P3-21L

Origin of Interfacial Reaction Constant for Si Thermal Oxidation

Toru Akiyama[1, 2] and Hiroyuki Kageshima[1]

[1]NTT Basic Research Laboratories, NTT Corporation
3-1 Morinosato-Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan
[2]Department of Physics Engineering, Mie University
1515 Kamihama, Tsu-shi, Mie 514-8507, Japan
Phone: +81-59-232-1211 (3978)   Fax : +81-59-231-9726
E-mail: akiyama@phen.mie-u.ac.jp

1. Introduction

Silicon thermal oxidation is of great interest and importance as a key process in fabricating silicon-based devices. Towards recent requirement in miniaturization of devices, the trend of Si technology is urging the precise control of SiO_2 interface structure: Gate dielectrics in metal-oxide-semiconductor field-effect transistors require the control of thin oxide films on atomic scale[1]. Even if conventional gate oxides are replaced by oxynitride or high permittivity dielectrics, thin oxides could play a role as a buffer layer to reduce defect levels at the interface. Oxide films are also used in order to obtain quantum confinement effect and surface buried layers in the future promising Si nano-devices[2]. Therefore, an atomic scale understanding of Si oxidation, which still remains controversial, should be required from technological viewpoints.

In ordinary dry oxidation, it is widely believed that silicon oxidation consists of a diffusion process of oxidant in the oxide and its reaction process at the interface[3]. As for the interfacial reaction, experiments evaluating reaction constant B/A in the Deal-Grove (D-G) model have reported that the activation energies for the reaction process are 1.76-2.00 eV[3,4], implying that the dominant process in this process is the severance of Si-Si bonds by O atom insertion[5]. However, recent experiments for ultrathin oxide using the auger electron spectroscopy (AES) and the scanning reflectance microscopy (SREM)[6], and reflectance difference spectroscopy (RDS)[7] report lower activation energies which cannot correspond to the energy of Si-Si bond: The atomic scale mechanisms such as the reaction pathways and its energy barrier for oxygen insertion at the interface are still not clear.

In this work, we perform first-principles total-energy electronic-structure calculations to clarify the reaction mechanisms of oxygen molecules at the SiO_2/Si(100) interface. We investigate the correspondence of energy barriers to the Si-Si bond energy, and elucidate the origin of B/A in the D-G model.

2. Calculation Method

All calculations have been performed by using the generalized gradient approximation (GGA) in density functional theory, ultrasoft pseudopotentials, and the conjugate-gradient minimization technique[8]. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 25 Ry. As a representative of SiO_2/Si(100) interface, we adopt quartz/Si(100) model containing two SiO_2 molecule layers and six Si atomic layers. The lateral size of unit cell is 2×2 ($a=7.73$ Å). We use the Γ-point sampling in the Brillouin zone integration. Details of calculation method will be provided elsewhere.

3. Results and Discussions

As shown in Fig. 1(a), we find that the O_2 molecule in the oxide region of the interface is stably located at the opening space of SiO_2 with the O-O axis almost parallel to the c axis. The calculated bond length of O-O of 1.29 Å slightly larger than the calculated bond length of gas-phase O_2 molecule of 1.25 Å. The energy of the O_2 molecule is lower than the energies of O atoms by ~1.0 eV.

Figure 1 also shows the energy variation and changes of geometries for O_2 incorporation into the Si substrate. In this figure, the O_2 molecule is incorporated along the energetically lowest pathway (adiabatic path). Starting from the initial structure mentioned above, the O_2 molecule becomes the metastable structure [Fig. 1(c)] through the transition state structure shown in Fig. 1(b). The energy of the transition state structure is 0.2 eV higher than the initial structure. In the metastable structure, each of the top Si atoms forms weak bond (floating bond) with each of the O_2 molecule. From this metastable structure, two individual Si-O-Si bonds [Fig. 1(e)] are finally formed. It is thus shown the energy barrier along the adiabatic path, which corresponds to the formation of floating bonds, is 0.2 eV.

In order to assess the change of energy barrier by displacement from the adiabatic path, we also perform the calculation of O_2 incorporation under the constraint of freezing host atom positions. Figure 2 shows energy variation and changes of geometries. In the transition state structure shown in Fig. 2(a), each of O_2 molecule forms floating bonds with top Si atoms. Then, these O atoms insert into the Si-Si bond [Fig. 2(b)]. If the reaction pathway in actual thermal oxidation around 1000°C is displaced from the adiabatic path, the energy barrier increase up to 1.3 eV. The microscopic process corresponding to the energy barrier for this non-adiabatic path is also the formation of the floating bonds.

From the changes of geometries, it has been shown that the energy barriers of oxygen incorporation do not correspond to the severance of the Si-Si bond, but the formation of Si floating bonds. The floating bonds between O and Si atoms seem to be formed even if Si with different
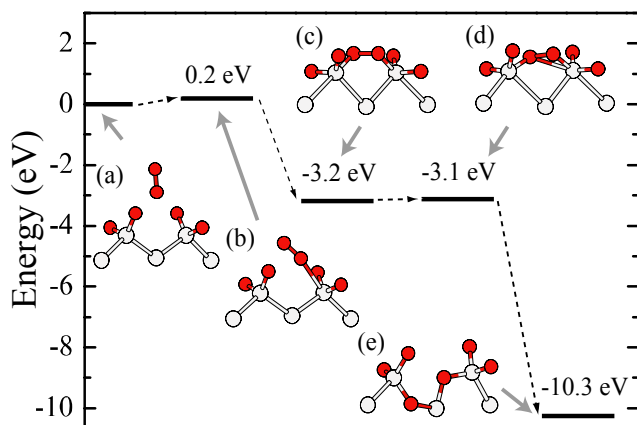
Fig. 1 Energy variation and geometries for O_2 incorporation along the energetically lowest reaction pathway (adiabatic path). The zero of energy is set to the energy of stable O_2 in the oxide. The empty and filled circles represent Si and O atoms, respectively. Only a part of atoms in a unit cell are shown for simplicity.

Fig. 2 Energy variation and geometries for O_2 incorporation of under the constraint of freezing host atom positions. The initial structure becomes (b) the metastable structure through (a) the transition state structure under this constraint. The geometry shown in Fig. 1(e) is finally formed by a sort of oxygen-pair diffusion from (c) the optimized structure. The notation is the same as that of Fig. 1.

orientation such as Si(111) surface is used in thermal oxidation. Therefore, the activation energy of oxygen incorporation might be unchanged depending on the surface orientation, being consistent with experiments.

The present energy barriers for O_2 incorporation are found to be lower than those of O atoms[9]. These results show that oxygen molecules diffusing in the oxide directly react with the substrate: Oxygen molecules are the dominant reaction species in dry oxidation. Moreover, the calculated energy barrier along the adiabatic path (0.2 eV) and off the adiabatic path (1.3 eV) are agree well with the experimentally reported activation energies for ultrathin oxide films obtained from AES and SREM (0.3 eV[6]), and from RDS (1.1 eV[7]), respectively. This excellent correspondence also shows that O_2 molecules are the dominant reaction species.

The activation energies of 1.76-2.00 eV obtained from B/A in the D-G model[3,4] are larger than the present energy barriers. Therefore, it is indicated that the activation energy of B/A is not come from the severance of the Si-Si bond, but from the effects of large strain on the formation of floating bonds. Since the volume of a SiO_2 unit in the oxide is about 2.25 times larger than that of a Si atom in the substrate, the oxygen incorporation process induces a large volume expansion and a large strain at the interface. With increase of oxide thickness during oxidation, the accumulation of strain might cause the increase of energy barriers. It is also possible to consider that the strain causes other microscopic processes such as Si-emission[10,11], and those processes are the alternative origin of B/A.

4. Conclusions

We have presented first-principles calculations that clarify mechanisms of reaction of oxygen molecules at SiO_2/Si(100) interface. The energy barriers for the reaction of oxygen at the interface corresponds to the floating bond
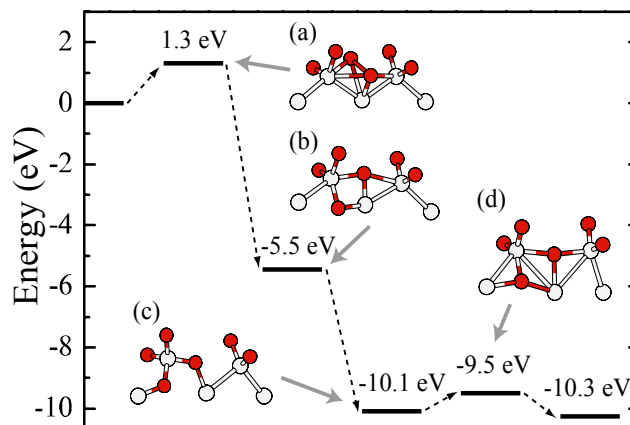
formation process between the oxygen of oxidant and the host Si atom at the interface, and agree well with the experimentally reported activation energies for ultrathin oxide. The present results imply that the accumulation of strain induced by oxidation crucially affect the interfacial reaction. It has been indicated that the origin of the activation energy of B/A in the D-G model due to this effect.

References
[1] M. L. Green *et al*., J. Appl. Phys. **90**, 2057 (2001).
[2] Y. Takahashi *et al*., IEEE Trans. Electron Devices **43**, 1213 (1996); Y. Kanemitsu *et al*., Phys. Rev. B**55**, R7375 (1997).
[3] B. E. Deal and A. S. Grove, J. Appl. Phys. **36**, 3770 (1965).
[4] H. Z. Massoud *et al*., J. Electrochem. Soc. **132**, 1745 (1985).
[5] B. E. Deal, J. Electrochem. Soc. **125**, 576 (1978).
[6] H. Watanabe *et al*., Phys. Rev. Lett. **80**, 345 (1998).
[7] T. Yasuda *et al*., Phys. Rev. B**67**, 195338 (2003).
[8] Calculation codes used in this work are based on Tokyo *Ab-initio* Program Package (TAPP), which has been developed by us: J. Yamauchi *et al*., Phys. Rev. B**54**, 5586 (1996); H. Kageshima and K. Shiraishi, Phys. Rev. B**56**, 14985 (1997).
[9] T. Akiyama and H. Kageshima, Appl. Surf. Sci. **216**, 270 (2003).
[10] H. Kageshima and K. Shiraishi, Phys. Rev. Lett. **81**, 5936 (1998); H. Kageshima, K. Shiraishi, and M. Uematsu, Jpn. J. Appl. Phys. **38**, L971 (1999).
[11] M. Uematsu, H. Kageshima, and K. Shiraishi, Jpn. J. Appl. Phys. **38**, L699 (2000).