Hole Trapping Due to Impurities in Amorphous Silicon Dioxide

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The roles of impurities in hole trapping in amorphous silicon dioxide (a-SiO$_2$) film are investigated employing the *ab initio* molecular orbital method applied to a cluster model. The calculations are carried out for OH, H, F, and Cl atoms terminating a silicon dangling bond in a-SiO$_2$. It is shown that a Cl atom acts as a trap for a hole. On the other hand, H atom itself does not serve as a trap site for a hole. The hole, however, weakens the Si-H bond by occupying the Si-H bonding orbital. It is found that F and OH have no significant effects on the hole trapping.

1. INTRODUCTION

The dielectric breakdown of thin gate oxides is a major cause of circuit failure. Trap generation in amorphous silicon dioxide (a-SiO$_2$) is receiving much attention because of its importance to the degradation and the dielectric breakdown of the gate oxides in metal-oxide-silicon (MOS) devices.[1-3] The generation mechanism, the structure, and the related properties of the traps, however, are still not well understood.

Some kinds of defects in a-SiO$_2$ are considered to induce charge trapping. They can be categorized into two groups. The first one is related to intrinsic defects, for example oxygen vacancy[4] and local distortion in a-SiO$_2$ network. It has been shown that the stretching of a Si-O-Si structure induces the hole trapping in the central oxygen.[5] The second is related to the impurities, i.e., extrinsic defects. Hydrogen-related impurities are commonly introduced into a-SiO$_2$ during the oxidation and the following processes. From a large amount of experiments, it has become clear that hydrogen plays several complex roles in the behavior of MOS devices.[6,7] The hydrogen is considered to contribute to both generation and annihilation of trap centers.

In this paper, we investigate the stable configuration and the electronic properties of impurities in a-SiO$_2$ employing the *ab initio* molecular orbital method applied to a cluster model. The calculations are carried out for H and OH terminating a silicon dangling bond in a-SiO$_2$. F and Cl in the same atomic configuration are also calculated. The roles of the impurities in the hole trapping in a-SiO$_2$ are discussed based on the electronic structures.

2. CALCULATION METHOD

The *ab initio* molecular orbital calculations are performed using the program package, Gaussian 92[8] within the framework of the unrestricted Hartree-Fock (UHF) method with the 6-31G** basis. The Si$_5$O$_{16}$H$_{12}$ cluster shown in Fig. 1(a) is used as the model of a-SiO$_2$ without impurities. In this cluster, the hydrogen atoms are placed to terminate the dangling bonds of silicon atoms and to simulate the effect of the a-SiO$_2$ outside the cluster.

In the following calculation, we use the stable atomic configuration of the Si$_5$O$_{16}$H$_{12}$ cluster determined by our previous calculation.[5] In the optimized configuration, all the atoms in the cluster are inequivalent as in the amorphous structure. The Si-O bond lengths and the bond angles around oxygen atoms distribute in the ranges 1.60 - 1.63 Å and 142 - 144° respectively. These values are in agreement with the experimental values.[9]

The models for OH, H, F, and Cl terminating a silicon dangling bond in a-SiO$_2$ are constructed by replacing one OSi(OH)$_3$ branch in Fig. 1(a) by one of the impurity atoms (Fig. 1(b)). The stable atomic configuration of each cluster containing an impurity is determined by freely relaxing the impurity and the surrounding four silicon and three oxygen atoms to the energy-minimum configuration without any restrictions on the symmetry. The positions of the hydrogen and oxygen atoms in outer part of the cluster are fixed at the same positions with those in the Si$_5$O$_{16}$H$_{12}$ cluster, throughout the calculation.
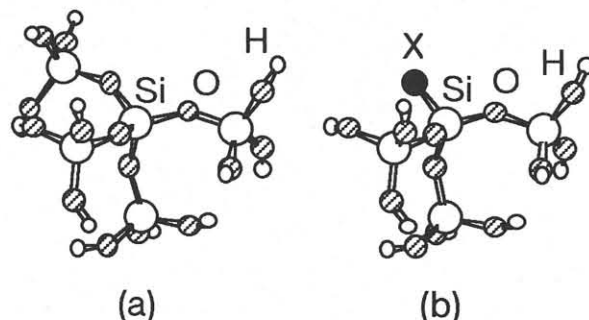

Fig. 1 Model clusters for a-SiO$_2$ (a) without and (b) with an impurity atom X (X = H, OH, F, or Cl).

3. ELECTRONIC STRUCTURES OF IMPURITIES IN a-SiO$_2$

The stable Si-X (X = OH, H, F, or Cl) distances in the neutral state are listed in Table 1. The change of the atomic configuration of SiO$_2$ caused by incorporating the impurities are small (less than 0.01 Å in bond lengths). The one-electron levels near the band gap for the stable atomic configurations with and without impurities are shown in Fig. 2. Since we model the infinite a-SiO$_2$ network by finite-size cluster, only qualitative discussion is possible on the positions of the levels. The levels related to the impurities are indicated in the figure. The

Table 1 Stable Si-X (X=OH, H, F, or Cl) distances in the neutral and positively charged states. For OH, the Si-O distance is listed.

Impurity	Si-X distance (Å)	
	Neutral	Positive
OH	1.62	1.59
H	1.46	1.45
F	1.58	1.56
Cl	2.05	2.42

impurity levels due to the OH and F atoms are deep in the valence band. These levels would not contribute to the hole trapping. On the other hand, the H atom generates the impurity level just below the valence-band edge. The Cl atom generates two nearly-degenerate impurity levels near the valence-band edge in the gap. The electrons occupying these two levels are strongly localized on the nonbonding 3p orbitals of the Cl atom. The impurity levels near the valence-band edge or in the band gap can contribute to hole trapping.
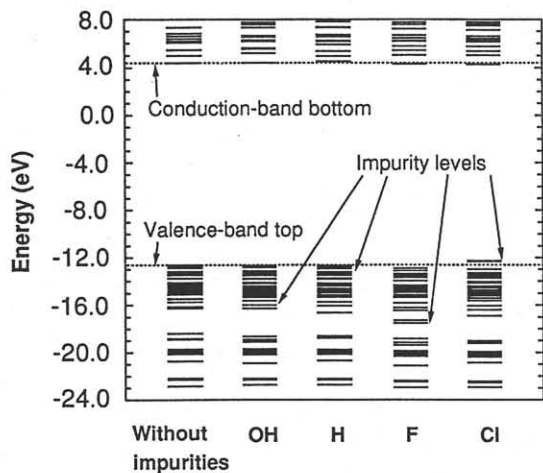
Fig. 2 One-electron levels around the band gap for various clusters with or without impurities.

4. EFFECT OF IMPURITIES ON HOLE TRAPPING

When a hole is introduced into each cluster, the stable configuration in the neutral state is no longer stable. The new stable atomic configuration involving a hole is calculated for each impurity cluster. The stable Si-X (X = OH, H, F, or Cl) distances in the positively charged states are shown in Table 1 compared with those in the neutral state.

4.1 OH and F

The change of the Si-X bond lengths is small for OH and F. For these impurities, the localization of the injected hole at the impurity site is not found. Thus, F and OH have no significant effects on the hole trapping.

4.2 Hole Trapping by Cl

In Table 1, it is found that the Si-Cl bond length increases largely by the hole injection. The injected hole is

trapped in one of the nonbonding 3p orbitals of the Cl atom and causes the large displacement of the Cl atom as shown in Fig. 3. The one-electron levels near the band gap for the clusters including a Cl atom are illustrated in Fig. 4, compared with those of the pure a-SiO$_2$ cluster without a hole. Valence-band top of a-SiO$_2$ in each cluster is set to the same level. Because of the hole trapping and the large structural change, one of the impurity levels corresponding to the nonbonding 3p orbital of the Cl atom moves from the vicinity of the valence-band edge to the midgap. The hole is trapped at this deep level. Thus, the hole will act as a trap for electrons.
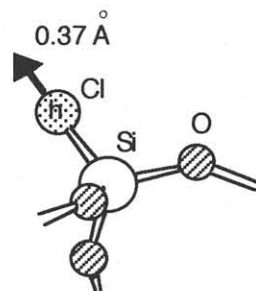
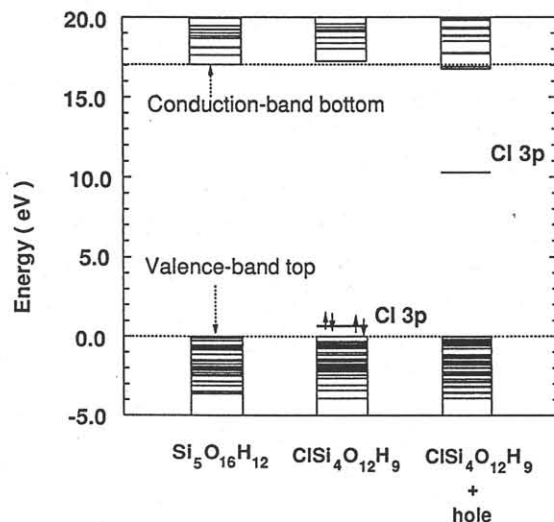Fig. 3 Displacement of the Cl atom with a hole.

Fig. 4 One-electron levels for Si$_5$O$_{16}$H$_{12}$ without a hole, ClSi$_4$O$_{12}$H$_9$ without a hole, and ClSi$_4$O$_{12}$H$_9$ with a hole.

4.3 Carrier-Enhanced Dissociation of H in SiO$_2$

In the case of H, the mechanism is somewhat different from Cl. The H atom causes a level just below the valence-band edge. Main component of the wave function corresponding to this level is the Si-H bonding orbital. As the Si-H bond length increases, this level is pushed up from the position just below the valence-band top into the band gap (Fig. 5), and the wave function is localized more strongly at the Si-H bond. This induces hole trapping at the Si-H bond. If the Si-H bond is slightly stretched, the injected hole can occupy the Si-H bonding orbital more easily to weaken the Si-H bond. Such a slight stretching will occur even during impurity vibration. The bond dissociation energy of the Si-H bond is 3.7 eV in the neutral state. This decreases to 0.6 eV when the hole is

injected. The activation energy for the dissociation of the H atom is less than 0.8 eV in this positively charged state (Fig. 6). Thus, in this state, the dissociation occurs easily even at room temperature. The H atom dissociates as a neutral atom leaving the hole at the Si atom. When the positively charged H atom dissociates leaving a neutral Si dangling bond, the total energy is 7.8 eV higher than in the case of neutral H atom. It should be noted that the H atom itself does not trap a hole. This point is different from the case of Cl.

It is well-known that H released from water-related species in SiO_2 can migrate across the oxide and accumulate at the Si/SiO_2 interface during the electron injection.[10] Although the hot-carrier capture process is not the unique step to the release of H atom, it is one of the possible step as mentioned above. As the released atomic H can easily react with various defects, it might contribute to the generation of new defects in a-SiO_2. Such behavior of H near the interface has already been reported.[11]

In our calculation, only the hole trapping was examined. The release of the H atom, however, might be caused also by electron trapping. In Fig. 5, it is found that the stretching of the Si-H bond pushes down the level at the
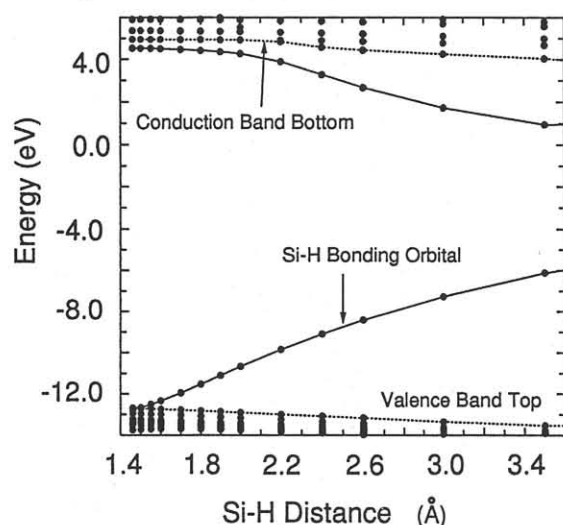

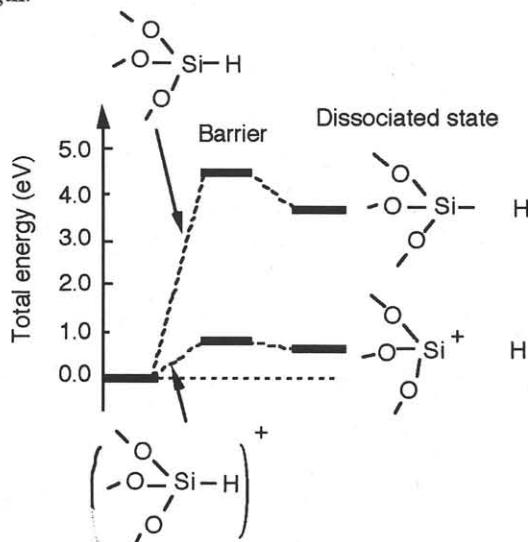Fig. 5 Change of orbital energies for the Si-H bond length.

Fig. 6 Change of bond dissociation energy of Si-H

conduction-band bottom into the band gap. The wave function corresponding to this level contains the component of the Si-H antibonding orbital, although it is not localized strongly. (Unfortunately, our model cluster is too small to describe such an extended wave function appropriately.) The localization, however, becomes slightly stronger as the Si-H bond length increases. The electron occupying this level may weaken the Si-H bond as the hole does.

5. CONCLUSION

The roles of impurities in hole trapping in a-SiO_2 film have been investigated employing the *ab initio* molecular orbital method applied to a cluster model. It has been shown that a hole injected into a-SiO_2 containing Cl impurity is trapped in one of the nonbonding 3p orbitals of the Cl atom, causing a large displacement of the Cl atom. The injected hole is not trapped in the H atom itself but can weaken the Si-H bond by occupying the Si-H bonding orbital. The bond dissociation energy of the Si-H bond decreases to 0.6 eV when the hole is injected. The activation energy for the dissociation of the H atom is less than 0.8 eV. Thus, the dissociation occurs easily even at room temperature. The H atom dissociates as a neutral atom leaving the hole left at the Si atom. We have found that F and OH have no significant effects on the hole trapping.

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