Extended Abstracts of the 1999 International Conference on Solid State Devices and Materials, Tokyo, 1999, pp. 316-317

Dielectric Degradation Mechanism of SiO_2 Examined through First-Principles Calculations: Electric Conduction Associated with Electron Traps and Its Stability under an Electric Field

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1. Introduction

The mechanism of the dielectric degradation that causes dielectric breakdown (BD) under electric stress must be clarified to accurately predict the lifetime of a gate insulator. We have studied the effect of electron traps (ETs) on the electronic conduction in silicon-dioxide and the stability of ETs under electric stress by using a first-principles method. A scaling theory developed for the conductance of localized system was successfully applied to interpret the conduction behavior of the ETs.

2. Analysis

Models

In our band calculation, we used a one-dimensional (1D) periodic silicon-dioxide chain with an oxygen vacancy as a silicon-dioxide-model (Fig. 1(a) and Table 1). We set the charge state of the oxygen vacancy as positive. The chain length L of each model corresponded to the distance between oxygen vacancies. To avoid additional interaction between chains, the unit cell size in the electronic calculations was set to 10 x 10 x L (Å^3).

To discuss the stability of ETs under electric stress, we used a dimerized two-oxygen-vacancy model, which is the simplest inhomogeneous distribution system, and calculated the polarizability of this model by molecular orbital (MO) calculation. The two dimerized oxygen vacancies in the 1D model are shown in Fig. 1(b). In this model the chain length L is fixed and the dimerized length D is varied (see Table 2).

Computational programs

The first-principles band calculations were done using the CASTEP total-energy pseudopotential program.[1] The Kleinman-Bylander form of the pseudopotential [2] was applied. The exchange-correlation energy was expressed through generalized gradient approximations with spin polarization.[3] The ab-initio Hartree-Fock MO calculations were carried out using *Gaussian94*.[4] The basis set STO-3G was used.

3. Results and Discussion

Electric conduction associated with ET

The bandwidth W of the lowest unoccupied electronic band that can accommodate electron carriers is considered the measure of the electric conduction associated with an ET, (i.e., a hole-trapped oxygen vacancy). As shown in Fig. 2, W decreases rapidly at the critical distance L_c which is 12 Å in 1D models. Such behavior cannot be expressed by a simple exponential function, so there are probably two different mechanisms causing it. The charge density of an ET around the oxygen vacancy is shown in Fig. 3. In the 3Si model, the charge density of the ET spreads along the entire SiO_2 chain, and as in the 5Si and 11Si models, the spread is less than 10 Å. This indicates that the spread of the ET charge density is independent of the distance between vacancies. Thus, the ET is strongly localized at the oxygen vacancy site in all these models.

BD can be regarded as an abrupt increase of conductance. We believe this sudden change in conductance is caused by an increased density of ETs and thus a shorter distance L between ETs. Applying the scaling function of conductance[5,6], $A \exp(-\alpha L)$, to the range of $L_c < L$ yields the exponent α, 0.079. This function is shown as the lower solid line in Fig. 2. However, when L is smaller than L_c, the distance dependence of W is similar to $1/L$ (the upper solid line in Fig. 2). In this region, the conductance behavior becomes metallic. That is, metallic conductance dominates when $L < L_c$ and hopping conductance dominates when $L > L_c$, which agrees with the results concerning the percolation concept.[7]

Stability of ET under electric field

The ET density at the critical charge Q_{BD} has been observed to be about 10^{19} cm^{-3} [7]. By assuming a uniform distribution of ETs in silicon dioxide, we estimated the average distance between traps to be 40 Å. This length is too long for intrinsic BD, which suggests that the ET distribution is inhomogeneous. We next considered the polarization effect under electric stress as a possible cause of such inhomogeneity. The total energy of silicon dioxide is as follow:

$E(F) = E(0) - 1/2\, L\alpha\, F^{*2}$,

where F is the external electric field and F^* is the local electric field ($F^* = (1+L\langle\alpha\rangle/\varepsilon_0)F$; L: Lorentz coefficient = 1/3), $E(0)$ is the total energy at zero electric stress, and α is polarizability. We calculated $E(0)$ and α for neutral (0) and positive (+1) charge states. Figure 4(a) shows that while $E(0)$ for the neutral state is independent of D, $E(0)$ for the +1 charged state of the most closely dimerized chain (D = 5.01 Å) was slightly lower than the chains with a longer D. In both charged states, α of the most closely dimerized chain was largest (Fig. 4(b)). Figure 4(c) shows that the ETs in the most closely dimerized chain were stable when F^*>40 MV/cm and the conductance of dimerized ETs was metallic because the distance between ETs (5.01 Å) was shorter than L_c. In this calculation, the external electric field, which corresponds to $F^* \sim 40$ MV/cm, was about 7 MV/cm.

Therefore, under electric stress, ETs come closer together to become stabilized, and so the ET distribution becomes inhomogeneous. More injected holes make the distribution more inhomogeneous and create a larger metallic conductance region. In this situation, the abrupt change in the scaling behavior of the conductance between metallic regions, which is caused by microscopic fluctuations, leads to non-linear conductance observed as a random-noise-like leakage current. In the final stage, intrinsic BD results from this degradation process.

4. Conclusions

We have shown that ETs tend to aggregate and an inhomogeneous distribution develops under electric stress, ultimately leading to dielectric degradation.

5. References

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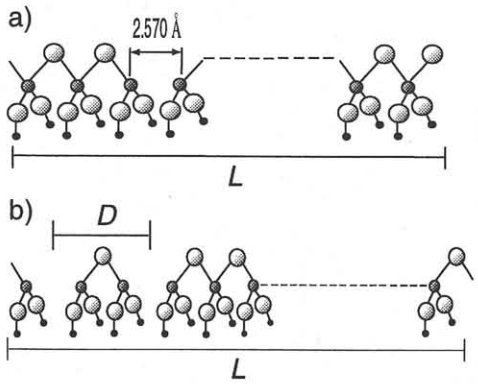

Fig. 1 One-dimension models of silicon dioxide. In each chain, all Si-Si distances are 2.570 Å. The large circles, small dark circles, and small black circles indicate O, Si, and H atoms, respectively. Model (a) has one oxygen vacancy per unit cell and a periodic boundary condition, and model (b) has two vacancies in each cluster. Parameter *D* indicates the dimerized length between two oxygen vacancies.

Table. 1 Chain length *L* of one-oxygen-vacancy models. (See Fig. 1(a)). *n*Si indicates chains that include *n* Si atoms (*n*=3 to 11).

	L [Å]
3Si	7.83
5Si	12.84
9Si	22.87
11Si	27.88

Table. 2 Chain length *L* and dimarized length *D* of two oxygen vacancy models. See Fig. 1(b). *n*Si indicates the chains which include *n* Si atoms between vacancies (*n*=2, 3, 4, 5), respectively.

	L	*D* [Å]
2Si	25.07	5.01
3Si	25.07	7.52
4Si	25.07	10.03
5Si	25.07	12.54 (=1/2 *L*)

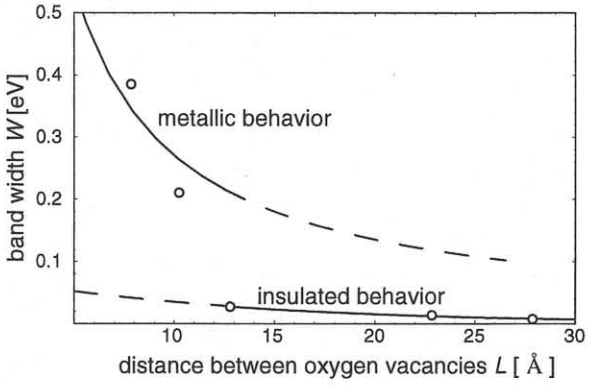

Fig. 2 Bandwidth *W* vs. distance between oxygen vacancies *L*. The open circles show calculated data, and the upper (lower) solid lines indicate the distance dependence of metallic (insulated) behavior.

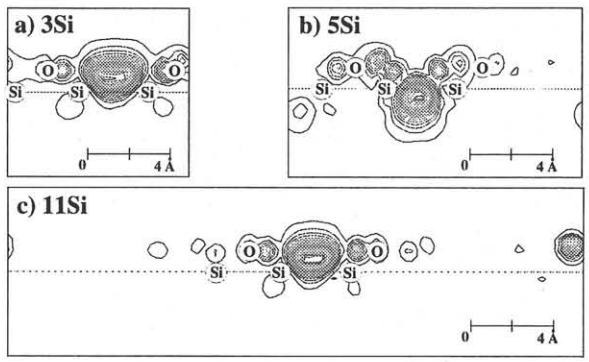

Fig. 3 Charge maps of the electron-trap level in 3Si, 5Si and 11Si chains. The distance between contour lines is 0.004 *e*/Å^3.

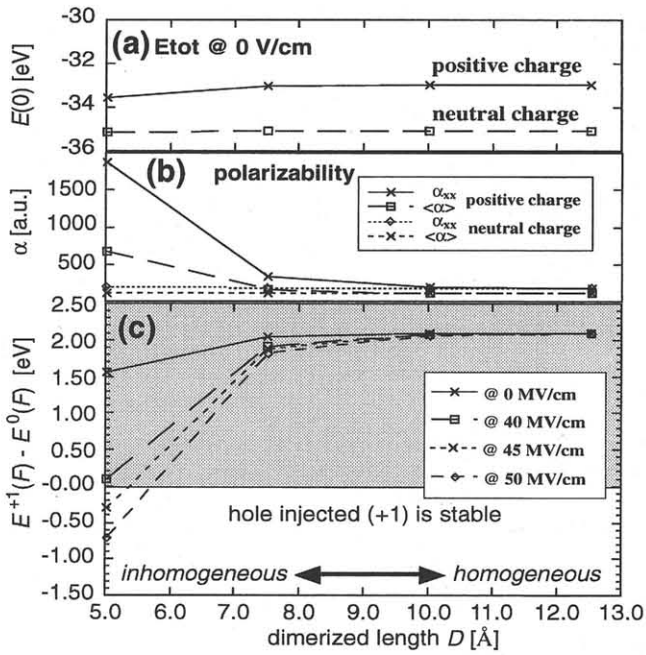

Fig. 4 (a) Total energy at zero stress, (b) polarizability, and (c) energy difference between positive and neutral charge states at each stress level (0 to 50 MV/cm).