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Fast Diffusion of Water Molecules into Chemically Modified SiO_2 Films Formed by Chemical Vapor Deposition

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We investigated water permeation properties into silicon oxide (SiO_2) and chemically modified SiO_2 films. The water permeability of fluorinated SiO_2 (SiOF) is higher than that of SiO_2, indicating that SiOF may have fast diffusion paths constructed from SiO–F structures formed by the breaking of Si–O–Si networks by F atoms. It is suggested that the presence of these fast diffusion paths can explain the reason for the high water permeability of various kinds of SiOF and other low-k films.

In semiconductor manufacturing processes, it is important to understand the water behavior in silicon oxide (SiO_2) insulation films. Currently, chemical mechanical polishing (CMP) is widely applied. Since the CMP technique is a wet process, water permeation into the films and adsorption on the surfaces sometimes cause device manufacturing failures. It is important to know the mechanism of water permeation in to SiO_2 and chemically modified SiO_2 films. However, the mechanisms of water diffusion into SiO_2 films are not sufficiently understood even now. Early studies by Deal and Grove[1] used the empirical method to lucidly express the oxidation rate of silicon and the diffusion process of oxidants into oxide films formed by thermal oxidation. Doremus[2] proposed a mechanism of water diffusion into SiO_2 films through the repetition of two-step reactions, i.e., 1) a condensation reaction of two SiOH structures and 2) hydrolysis of Si–O–Si by water molecules. Tomozawa[3] showed that fast moving molecular water in oxide is responsible for the silicon wet oxidation process. However, the diffusion mechanisms of water molecules in SiO_2 and chemically modified SiO_2 have not yet been thoroughly investigated and are still the subject of investigations.[4–6] In particular, theoretical methods in high accuracy molecular orbital (MO) calculations are not being used in these investigations.

We, therefore, calculated the energy for adsorption of water molecules by Si–O–Si clusters and fluorinated Si–O–Si clusters by means of an MO method based on density functional theory and related to experimental results obtained in thermal desorption spectrum (TDS). The mechanisms of water diffusion into SiO_2 and chemically modified SiO_2 (fluorinated SiO_2) were discussed. We have developed a molecular orbital program for the density functional theory called the electronic structure calculation program for atomic clusters (ESPAC). The details of ESPAC have already been reported.[7,8] Characteristically, ESPAC uses the inequality of Schwartz which can reduce unnecessary numerical calculations and enable fast calculation and high accuracy[7] (i.e., error in total energy is below 10^{-5} eV for C60).

We assumed many kinds of coordination structures of water molecules to SiO_2 and fluorinated SiO_2 (SiOF) cluster models and calculated hydrogen-bond energies for these structures. The structures were optimized in local density approximation, and energies were calculated by the generalized gradient approximation. Basis sets are Slater-type orbitals which include all electrons and polarization functions, and valence orbitals were doubled. All SiO_2 cluster groups were terminated with hydrogen atoms instead of dangling bonds since dangling bonds produce negative effects such as convergence of calculations and estimations of the chemical nature of silicon dioxide films. Sample SiO_2 and SiOF films were deposited on a bare silicon wafer by plasma.

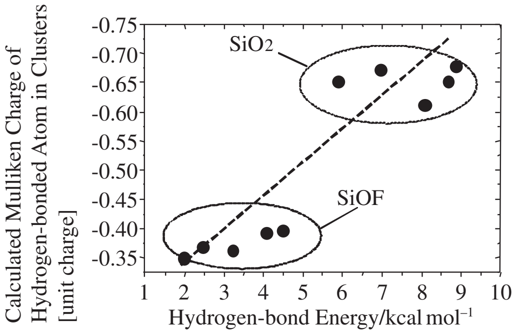

Figure 1. Hydrogen-bond energies and Mulliken charge.

We show 10 typical patterns of hydrogen-bond energies coordinating water molecules to SiO_2 and SiOF clusters in Figure 1. The hydrogen-bond energies are 2.02–8.90 kcal mol^{-1}, and the bond lengths are 0.21–0.29 nm. Calculated negative Mulliken charge almost totally depends on the hydrogen-bond energies. This suggests that fluorinating SiO_2 reduces hydrogen-bond energies caused by a decrease in the negative charge of oxygen atoms in clusters due to the high electronegativity of fluorine. The hydrogen-bond energies depend on Mulliken charge and do not depend on molecular coordination.

Figure 2 shows the TDS spectra of SiO_2 and SiOF films. Each peak corresponds to activation energies for water desorption from SiO_2 and SiOF films deposited by CVD. While the spectrum for the SiO_2 film has only one peak, that for the SiOF film has two. The desorption energy for first and second peaks, E_1 and E_2, are estimated to be 7–10 and 20–22 kcal mol^{-1}, respectively. The amount of desorbed water from SiOF films is larger than that from SiO_2 films, which is consistent with our calculation that fluorination reduced the adsorption energies of water molecules as shown in Figure 1. Since the first peak appeared only for the SiOF film, we would like to propose the following model that water diffuses in a stepwise manner into the SiOF film as shown in Figure 3. 1) First, water molecules are

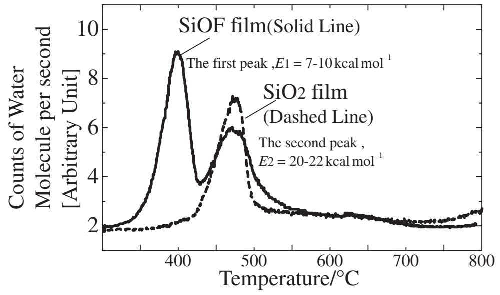

Figure 2. TDS of SiO_2 and SiOF (dipped three days in water).

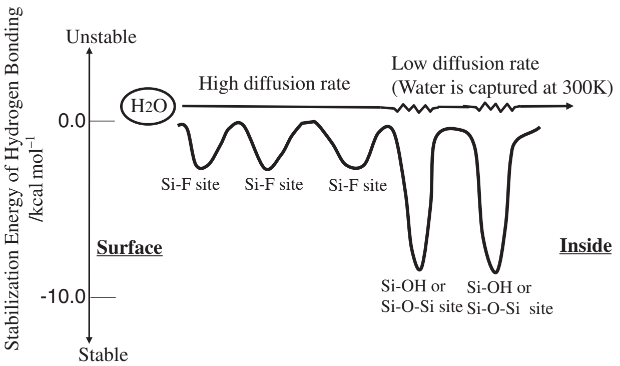

Figure 3. Schematic figure of energy diagram for water permeation into SiOF film based on MO calculations.

absorbed onto the SiOF film surface. 2) The SiOF film has fast diffusion pathways since F atoms have only one chemical bond and thus terminate Si–O–Si networks. Since the hydrogen-bond energy is lower than 4.52 kcal mol^{-1}, the water molecules easily diffuse through the fast pathway at 300 K without being trapped by Si–OH groups. The potential wells of the hydrogen bonds near the bonds of Si–F areas are shallow relative to SiO_2, so the diffusion rate is high and water molecules permeate into the film. In contrast, the potential wells of the hydrogen bonds near Si–O–Si structures or Si–OH bonds are deep (5.91–8.90 kcal mol^{-1}), so the water molecules are captured and have a low diffusion rate.

The results showed that the lifetime of water captured by SiO_2 clusters is almost a thousand times longer than that of water captured by SiOF clusters in Arrhenius approximation. Thus, it can be said that Si–OF structures provide a fast pathway for water molecules and that the molecules are finally captured by Si–OH or Si–O–Si structures. 3) Diffusing water molecules in the SiOF film are finally trapped by Si–OH groups in the film and stored up in the film. The schematic potential-energy diagram and diffusivity of water are shown in Figure 4. The potential wells of the hydrogen bonds near the bonds of Si–F areas are shallow (below 4.52 kcal mol^{-1}), so the diffusion rate is high and water molecules permeate into the film. In contrast, the potential wells of the hydrogen bonds near Si–O–Si structures or Si–OH bonds are deep (5.91–8.90 kcal mol^{-1}), so the water molecules are captured or have a low diffusion rate. We used the Arrhenius equation to calculate the relative lifetime of water molecules captured in these wells, assuming the same frequency factors for SiO_2 and SiOF. The results showed that the lifetime of water captured by SiO_2 clusters is almost a thousand times longer than that of water captured by SiOF clusters. Thus, it can be said that Si–OF structures provide a fast pathway for water molecules and that the molecules are in the end captured by Si–OH or Si–O–Si structures.

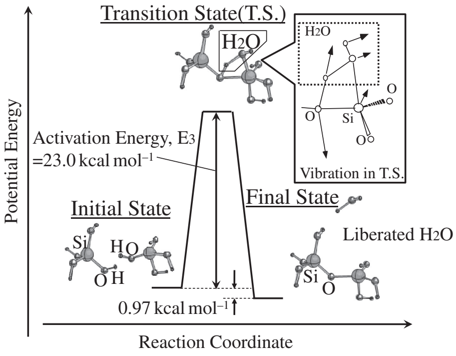

Figure 4. Equilibrium reaction of water with SiO_2 cluster.

The second peak in Figure 2 has apparently high energy relative to the energy of a hydrogen bond, can be attributed to condensation of two Si–OH structures and hydrolysis of the Si–O–Si structure. We used ESPAC to calculate the total electronic energy and the initial, final, and transition states for the reaction. This is shown in the energy diagram given in Figure 4. In the initial state, two Si–OH structures approach each other using thermal energy around the environment. These two clusters form the transition state that has vibrational states exhibiting water liberation. Finally, the transition state forms a Si–O–Si bond and H_2O at the final state. The theoretical activation energy, E_3 is 23.0 kcal mol^{-1}, and reaction enthalpy is a slightly endothermic -0.97 kcal mol^{-1}. Since the enthalpy is less than 1 kcal mol^{-1}, this reaction can be presumed to be an equilibrium reaction and thus reversible. We consider that the reaction represents water diffusion at a high-temperature region (20–22 kcal mol^{-1}) in TDS observation. The calculated activation energy agrees well with the experimentally evaluated energy. Since the trapping energy of a SiO–F structure is lower than that of Si–O–Si or Si–OH structures, the water molecules easily permeate into SiOF films. Consequently, the SiOF films have lower water resistivity than SiO_2 films. We hypothesize that the low water resistivity of the SiOF films, which is similar to that of low-k SiOC films, is caused by these fast diffusion pathways.

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