Hopping-Conduction Energy of Holes in SiO$_2$ Determined Accurately by Molecular Orbital Calculation

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1. Introduction

The trapping and conduction of holes is one of the major mechanisms that degrades dielectric characteristics of tunnel and gate oxides. The oxides used in ULSI are becoming thinner - now less than 5 nm, i.e., fewer than 50 atomic layers. Accordingly, to realize highly reliable ULSI devices, such problems should be treated specially as atomic-scale phenomena.

The conduction process of holes in SiO$_2$ has been treated by the stochastic approach with less clear atomic images[1,2]. Recently, the molecular orbital (MO) theory has revealed the features of the hole-trapping mechanism, e.g., Si-O bond stretching[3]. However, treatment of hole-hopping conduction from molecular point of view has not yet been reported.

With this as background, we report calculation of the energies required for hole-hopping based on MO theory. In our study, the configuration interaction (CI) method was utilized to accurately treat the change of electron distribution caused by hole-hopping.

2. Method of Calculation

Ab initio MO calculations were performed using the HONDO 7.0[4] program, based on generalized valence bond (GVB) total energy formalism and the CI method, using STO-3G basis set.

As SiO$_2$, Si$_2$O$_5$H$_{10}$ (Fig.1(a)) and Si$_3$O$_7$H$_{16}$ (Fig.1(b)) cluster models were used with vacancy-free and/or oxygen vacancy structures, respectively.

![Cluster models used for MO calculation](image)

(a) vacancy-free  (b) with oxygen vacancy

In order to obtain an energy-relaxed, hole-trapped structure, we introduced an excess hole into Si$_2$O$_5$H$_{10}$ and Si$_3$O$_7$H$_{16}$ of SiO$_2$ clusters. Then the atoms were allowed to moved freely until the total energy of the structure reached the minimum state.

With the vacancy-free SiO$_2$ structure, all atoms in the cluster (Fig. 1(a)) moved freely during the energy-relaxation process. Considering the variation in oxygen vacancy structures, we prepared two sizes of clusters (Fig.1(b)) before the energy-relaxation process. One was "large cluster", with a long Si-Si bond of 2.9 Å, and the other was "small cluster" with a short Si-Si bond of 2.5 Å. During the energy-relaxation process, only the atoms in the O$_3$Si-SiO$_2$ part of the cluster moved freely.

The hopping conduction process of holes in SiO$_2$ is shown in Fig. 2. First, the hole at site 1, when given the energy of $E^h$, moves to site 2 with no resultant change in the SiO$_2$ structure. Then, the SiO$_2$ gradually changes to the relaxed structure, keeping the hole at site 2. This process corresponds to the movement from A to B through C shown in Fig. 2.

![Schematic diagram of hole hopping from site 1 to site 2](image)

The hole-hopping energy of $E^h$, i.e., the electronic excitation energy, determines the critical path of this process. In order to calculate this energy, the CI method[5] was utilized. The wavefunction used in this method is written as the linear combination of electronic configuration state functions (CSFs).

\[
\Psi = \sum_{i,\alpha} C_{i,\alpha} \Phi_{i \rightarrow \alpha}
\]

(1)

Here the CSF $\Phi_{i \rightarrow \alpha}$ is a Slater determinant in which one electron is excited from MO $\Phi_i$ to $\Phi_\alpha$. More than 25,000 CSFs were used in the present calculation.

In addition, the ground and j-th excited states are obtained by solving the equation below:

\[
H \Psi' = E' \Psi'
\]

(2)

If the ground state $\Psi'$ and j-th excited state $\Psi'$ respectively...
express the hole trapped at site 1 and site 2, the hole-hopping energy $E^h$ is calculated as the difference in the energies of the two states:

$$E^h = E - E^0$$

(3)

3. Results and discussion

(1) Hole-trapped structure in SiO$_2$

Our calculation indicated that one of the 2$p$ lone pair within MO of oxygen (O(5) in Fig. 1(a)) was occupied by only one electron, which means that the oxygen atom was occupied by a hole. The length of the Si-O bonds after hole-trapping (Si(2)-O(5) and Si(3)-O(5)) was estimated as 1.8 Å, which was 10% longer than that of the other Si-O bonds. These results agreed well with those reported previously [3].

(2) Hole-hopping energy

In the case of the vacancy-free SiO$_2$ cluster, the hole moved from one oxygen atom (O(5) in Fig. 1(a)) to another oxygen atom (O(4)), as schematically shown in Fig. 3. This resulted in a large hole-hopping energy value of 2.84 eV. Conversely, in the case of the oxygen vacancy clusters, the hole moved from one oxygen atom (O(5)) to the MO site that had the Si-Si bonding property. This resulted in small energy of values 1.09 eV for the "small cluster" and 1.26 eV for the "large cluster".

![Energy Diagram](image)

Fig. 3: Energies necessary for hole-hopping as a function of Si-Si distance. Calculation was performed for various SiO$_2$ structures.

From these results, we can derive the following scenario for the conduction of holes in SiO$_2$ When a hole is injected into SiO$_2$ having a large kinetic energy, it moves more smoothly into the oxygen vacancy area than into the non-vacancy area, because the difference in hole-hopping energy between the two areas is more than 1.5 eV. In actual device operation, a certain electric field, 10 MV/cm for example, is usually applied to the small area (about 5Å) of oxide that contains the two hole-trapping sites as shown in Fig. 3. Consequently, the hole can pick up 0.5 eV of energy which will lower the hole-hopping energy we have calculated to less than 0.8 eV.

These findings well explain the experimental fact that the hole density after Fowler-Nordheim stress is very high in the vicinity of the Si/SiO$_2$ interface, where many oxygen vacancies are expected[6].

4. Conclusion

The critical energies required for hole-hopping in SiO$_2$ were calculated for the first time on the basis of MO theory which can treat excitation very accurately. The calculation showed large energy values in vacancy-free SiO$_2$ structures and small ones in oxygen vacancy SiO$_2$ structure. These results well explain the experimental results, which indicate that hole-hopping energy plays an important role in determining the hole distribution in the SiO$_2$ and Si/SiO$_2$ interface region.

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References

4) HONDO ver. 7.0: M. Dupuis et al., QCPE #544, Indiana University, Bloomington, Indiana, USA (1987)
5) A. Szabo and N. S. Ostlund: Modern Quantum Chemistry; Macmillan Publishing (1982)