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Onefold coordinated oxygen atom: an electron trap in the silicon oxide

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Abstract

It has been long suggested that the ≡SiOH defect is an electron or "water" trap in silicon dioxide based on some indirect evidences. In this work, quantum calculation on the capturing properties of non-bridging oxygen hole center with unpaired electron ≡SiO· and hydrogen defect ≡SiOH in silicon oxide are performed with the ab initio density-functional method. It was found that the ≡SiO· defect is an electron trap and this defect should be the responsible candidate for better hardness against radiation for the metal–oxide-semiconductor gate oxide produced by wet oxidation. We found that the ≡SiOH defect could not be an electron trap according to the present calculation results.
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1. Introduction

The reductions of gate dielectric thickness and the channel length in metal–oxide-semiconductor (MOS) devices have resulted in the significant increase of electric field in the dielectric film and silicon substrate and hence the probability of electron and hole injection into the silicon oxide is enhanced. When the injected carriers are captured by the oxide traps, the electrical properties of MOS devices degrade. Hence detailed understanding of the nature of dielectric traps is crucial to improve the device reliability and lifetime for the future nano-scale MOS devices. There are many kinds of oxide traps and their atomic structures had been proposed for several decades. However, since atomic structures of these traps cannot be investigated directly, there are still many uncertainties about the origins and physical properties of these traps. Over the four-decade history of silicon microelectronics, only one trap, the Si–Si bond or oxygen vacancy, in silicon oxide have become fully ascertained. Si–Si bond was found to be a hole trap and to be responsible for the accumulation of positive charge during ionizing radiation in silicon oxide [1–6]. To reduce the positive charge accumulation in silicon oxide, compensation of positive charge accumulation by negatively charged electron traps was used [7]. This method made use of the negatively charged "water traps" (WT) to compensate the positive charge accumulated on Si–Si defects. Recently, it was found that the WT can induce degradation to the floating gate memory devices [8,9]. However, the nature of WT in silicon oxide is still unclear so far [10–13]. The aim of this paper is to study the electronic structure of ≡SiO· and ≡SiOH defects by numerical simulation so as to understand the roles and properties of these defects.

2. Experimental results

It was shown that the neutral electron traps (with cross-section $\sigma \approx 10^{-17}$ cm^2 and near the surface of the

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oxide) could be created due to the water diffusion into thermal oxide [10–13]. Infrared spectroscopy further showed a high density of ≡SiOH defects near the surface of oxide after water incorporation [12]. For these reasons, the ≡SiOH defects were ascribed to the WT in oxide [12]. With this connection, we conduct a systematic investigation on the electroluminescence of Si/SiO_2/electrolyte system with oxide prepared using several different methods. As shown in Fig. 1, the blue cathodoluminescence at 2.7 and 4.4 eV photoluminescence (PL) emission can be attributed to the triplet–singlet transitions in twofold coordinated silicon atom with two unpaired electrons (=Si:). Previous quantum calculation on the =Si: defect was also performed with the 17-atom $Si_3O_8H_6$ cluster [14]. Results show that the electron capture in =Si: defect is energetically unfavorable. The dicoordinated Si centre should be responsible for the positive charge accumulation in MOS devices during ionizing irradiation. In addition, all kinds of oxide lead to a strong red luminescence peak at energy of 1.9 eV (see Fig. 1). This peak was previously identified as onefold coordinated oxygen atom with an unpaired electron (≡SiO·) or non-bridged oxide hole center (NBOHC), or *R* center [14,15]. Electron spin resonance (ESR) experiments and quantum-chemical simulation [16–22] further confirm that the 1.9 eV peak is due to ≡SiO·. This kind of defects is also found in oxynitride with more complicated behaviors. In oxynitride, the silicon atoms in these defects can be randomly coordinated by different number of oxygen and nitrogen atoms, i.e. $O_{3-\beta}N_{\beta}SiO^{\cdot}$ or $O_{3-\beta}N_{\beta}SiN^{\cdot}$ where $\beta = 0,1,2,3$. As a result, a slight difference is found in peak energy from the conventional *R*-center [14]. We found from electroluminescence experiments that both the density of hydrogen (≡SiOH defects) and the intensity of red luminescence increase in wet oxide [12]. In addition, etching back experiment indicates that both the ≡SiOH defects [12] and the *R* centers are located near the oxide surface. However, since the distributions of ≡SiOH and ≡SiO· defects are the same and their densities have similar dependence on oxidation method, ≡SiOH defect may not be the only possible candidate for the "water traps" observed in Hartstein and Young's study [12]. Hence, it is better to study the electronic structure of these defects using quantum-chemical method so as to differentiate their effects on the device properties.

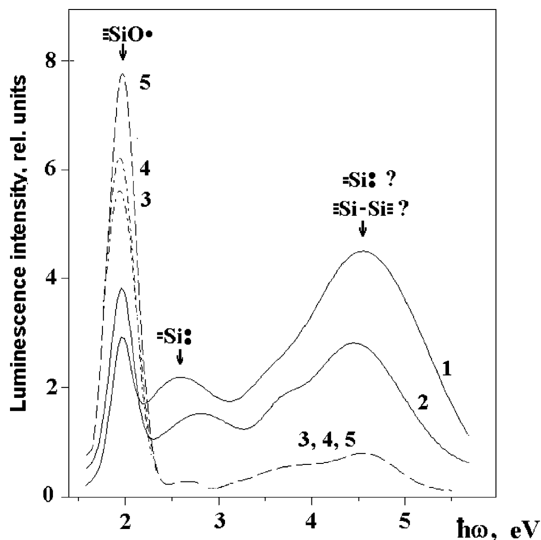

Fig. 1. Electroluminescence spectra of silicon oxide on Si produced by different methods: (1) anodic oxidation, (2) dry thermal oxidation and wet oxidation at (3) 1050, (4) 950 and (5) 900 °C. The arrow shows the luminescence band of NBOHC (≡SiO·, 1.9 eV), dicoordinated Si center (=Si:, 2.7 eV), and (=Si:, or/and ≡Si–Si≡ bond, 4.4 eV).

3. Quantum calculation

Electronic structure of neutral ≡SiO· and ≡SiOH defects in silicon oxide had been studied using recursion and ab initio method [20–22]. Unfortunately the roles (electron or hole traps) of these defects were not reported in these papers. Pachioni and Ierano [22] studied the optical properties of SiO defect in neutral state. Charged state properties of the defects are still derived from some indirect experimental results. Skuja [15] found that the 1.9 eV luminescence band of ≡SiO· defect could be excited at either 2.0 or 4.8 eV. The large difference (Stokes shift) between excitation (4.8 eV) and luminescence energy (1.9 eV) is an evidence of strong electron–phonon coupling in the oxide. Semiemprical MINDO/3 method further confirmed that the ≡SiO· defect is an electron trap [1,6]. Pantelides proposed that the ≡SiOH defect is also an electron trap based on some indirect evidences [20] and needs further confirmation.

In this work, we performed computer simulation of the electronic structures of these two defects using Amsterdam Density Functional (ADF) program [21] with ab initio density functional theory (DFT). Cluster models were used in the calculations. The fragments of crystalline α-quartz were used and the cluster dangling bonds were saturated with hydrogen atoms. For simulating the bulk properties, cluster $Si_5O_{16}H_{12}$ consisting of 33 atoms, was used (see Fig. 2a). Cluster H_9O_9-$Si_3O_3SiO^{\cdot}$ was used for simulating the ≡SiO· defect (see Fig. 2b). In this cluster the defect tetrahedron is terminated by two additional coordination spheres. The charge capture properties of ≡SiOH defect were studied with the $H_9Si_3O_3SiOH$ cluster. This cluster contains only one ≡SiOH group.

In the calculation, the Kohn–Sham molecular orbits were constructed using Slater-type exponential basis functions. The basis set includes a double-zeta basis with

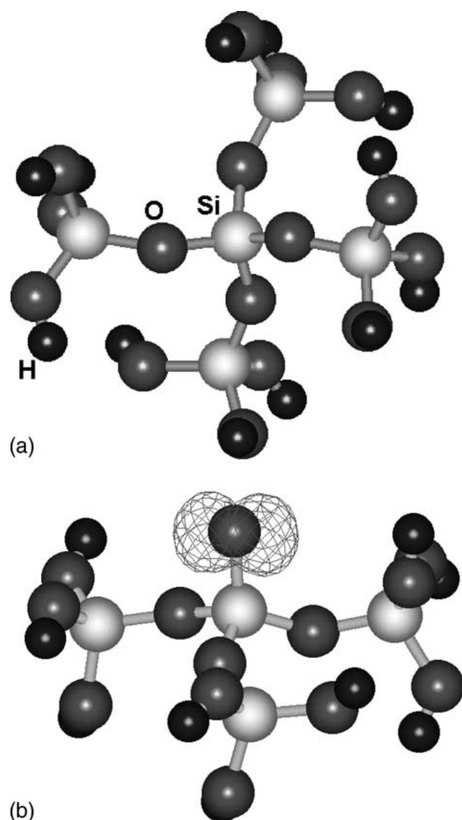

Fig. 2. Clusters used in simulation: (a) SiO_2 bulk and (b) $\equiv$SiO· defect with spin distribution in neutral cluster on O $2p_\pi$ non-bonding orbital.

polarization function for all atoms. It corresponds to basis set III in ADF terminology and all electrons were included in valence basis. The position of all Si and O atoms were fully optimized in all charge states at the non-local DFT level using Becke [23] form of exchange and Lee–Yang–Parr [24] form for correlation function. Positions of terminal H atoms were fixed to represent the embedding nature in solid. MNDO method (MOPAC 7.0 program) was used to validate the semiempirical ab initio results.

To evaluate the capability of the clusters for capturing electron or hole, we calculate the bonding energy at different charge states and find the energy gain using the Koopman formula given below:

$$\Delta E^{e} = (E^{0}_{bulk} + E^{-}_{def}) - (E^{-}_{bulk} + E^{0}_{def}) \quad (1)$$

$$\Delta E^{h} = (E^{0}_{bulk} + E^{+}_{def}) - (E^{+}_{bulk} + E^{0}_{def}) \quad (2)$$

where E^{0}_{bulk}, E^{-}_{bulk}, E^{+}_{bulk} and E^{0}_{def}, E^{-}_{def}, E^{+}_{def} denoted the bonding energy of neutral, positively and negatively charged bulk clusters and defect clusters, respectively. Negative value ΔE^{e} and ΔE^{h} indicate the capturing capability of electron and hole, respectively. Similar approach was used to calculate the charge capturing properties of Si–Si bond in silicon nitride and good agreement with the ESR results is obtained [25].

4. Calculation results and discussion

Validity of the cluster approximation method has received a lot of concerns. It is found experimentally that although the short-range order of crystalline and amorphous silicon oxide may have large variation, their electron structure, e.g. band gap, valence band density of states, are strikingly similar. These results suggested the possibility of representing the "infinite solid" with finite size of cluster in quantum calculation. Pacchinoni and Ierano [20] found that the band gap energy calculated with the small cluster $(OH)_3SiOSi(OH)_3$ is 8.8 eV which is very closed to experimental band gap value. For defect calculations, the cluster approximation is even better because the defect wave function is strongly localized the band gap of bulk silicon oxide is large [1,20]. Hence small clusters (two Si atoms) are often used to calculate the defect properties of $\equiv$Si–Si$\equiv$ defects, di-coordinated Si (=Si:) and E' centers and good agreement between the calculation and experimental results were obtained [20].

Noted that the clusters ($Si_5O_{16}H_{12}$ for bulk and $H_9O_9Si_3O_3SiO$· for $\equiv$SiO·) used in this work are considered as large clusters in other similar studies [1,20,25]. For example, to study the double oxygen vacancy, Pacchioni and Ierano used both small cluster ($Si_3O_8H_8$) and large cluster ($Si_5O_{14}H_{12}$) for quantum calculation. They found that only a small difference (0.07 Å) for the Si–Si distances between these two clusters [26]. Edwards and Fowler also found that there are only small differences between the calculated properties from the small clusters and those of large clusters [1]. Hence the small cluster models are still accurate enough in many cases. Instead, large differences do find in the different computational methods. Recent developed ab initio calculation based on Hartree–Fock method has significantly improved the accuracy of the calculation [26]. Hence our qualitative results based on this method should be reliable. Our results show that the unpaired electron in the neutral $\equiv$SiO· defect is localized on the oxygen O $2p_\pi$ orbital (see Fig. 2). The energy level of this defect is near the top of oxide valence band. Similar conclusion was obtained by recursion, MINDO/3 and ab initio methods [1,6,21,22]. This result agrees with the experimental observation that the $\equiv$SiO· defects are paramagnetic [18]. In addition, simulation results also show that the capture of electron in $\equiv$SiO· defect is energetically favourable. The energy gain of an electron capture on $\equiv$SiO· defect is 3.9 eV (from DFT calculation) or 3.2 eV (from MNDO calculation). Our calculations further show that

hole capture on ≡SiO· is energetically unfavourable (ΔE^h is negative). Thus the ≡SiO· defect in oxide should be an electron trap only. The electron captured on the neutral paramagnetic ≡SiO· defect is also localized on the oxygen unpaired O $2p_\pi$ orbital. Localization of the second electron results in the zero spin of the system according to following the reaction:

$$\equiv\text{SiO}^{\cdot} + \text{e} \rightarrow \equiv\text{SiO:} \quad (3)$$

According to the simulation, electron capturing results in the oxygen atom shifts to silicon atom by 0.08 Å and the charge change on the oxygen atom after the electron localization in clusters $H_9O_9Si_3O_3SiO^{\cdot}$ is 0.47e. It implies that the captured electron is localized mostly on the onefold coordinated oxygen atom. The electron trap with energy of 2.4–2.5 eV in wet oxide [27] is probably due to this kind of traps. Since the value of capture cross-section (σ) of WT is about 10^{-17} cm^2 [8], their corresponding effective trap radius ($R = \sqrt{\sigma/\pi}$) is about 0.2 Å. This value qualitatively agrees with the highly localized character of non-bonding O $2p_\pi$ wave function.

For ≡SiOH defect, our calculation, with the $H_9Si_3O_3SiOH$ cluster, shows that neither electron nor hole capturing is energetically favourable (both ΔE^h and ΔE^e are negative). It indicates that the ≡SiOH defect in silicon oxide should not be a trap under normal device operation condition. However, the hydrogen bond may be broken at high electric field stress or after hot-carrier irradiation and become a trap center [14].

Our further concern is the possible mechanism for the creation of ≡SiO· defects. The creation of ≡SiO· defects can be a result of ≡SiOH defects decomposition. The ≡SiOH defect may be formed when water diffuses into the silicon oxide, i.e.,

$$SiO_2 + H_2O \rightarrow \equiv\text{SiOH} \quad (4)$$

The ≡SiOH defect may then be broken into ≡SiO· according to the following reaction [16]

$$\equiv\text{SiOH} \rightarrow \equiv\text{SiO}^{\cdot} + \text{H} \quad (5)$$

It was shown that the amount of WT can be reduced by annealing of the water contained oxide in hydrogen [10,11]. This effect can be explained with the recombination of ≡SiO· defect with hydrogen.

With 7.9 eV photon illumination, Nishikawa et al. [28] found with ESR that the generated ≡SiO· defect density in the fused silicon oxide is only 5×10^{16} cm^3. This amount is significantly lower than the ≡SiOH defect density (4×10^{19} cm^3) before photon illumination. This observation can be explained as follow. The generated electrons during the irradiation can charge ≡SiO· defects. As a result, some of the ≡SiO· defects may transfer into the non-paramagnetic state (≡SiO:) and cannot be detected with ESR.

5. Conclusions

In conclusion, we have studied the ≡SiO· and ≡SiOH defects in different charged states using the ab initio DFT quantum chemical simulation. According to simulation results, the ≡SiO· defect in silicon oxide is an electron trap. It suggests that the experimentally observed oxide "water trap" is due to the ≡SiO· defect rather than the ≡SiOH defect as the ≡SiOH defect cannot capture any charge carriers without breaking the chemical bond in this defect. The defect centers in silicon oxide are often studied indirectly with the electrical measurements and the real origins and properties of the dielectric traps are often derived more or less based on some hypotheses or some kinds of reasoning. Quantum chemical simulation is a good approach to verify and to confirm the hypotheses.

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References

[1] Edwards AH, Fowler WB. Semiempirical orbital studies of intrinsic defects in a-SiO_2. In: Walrafen GE, Revesz AG, editors. Structure and bonding in noncrystalline solids. New York: Plenum Press; 1986. p. 139–55.

[2] Chu AXC, Fowler WB. Theory of oxide defects near the Si–SiO_2 interface. Phys Rev B 1990;41:5061–6.

[3] Witham HS, Lenahan PM. Nature of the E' deep hole trap in metal–oxide-semiconductor oxides. Appl Phys Lett 1987;51:1007–9.

[4] Gritsenko VA, Xu JB, Ng YH, Kwok RM, Wilson IH. Short range order and the nature of defects and traps in amorphous silicon oxynitride governed by the Mott rule. Phys Rev Lett 1998;81:1054–7.

[5] Pacchioni G, Ierano G. Optical absorption and nonradiative decay mechanism of E' center in silica. Phys Rev Lett 1998;81:377–80.

[6] Morokov YuN, Novikov YuN, Gritsenko VA, Wong H. Twofold coordinated nitrogen atom: an electron trap in MOS devices with silicon oxynitride as the gate dielectric. Microelectron Eng 1999;48:175–8.

[7] Shanfield Z, Moriwaki MM. Characteristics of hole traps in dry and pyrogenic gate oxides. IEEE Trans Nucl Sci 1984;31:1242–8.

[8] Ranaweera J, Ng WT, Salama CAT. Simulation. fabrication and characterization of a 3.3 V flash Ze(2) PROM array implemented in a 0.8 μm CMOS process. Solid-State Electron 1999;43:263–73.

[9] Huang KC, Fang YK, Yeung YN, Chen CW, Sung HC, Kuo DS, et al. The impacts of control gate voltage on the cycling endurance of split gate flash memory. IEEE Electron Device Lett 2000;21:359–61.

[10] Nicollian EH, Berglund CN, Shmidt PF, Andrews JM. Electrochemical charging of thermal SiO_2 films by injected electron currents. J Appl Phys 1971;42:5654.
[11] Young DR, Irene EA, DiMaria DJ, De Keersmaecher FF, Massoud HZ. Electron trapping in SiO_2 at 295 and 77-degrees-K. J Appl Phys 1979;50:6366–72.
[12] Hartstein A, Young DR. Identification of electron traps in thermal silicon dioxide films. Appl Phys Lett 1981;38:631–3.
[13] Fleetwood DM, Reber Jr RA, Winokur PS. Trapped-hole annealing and electron trapping in metal–oxide-semiconductor devices. Appl Phys Lett 1992;60:2008–10.
[14] Wong H, Gritsenko VA. Defects in silicon oxynitride gate dielectric films. Microelectron Reliab 2002;42:597–605.
[15] Skuja L. The origin of the intrinsic 1.9 eV luminescence band in glassy SiO_2. J Non-Cryst Solids 1994;179:51–69.
[16] Gritsenko VA. Electronic properties of amorphous dielectrics in silicon MIS structure. Novosibirsk, Russia: Science; 1993. p. 280.
[17] Skuia L. Optically active oxygen-deficiency-related centers in amorphous silicon dioxide. J Non-Cryst Solids 1998; 239:16–48.
[18] Griscom DL. Defect structure of glasses—some outstanding questions in regard to vitreous silica. J Non-Cryst Solids 1985;73:51–77.
[19] O'Reilly EP, Robertson J. Theory of defects in vitreous silicon dioxide. Phys Rev B 1983;27:3780–95.
[20] Pantelides ST. The electronic-structure of impurities and defects in SiO_2. Thin Solid Films 1982;89:103–8.
[21] Kanashima T, Okuyama M, Hamakawa Y. Analysis of Si–H, Si–O–H and Si–O–O–H defects in SiO_2 thin film by molecular orbital method. Jpn J Appl Phys 1997;36:1448–52.
[22] Pacchioni G, Ierano G. Ab initio theory of optical transitions of point defects in SiO_2. Phys Rev B 1998; 57:818–32.
[23] Becke AD. Density-functional exchange-energy approximation with correct asymptotic-behavior. Phys Rev A 1988;38:3098–100.
[24] Lee C, Yang W, Parr RG. Development of the Colle–Salvetti correlation-energy formula into a functional of the electron-density. Phys Rev B 1988;37:785–9.
[25] Gritsenko VA, Novikov YuN, Morokov YuN, Wong H. Simulation of electronic structure of Si–Si bond traps in oxide/nitride/oxide structure. Microelectron Reliab 1998; 38:1457–64.
[26] Pacchioni G, Ierano G. Ab initio formation energies of point defects in pure and Ge-doped SiO_2. Phys Rev B 1997;56:7304–12.
[27] Kapoor VJ, Feigle FJ, Butler SR. Energy and spatial-distribution of an electron trapping center in mos insulator. J Appl Phys 1977;48:739–49.
[28] Nishikawa H, Nakamura R, Ohki Y. Correlation of preexisting diamagnetic defect centers with induced paramagnetic defect centers by ultraviolet or vacuum-ultraviolet photons in high-purity silica glasses. Phys Rev B 1993;48:15584–94.