

Peroxy Linkage Defects in SiO₂ Examined through First-Principles Calculations: Defect Formation, Boron Binding, and Charged States of the B Adduct.

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1. Introduction

Peroxy linkage defects represent one of the fundamental defect structures in SiO₂ and their role as a B atom diffusion center in ultrathin gate oxides for MOS devices, as shown in Fig. 1, is of interest to researcher due to their impact on the reliability of MOS devices[1]. We have extensively examined the peroxy linkage defect through first-principles calculations to reveal its atomistic features more clearly than was done through previous semiempirical calculations[2].

2. Analysis

Models

A cluster model, (HO)₃-Si-O-Si-(OH)₃, was used as a SiO₂ model without any geometrical constraints while a periodic model based on a β -cristobalite crystal was used as geometrically constrained SiO₂ model. Although there could be several pathways for the formation of peroxy linkage in SiO₂, as shown in Fig. 2[3,4], the simplest scheme—insertion of interstitial oxygen into SiO₂ network—was assumed to be the primary process.

Computational programs

For the cluster-model calculation, we used an ab initio molecular orbital program, Gaussian 94[5], at the HF/MP2 level with a 6-31G* basis set. For the periodic model, we employed an ab initio local-density program, CASTEP[6], with pseudopotentials for Si, O, and B. Plane-wave basis sets with a cutoff energy of 500 eV were used for CASTEP. The geometrical prediction of the peroxy linkage in β -cristobalite with CASTEP was carried out using only the Γ point for the momentum-space integration while relaxing all freedoms of the cell parameters.

3. Results and Discussion

Peroxy linkage formation

The geometry of the transition state of the peroxy linkage formation that we analyzed with the SiO₂ cluster model is shown in Fig. 3 along with the product peroxy structure. The transition state contains Si fivefold coordinated with oxygen atoms. The activation energy for this insertion process of interstitial oxygen into the Si-O bond is 4.1 eV and the heat of reaction is 2.7 eV. This means that the transition state is located near the product system as the reaction is endothermic. The insertion process of the interstitial oxygen into the SiO₂ network was simulated by incorporating the oxygen into the SiO₂ bond in β -cristobalite crystal. The optimized structure of peroxy linkage in β -cristobalite is shown in Fig. 4. After the peroxy formation, the b axis was elongated by 0.03 Å while the a and c axes were shortened by 0.09 Å and 0.18 Å, respectively. The electronic structure of peroxy linkage in β -cristobalite is shown in Fig. 5. The profile of the valence bands and conduction bands differs slightly from that of the original

β -cristobalite. Two new states appeared that had very little dispersion in the forbidden gap of the β -cristobalite. The origin of these two new bands can be attributed to the localized lone pair orbitals of oxygen.

B atom binding to peroxy linkage

The optimized structures of B adducts to peroxy linkage in the SiO₂ cluster model are depicted in Fig. 6 for both the neutral state and positively charged(radical) states. The binding energy of B atom to the peroxy bond was 8.9 eV for the neutral state but rose to 12.4 eV for the radical state. In both cases, the binding energy was so large that the trapped B atom would be unable to escape from the binding site. We also analyzed the B incorporation into the peroxy bond in β -cristobalite, as shown in Fig. 4, for both charged states to determine the effect of geometrical constraints imposed by the crystal periodicity. The binding energies of B atom based on the β -cristobalite calculation are summarized in Table 1 along with those based on the cluster model. The crystal periodicity increased the binding energy by a few electron volts. These results indicate that the B diffusion model via peroxy linkage will not suffice as a realistic diffusion mechanism and more computational efforts are needed to reveal the atomistic diffusion mechanism.

Charged states of B

We analyzed the stability of the charged states of B incorporated in the peroxy bond using the method described by Yokozawa and Miyamoto[7]. Figure 7 shows the relative total energies of the charged states. For a low Fermi energy level, the positively charged state is preferred, while the negatively charged state is preferred once the Fermi energy level rises above 4.2 eV.

4. Conclusions

We have used first-principle calculations to extensively analyze formation energy, B atom binding, and the charged states of B in the peroxy bond for the peroxy linkage defect in SiO₂. Our results show that the intrinsic B atom diffusion mechanism in SiO₂ via the peroxy linkage does not reflect the actual diffusion phenomena and more work is needed to reveal the diffusion mechanism in ultrathin SiO₂ films. The B atom in a peroxy bond could behave as an electron trap or hole trap depending on the position of the Fermi level.

References

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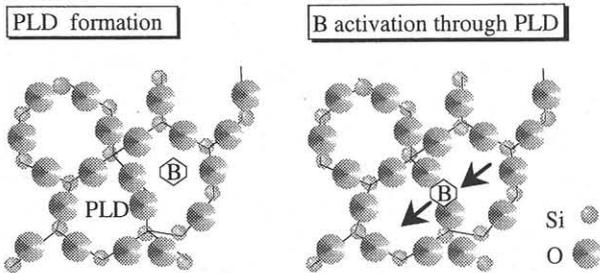


Fig. 1 Atomistic model proposed by Fair for the intrinsic B atom diffusion in pure SiO₂ via a peroxy linkage defect (PLD); Initial formation of PLD and subsequent activation through the PLD was assumed.

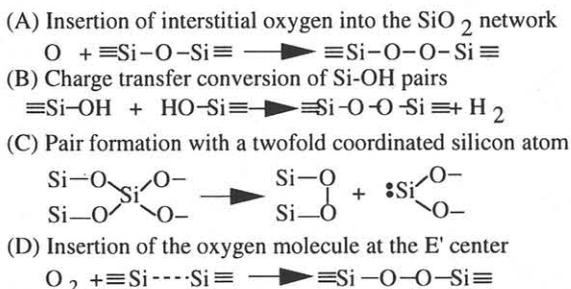


Fig. 2 Possible pathways for the PLD formation; Insertion of an interstitial oxygen atom into the SiO₂ network was assumed to bring about a PLD in the SiO₂ film in this study.

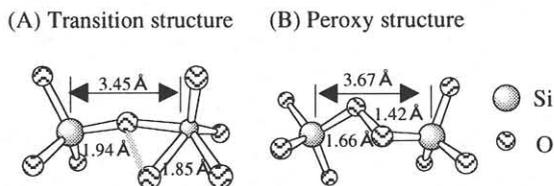


Fig. 3 Geometry of the transition structure for the PLD formation reaction caused by the insertion of an oxygen atom into the Si-O bond and the resultant PLD structure. The activation energy for this reaction was 4.1 eV and the heat of reaction was 2.7 eV (endothermic reaction).

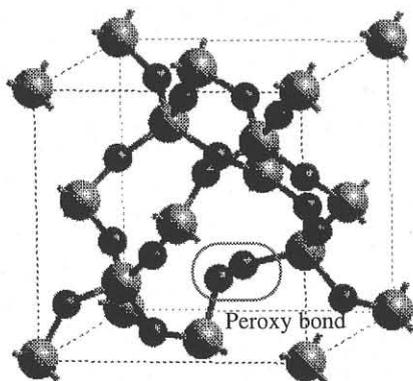


Fig. 4 The optimized structure of a peroxy linkage defect formed in β -cristobalite crystal. All freedoms, including the unit cell parameters, were fully relaxed. A slight elongation of the b-axis and a slight shrinkage of the a-axis and c-axis were observed after optimization.

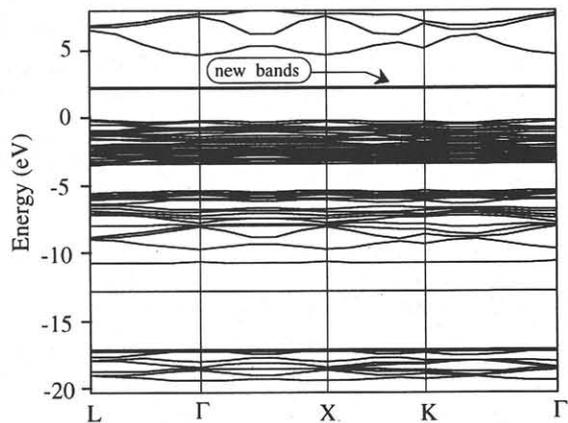


Fig. 5 The calculated band structure of β -cristobalite with one peroxy linkage defect (as shown in Fig.4) in the neutral state. Two bands with low dispersion appeared in the forbidden gap of the cristobalite. These bands were formed mainly by the oxygen atom of the peroxy bond.

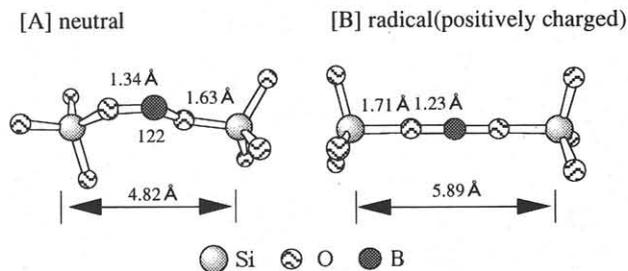


Fig. 6 The optimized structures of B adducts to peroxy linkage in different charged states: [A] neutral, and [B] positively charged. These structures were obtained with cluster models. The heat of reaction was -8.9 eV for [A] and -12.4 eV for [B].

Table 1 Summary of the heat of formation (eV) for the B adduct to the peroxy linkage evaluated with the flexible cluster model and the periodic model based on β -cristobalite as shown in Fig 4.

| Model | Neutral state | Positively charged state |
|----------|---------------|--------------------------|
| Cluster | - 8.9 | - 12.4 |
| Periodic | -13.9 | - 15.6 |

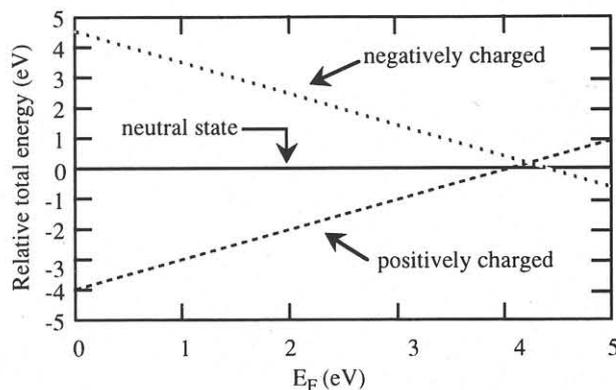


Fig. 7 The relative total energies of the three charged states --neutral, positively charged, and negatively charged -- for B adducts to the peroxy linkage formed in β -cristobalite as a function of the Fermi level. The total energy of the neutral state was set to zero.