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Theoretical Analysis of Oxygen-Excess Defects in SiO_2 Thin Film by Molecular Orbital Method

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Energy states of oxygen-excess defects in SiO_2 have been studied by theoretical analysis using molecular orbital calculation. The photoluminescence peaks at around 2.4, 3.5 and 4.4 eV have been observed in SiO_2 film grown by photo-CVD. Moreover, the annealing effects suggest that the origins of the peaks at 2.4 and 3.5 eV are oxygen-excess defects. The theoretical analyses have been carried out by using both the semi-empirical and *ab-initio* methods, and show that the transition energy from excited-singlet to ground is 2.32 eV for STO-3G basis set and 2.4 eV for 3-21G basis set which are closed to the measured value 2.4 eV.

1. Introduction

Recently, integration of semiconductor devices such as a memory and a processor are markedly high and the sizes of these elements are minute. So, precise properties of the films used in the devices become very important. SiO_2 thin films play very important role as a gate insulator and an insulator of wiring in these devices, and defects in the SiO_2 film affect electrical properties of the device remarkably. Then, it is important that the defects in SiO_2 films are identified precisely. It is reported that the photoluminescence and optical absorption due to the oxygen-vacancy (≡ Si − Si ≡) defect were analyzed theoretically and the structure was determined[1-2]. However, the theoretical analyses of photoluminescence about the oxygen-excess defects such as (≡Si−O−O−Si≡), (Si−O−O ・) and (Si−O ・) have not been reported yet. So, oxygen-excess defects have been studied by molecular orbital (MO) analyses. The transition energy between the ground and the excited states is one of the results by this MO calculation, and is compared with photoluminescence peak energy. Now, photoluminescence is one of the most sensitive method to characterize a defect, and optical properties yield good information about peroxy linkage and other defects.[3-6] We have reported some photoluminescence and absorption peaks found in SiO_2 prepared by photo-induced chemical vapor deposition (photo-CVD) films, and the origins of these peaks were classified into oxygen-excess and oxygen-vacancy defects.[7-9]

In this work, we construct the clusters of oxygen-excess defect, particularly peroxy linkage (≡ Si − O − O − Si ≡) defects, and examine this energy level of clusters using molecular orbital (MO) method. Moreover, the photoluminescence peaks are compared with the calculated energy levels.

Table I. Deposition conditions of SiO_2 films

Light source	D_2 lamp
Working pressure	27 Pa
Back pressure	1.0×10^{-3} Pa
Substrate temp.	RT. ~ 300℃
Si2H6/O2 flow rate ratio	0.103 ~ 0.241
Substrate	MgF_2 or n-Si (100)

2. Photoluminescence of photo-CVD SiO_2 film

2.1 Sample preparation

The SiO_2 films were deposited by photo-induced chemical vapor deposition (photo-CVD). In thin-film fabrication methods, photo-CVD has the advantage of low temperature process without damage. Deuterium lamp was used for a vacuum ultraviolet (VUV) light source, and the samples were deposited at room temperature to 300 ℃. The deposition temperatures are much lower than thermal oxidation. The substrates are MgF_2 to measure optical absorption and n-type Si (100) to measure photoluminescence. The detailed deposition conditions are shown in Table I.

2.2 Photoluminescence measurement system

The samples are set in vacuum in optical dewar at room temperature. The light source to excite SiO_2 film is ArF excimer laser. Wavelength of the laser light is 193 nm, the photon energy is 6.4 eV, the pulse width is about 17 ns and the fluence is about 1 mJ/cm^2. Photoluminescence was focused by a quartz lens was detected monochromator (NIKON G250) and photo-multiplier (hamamatsu R1509).

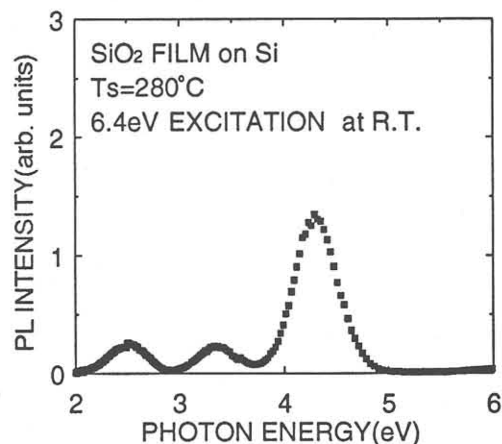

Fig. 1. Photoluminescence spectrum of SiO_2 film. The sample was deposited by photo-CVD at 280 ℃. The excitation is ArF excimer laser.

2.3 Photoluminescence spectra

Photon energy of the emitted light is less than the band gap of the SiO_2 (about 9 eV). Therefore, the origin of the photoluminescence is not recombination through direct interband transition, but radiation transition related to the levels created by defects in this case. Figure 1 shows the photoluminescence spectrum of the SiO_2 film deposited at 280 ℃. The peaks around 2.4, 3.5 and 4.4 eV are distinguished clearly.

The effects of annealing in O_2 and N_2 are measured to clarify the origin of the photoluminescence peaks. The annealing was done in N_2 or O_2 ambient at 400 ℃ for 1 hour. The photoluminescence peak at 4.4 eV decreases by annealing in O_2, but shows little change after annealing in N_2. This suggests that the 4.4 eV peak results from an oxygen-vacancy. The other peaks (2.4 and 3.5 eV) increase by annealing in O_2, but decrease by annealing in N_2. This suggests that these peaks (2.4 and 3.5 eV) are due to on oxygen-excess defect, and these defects are easily broken by heat.

3. Molecular orbital calculation and analyses

3.1 MO calculation method

MO calculations of the clusters of oxygen-excess defects have been carried out by using a semi-empirical method (MOPAC93[10]) and an *ab-inito* method (Gaussian92[11]) to clarify the structures of oxygen-excess defects. Table II shows the calculation programs and parameters.

3.2 Modeling of oxygen-excess defect

First, cluster model (1) shown in Fig. 2 was used. Initial geometry of used cluster is a part of c-SiO_2 in which an O atom is added between two Si atoms; Si-O distance is 0.16 nm, O-H distance is 0.1 nm. Si-O-Si angle is 144 degree, and dangling bonds were terminated by hydrogen atoms. Then, all bond lengths and angles were fully optimized by the semi-empirical MO method. This corresponds to enough relaxed SiO_2 structure, and neglect of surrounding atoms. After the optimization, it is thought that the bonding of two excess oxygen atoms is weaker. Dependence of energy of ground, excited triplet and excited singlet states on the Si-X lengths were calculated by semi-empirical MO method. The result is shown in Fig. 3. This cluster is quasi-stable at the point Si-X = 0.12 nm in the excited triplet state, and transition energy from the excited state to ground state is 1.8 eV. But, this value does not agree with experimental ones (2.4 and 3.5 eV).

Table II. MO calculation programs and parameters

Semi-empirical method
Program: MOPAC93
Parameters: PM3, C.I.
Ab-initio method
Program: Gaussian 92
Parameters: Basis set is STO-3G (3-21G). Single-excitation-C.I.

Next, another cluster model (2) shown in Fig. 4 was used. The initial geometry is the same one as model (1), but only the positions of two excess oxygen atoms between two Si atoms were optimized while the Si, H and other O atoms were fixed at the positions of c-SiO_2. This means the positions of Si atoms are fixed by influence of other atoms surrounding this cluster, but the excess oxygen atoms are movable. This cluster is quasi-stable at near Si-X = 0.16 nm, and transition energy from the excited state to ground state is about 2.3 eV. Moreover its geometry is in Si-Si coupled with O-O perpendicularly. This transition energy roughly agrees with 2.4 eV photoluminescence peak measured in photo-CVD SiO_2 film. Moreover, the dependence of ground state energy on the variation of the Si-X angle was calculated. The energy is independent of the small change of Si-X-Si angle.

3.3 Energy calculation on oxygen-excess defect

The transition energy of model (2) is calculated by ab-initio MO method to study the energy status precisely. Figure 5 shows that the dependence of energy of excited triplet and excited singlet state on the Si-X lengths. The cluster is quasi-stable at Si-X = 0.17 nm, the transition energy from excited singlet to ground state is 2.65 eV and this roughly agrees with experimental one. These

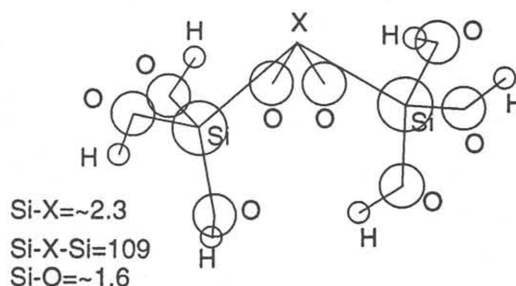

Fig. 2. The cluster model of oxygen-excess defect (1): The geometry was fully optimized.

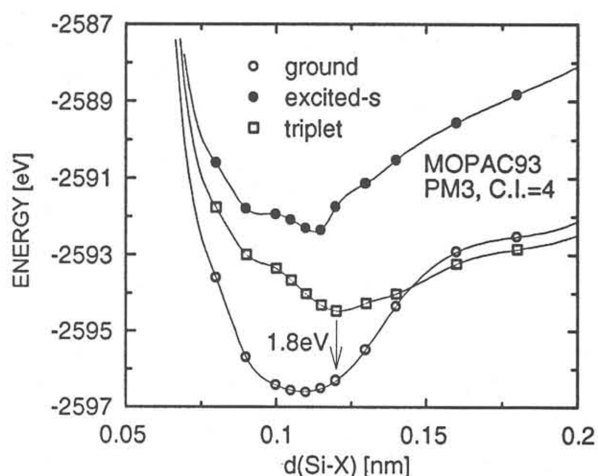

Fig. 3. The potential energy surface calculated by semi-empirical MO method about the cluster of oxygen-excess defect (1).

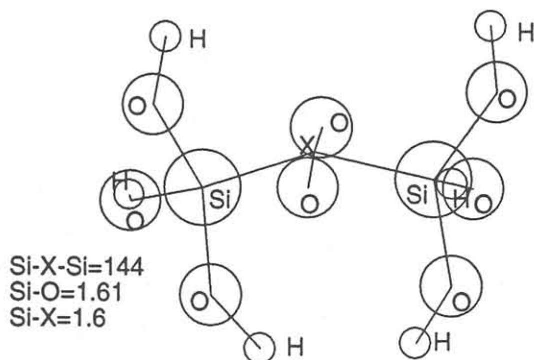

Fig. 4. The cluster model of oxygen-excess defect (2): Only the positions of two O atoms between Si atoms were optimized while other atoms are fixed.

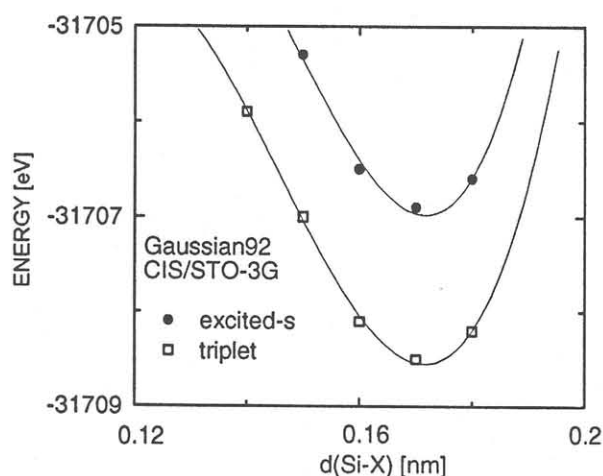

Fig. 5. The potential energy surface calculated by *ab-initio* MO method about the cluster of oxygen-excess defect.

theoretical results suggest that the defect which causes the 2.4 eV photoluminescence peak has atomic structure shown in Fig. 4 (cluster model (2)). Total amount of electron belonging to two excess oxygens is 0.77, although that belonging to single oxygen in defect-free structure is 0.33. Therefore, Si near oxygen-excess defect is ionized more than Si in defect-free structure. The *ab-initio* MO calculations with another cluster including more Si atoms and another basis set (3-21G) which is bigger than STO-3G basis set, were done to verify this transition energy. As a result, the cluster including three Si atoms has quasi-stable geometry, and the transition energy from excited singlet to triplet is 2.32 eV at this point. MO calculation with 3-21G basis set results that transition energy is 2.40 eV, and this agrees with the photoluminescence at 2.4 eV. Therefore, all calculated values are consistent, and these results suggest that the oxygen-excess defect relates to 2.4 eV photoluminescence peak.

On the other hand, the excitation energy of the cluster (1) was calculated, because the excitation energy evaluated by *ab-initio* MO method is different from one by semi-empirical MO method. *Ab-initio* MO calculation indicates that the transition energy from excited triplet to ground state is 1.74 eV, and the transition energy from excited singlet to ground is 4.06 eV. These results do not agree with experimental ones, although semi-empirical and *ab-initio* methods are different. It is thought, that *ab-initio* computations provide better quantitative prediction rather than semi-empirical method, because semi-empirical method has many parameters derived from experimental data. But, it needs a detailed discussion.

4. CONCLUSION

The oxygen-excess cluster ($Si_2O_2(OH)_6$) in SiO_2 was constructed, and this cluster's energy levels were calculated by *ab-inito* MO method. As a result, these clusters have quasi-stable geometry in coupled Si-Si with O-O perpendicularly. The transition energy is 2.40 eV (using 3-21G basis set) in this point, and the transition energies of another basis set and cluster are almost equal to 2.4 eV. Moreover, this transition energy agrees with photoluminescence peak at 2.4 eV which is assigned to oxygen-excess vacancy by annealing effects.

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