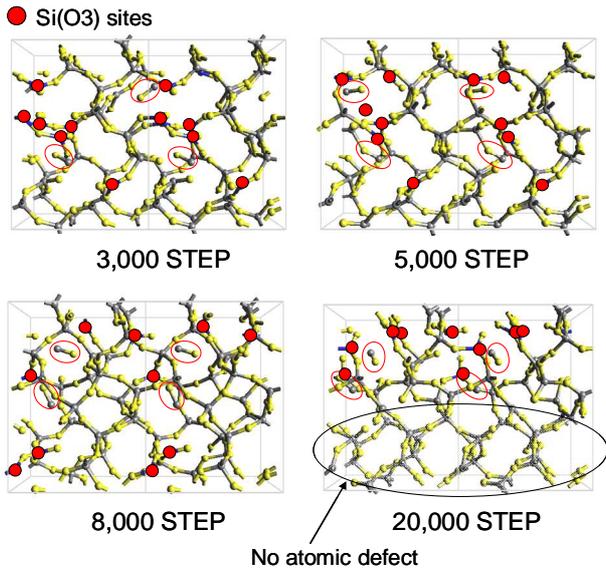


Figure 7: Change of SiO_2 structure with two oxygen vacancies and distribution of Si(O3) defect sites. Two unit cells are shown in this figure to make clear the clustering process of SiO molecules.

SiO molecule was located near the matrix. Hence, the large fluctuation of band gap value results from the change in the LUMO energy due to the change in the atomic configuration accompanying the migration of the liberated SiO molecule. The decrease of the magnitude of the band gap of SiO_{2-x} appeared under both tensile and compressive strain. Additional application of 7.5 % tensile strain value was lower than that of the perfect α -cristobalite structure by about 20 % in this simulation. We can conclude therefore, that both the existence of oxygen vacancies and tensile strain in SiO_2 films deteriorate the electronic reliability of the oxide film seriously.

Figure 7 shows the snapshots during the molecular dynamics simulation of α -cristobalite with two oxygen vacancies. Two free SiO molecules were generated independently and the defect sites such as Si(O3) and O(Si1) are also formed due to the formation of the free SiO molecules. The two SiO molecules started to cluster with each other and the defect sites of Si(O3) moved together with SiO molecules. This clustering process separates the damaged area with the perfect area as shown in this figure. The magnitude of the band gap of this structure was 7.1 eV on average, which is lower than that of the silicon dioxide without the oxygen vacancy by about 20 %. As we have mentioned before, the change in the atomic configuration due to the diffusion of the free SiO molecule seriously affects the shrinkage of the band gap. This clustering process of the two SiO molecules may indicate the generation of the well-known “weak spot” in the gate oxide film. Based upon our simulation results, we conclude that both the existence of oxygen vacancies and tensile strain in the SiO_{2-x} film deteriorate the electronic reliability of the film seriously.

IV. CONCLUSION

The effect of the strain and the intrinsic defects in the SiO_{2-x} film on both the electronic and structural characteristics of the film was analyzed using a tight-binding quantum chemical molecular dynamics method. Three dimensional periodic unit cell of α -cristobalite structure was used as a model of SiO_2 . The oxygen vacancy in the α -cristobalite structure generated free silicon-monoxide molecule that induced the large change of the atomic configuration of the film. The calculated band gap value of the SiO_{2-x} with one oxygen vacancy was 7.8 eV, which was significantly smaller than that of the perfect SiO_2 structure (8.9 eV). In addition, the value fluctuates widely from 6.3 eV to 8.6 eV depending on the distance between the liberated SiO molecule and the SiO_{2-x} lattice. The application of tensile strain to the SiO_{2-x} decreased the band gap further by about 10 %. With the increase of the number of the oxygen vacancy, the magnitude of the band gap decreases further. This is because that the generated plural SiO molecules start to cluster with each other. This clustering may be the reason for the formation of the well-known “weak spot” in the SiO_{2-x} film. We conclude therefore, that the magnitude of the band gap decreases seriously when both the number of oxygen vacancies and tensile strain increase in the SiO_{2-x} film. Such a decrease of the magnitude of the band gap causes the serious degradation of the electronic reliability of the gate oxide film in semiconductor devices.

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