# Dependence of Hopping-Conduction Energy of Holes on Distance between Trap Sites in SiO<sub>2</sub>: a Molecular Orbital Calculation

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## **1. Introduction**

Hole conduction in  $SiO_2$  is one of the most important processes affecting the dielectric degradation in tunnel and gate oxides. Both macroscopic and microscopic models have been proposed for this process. The macroscopic random-walk model has successfully predicted the time propagation of spatial charge distribution caused by hole conduction [1]. Meanwhile, the microscopic model described the hole conduction as direct hopping among localized trap sites [2].

In a recent experimental study based on substrate hot-hole injection, the mechanism which causes decrease of hole fluence to breakdown was discussed on the atomistic level in terms of Si-O bond breakage [3]. But the macroscopic and microscopic models mentioned above cannot give physical insight into this degradation process. To realize highly reliable devices using thin oxide, less than 5 nm thick, degradation phenomena should be understood from atomic and molecular points of view.

Using molecular orbital (MO) calculation, we recently showed that the existence of oxygen vacancy in  $SiO_2$  drastically reduces the energy necessary for hole hopping [4]. In the present paper, in order to understand the phenomenon in hole hopping conduction in more detail and explain the experimental results shown above, we calculated the dependence of hopping conduction energy on the distance between trap sites.

### 2. Method of calculation

The *ab initio* MO calculations, based on generalized valence bond (GVB) total energy formalism and the configuration interaction (CI) method with STO-3G basis set, were performed using GAMESS [5] program, .

We used a  $Si_4O_{13}H_{10}$  (Fig.1) cluster model as the  $SiO_2$  structure. In order to obtain an energetically-relaxed hole-trapped structure, all atoms were moved freely during the geometry optimization procedure.

Hopping conduction of holes in  $SiO_2$  was assumed to occur in two steps: (1) hole movement from one trap site to another by electronic excitation (without changing atomic structure) and (2) structural relaxation while the hole is kept at the new trap site.

The hole-hopping energy, i.e., the electronic excitation energy, determines the critical path of these two steps. The energy was calculated by the CI method [6] which is shown in Fig. 2.

#### 3. Results and discussion

We calculated hopping-conduction energies for two cases. In the first case, the hole trapped at a 2p lone pair orbital at one oxygen atom (O(2) in Fig. 1) moves to the nearest-neighbor oxygen atom, O(4). In the other case, the hole moves from O(2) to the second-nearest-neighbor oxygen atom, O(6). The 3D image of the hole-trapped MO is shown in Fig. 3.

The results are listed in Table I. In the nearest-neighbor site hopping, the hole-hopping energy was 2.77 eV, which is close to the value of 2.84 eV obtained with the small cluster model [4]. On the other hand, in the second-nearest-neighbor site hopping, the energy was as large as 4.38 eV.

This energy difference is explained in Fig. 4. In the nearestneighbor hopping, a small portion of the cluster moves during structural relaxation (B to C), which means that B is close to equilibrium C and hopping energy E(1) is small. On the other hand, in the second-nearest-neighbor hopping, the structural change is large (D to E), and this results in large hopping energy E(2).

These results suggest that in the vacancy-free oxide area, holes prefer to hop to the nearest-neighbor site because the hopping energy involved is less than that for the second-nearest-neighbor hopping. And when large energy is given to holes, hole-hopping between the second-nearest-neighbor sites occurs and increases hole conduction as a whole.

These hopping processes will enhance the hole-induced bond breakage in  $SiO_2$  (as proposed in the literature [3]) and result in the decrease of hole fluence to breakdown in substrate hothole injection.

#### 4. Conclusion

Using a calculation based on molecular orbital theory, we showed that hole-hopping energy depends on the distance between trap sites, where the energy is considered equivalent to electronic excitation energy. The results show that critical energy is very small in the case of nearest-neighbor site hopping and is large in the case of the second-nearest-neighbor site hopping. This explains the experimental result that hole fluence to breakdown largely depends on the kinetic energy given to holes in substrate hot-hole injection.

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Fig. 1 Cluster model used for MO calculation. (H-atoms for termination are not shown.)



Fig. 3 Hole-trapped molecular orbital.

Total energy

E(1)





Table I. Hole-hopping energies for nearest-neighbor and second-nearest-neighbor site hopping.





Fig. 4 Hole-hopping schemes and energies for nearest-neighbor and second-nearest-neighbor site hopping.