

Invited

# Chemical Structures of Ultrathin Silicon Oxide Film and Its Interface

Takeo Hattori

Musashi Institute of Technology

1-28-1 Tamazutsumi, Setagaya-ku, Tokyo 158

Studies on the structures of Si-SiO<sub>2</sub> interfacial transition layers are reviewed. It is necessary to clarify the intrinsic interface structures, which probably include intrinsic defects. Then, it may be necessary to modify and to stabilize the interface structures by the interface doping or by the introduction of interface layers. Our recent studies on the compositional and the structural transition layers using XPS will be also discussed.

## 1. Introduction

As a result of significant progress in microfabrication technology, it became possible to form 5 nm thick gate oxide film applicable to LSI<sup>1)</sup>. In such a small MOSFET, the properties of the oxide films are affected not only by the oxidation processes, but also by the structures of the transition layers at SiO<sub>2</sub>/Si and gate electrode/SiO<sub>2</sub> interfaces. In spite of the tremendous structural studies of these interfacial transition layers<sup>2,3)</sup>, there are many unsolved fundamental problems. For example, it is difficult to predict the interface state densities for the intrinsic interface structures. In addition to the structural studies, the study on the initial oxidation mechanism<sup>4)</sup> is also necessary in order to control the oxide film thickness precisely. The flatness of the interface was found to give drastic effects on the interface structures<sup>5)</sup>. In the present paper, the structures of the interfacial transition regions and the flatness of the interface will be discussed.

## 2. Si-SiO<sub>2</sub> Interfacial Transition Regions

The interfacial transition regions are formed on both sides of the interface in order to relax the stress produced by oxide formation. In these transition regions both the compositional and structural transition take place. The abrupt compositional transition was predicted theoretically<sup>6)</sup>, followed by the experimental observations<sup>7)</sup>. The structural transition in silicon substrate takes place with the displacement of two silicon layers next to the interface<sup>7)</sup>, while the structural transition in the oxide film is considered to take place within 3 nm from the interface<sup>8)</sup>.

## 3. Chemical bonds at the Si-SiO<sub>2</sub> Interface

The abruptness of the interface, the orientation dependence of the interface structures, the suboxide distribution in the oxide films have been studied extensively using XPS(X-ray photoelectron spectroscopy). However, the controversy exists on the composition of the interfacial transition layer. Namely, the orientation

dependent composition were deduced from the depth profiling measurements<sup>9,10,11</sup>), while the orientation independent composition was deduced from the nondestructive measurements<sup>12</sup>). However, it was found from the recent studies<sup>13</sup>) that the orientation dependent composition can be deduced from the the latter.

Another controversy exists on the mechanism for the change in the oxidation-induced chemical shifts in depth direction<sup>8,14,15</sup>). Recently, it was found that the O 1s chemical shift can be explained by considering the second nearest neighbour atoms<sup>16</sup>).

#### (1) Chemical Shift<sup>17)</sup>

Figure 1 shows the oxidation-induced chemical shifts as a function of dioxide film thickness obtained from destructive depth profiling using chemical etching. The oxide films used were prepared on Si (100) with following two oxidation conditions; (1) oxidation in dry oxygen at 800 °C, (2) oxidation in 10% dry oxygen diluted with argon at 1000 °C followed by the one hour annealing in dry argon at 1000 °C.

According to this figure, the chemical shifts are weakly affected by the stress relaxation in the oxide film. This is because the stress relaxation time<sup>18)</sup>  $\tau_s$  of  $1.9 \times 10^7$  sec at 800 °C is extremely larger than the oxidation time of 5400 sec, while  $\tau_s$  of 720 sec at 1000 °C is extremely smaller than the annealing time of 3600 sec. The same results were obtained for oxide films prepared on (110) and (111) surfaces. These results imply that Si-O-Si bond angle does not contribute to the change in chemical shift in contrast to the model proposed by Grunthaner et al<sup>8</sup>).

The oxide charge-induced band bending is less than 0.3 eV for the dioxide film

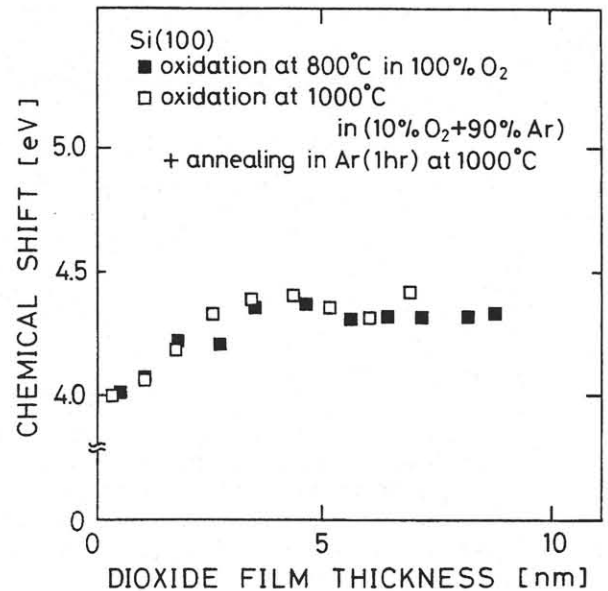


Fig. 1 Dependence of chemical shift on dioxide film thickness.

thickness of less than 10 nm. Then, the potential drop across the oxide film can be calculated to be less than 0.1 V. Therefore, the charge up of the oxide film does not contribute to the chemical shifts.

#### (2) Suboxides at Si-SiO<sub>2</sub> interface<sup>19)</sup>

Figure 2 shows the atomically flat interface on (100) surface. The number of photoelectrons  $N_i$  emitted from Si<sup>2+</sup> is proportional to the area density  $N_t$  of silicon atoms on (100) surface, while the number of photoelectrons  $N_s$  emitted from the silicon substrate is proportional to  $n_s \Lambda_s$ . Here,  $n_s$  is density of silicon atoms in the

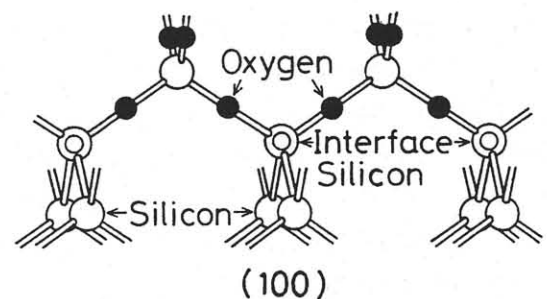


Fig. 2 Atomically flat interface structure on Si(100) surface.

substrate and  $\Lambda_s$  is the electron escape depth in silicon substrate. Also,  $Si^{x+}$  corresponds to the bonding configuration of  $Si-Si_{4-x}O_x$ . Then, the ratio  $N_i/N_s$  is equal to 0.057 for photoelectrons excited by Mg K $\alpha$  radiation. This value can be the measure to define the flatness of the interface. By considering material dependent background, the suboxide signals are successfully separated from the intense peaks for silicon in silicon dioxide and silicon substrate<sup>10)</sup>.

Figure 3 shows the dependence of (NI/NS) on the dioxide film thickness for the following three kinds of oxide films; (1) oxidation at 1000 °C in 100% dry O<sub>2</sub>; (2) oxidation at 1000 °C in 10% dry O<sub>2</sub>; (3) (2) followed by annealing at 1000 °C in dry Ar for one hour. Here, NI and NS is Si 2p spectra intensity for Si<sup>2+</sup> and silicon substrate, respectively. According to this figure, the flatness is the highest for the oxide film formed in 100% oxygen at 1000 °C, while the flatness is the lowest for the oxide film annealed in argon after

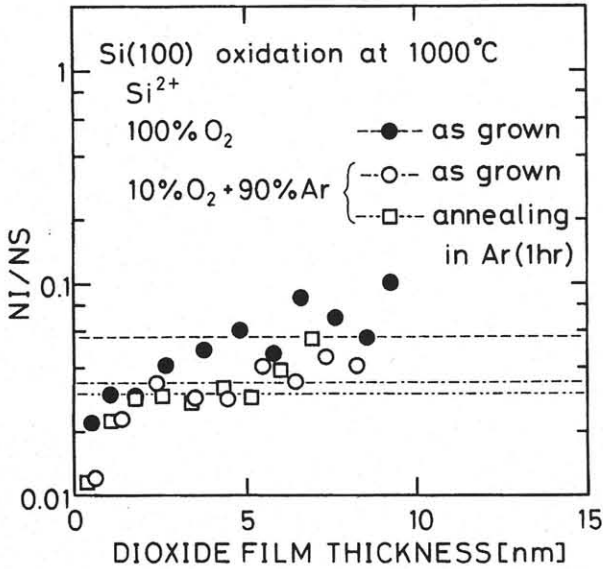


Fig. 3 Dependence of (NI/NS) on dioxide film thickness.

oxidation. These results imply that the flatness is decreased by annealing to relax the stress at the interface. The larger flatness is achieved if the oxidation rate is higher than the stress relaxation rate.

#### 4. Structural Transition Region<sup>19)</sup>

Figure 4 shows the change in the dioxide film thickness as a function of the chemical etching time for the oxide films discussed in Fig. 3. The change in the chemical etching rate in depth direction in this figure can be correlated with the structural change in depth direction.

#### 5. Summary and Future problems in Si-SiO<sub>2</sub> interface

The chemical shifts observed was found to be unaffected by the stress in the oxide film. The structural transition regions was detected as the change in the chemical etching rate.

The optimum conditions of precleaning process, the oxidation and the cooling after oxidation should be chosen such as to realize intrinsic interface structures. The impurities may produce the deviation from the intrinsic interface structures.

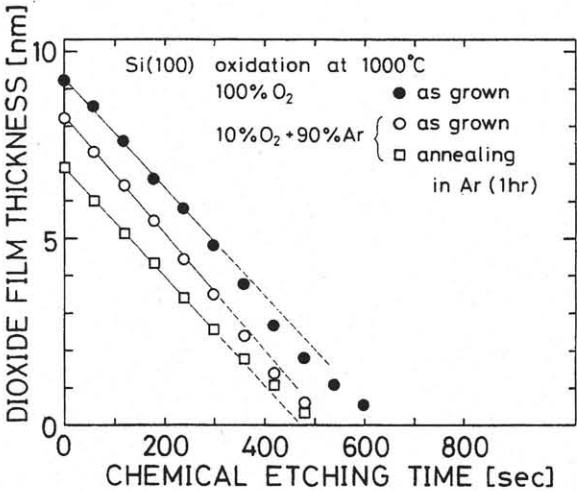


Fig. 4 Dependence of dioxide film thickness on chemical etching time.

The interface doping and the introduction of interfacial layers may be necessary to control and stabilize the interface structures. Although the existence of hydrogen and OH can be considered to be effective to stabilize the interface structures, the amounts of hydrogen and OH can not be evaluated accurately at present time.

#### References

- 1) T. Kobayashi and S. Horiguchi and K. Kiuchi: Tech. Dig. 1984 IEDM, p.414.
- 2) For extensive references, see The Physics of SiO<sub>2</sub> and Its Interfaces, ed.S. T. Pantelides (Pergamon, 1978).
- 3) R. S. Bauer et al.: Appl. Phys. Lett. 37 (1980) 1006.
- 4) E. A. Irene and E. A. Lewis: Appl. Phys. Lett. 51(1987)767.
- 5) A. Ourmazd et al.: Phys. Rev. Lett. 59 (1987) 213.
- 6) S. T. Pantelides: J. Vac. Sci. Tech. 14 (1977) 965.
- 7) R. Haight et al.: J. Appl. Phys. 53 (1982) 4884 and refereces therein.
- 8) F. J. Grunthaner et al.: Phys. Rev. Lett. 43 (1979) 1683.
- 9) T. Hattori and T. Suzuki: Appl. Phys. Lett. 43(1983)470.
- 10) T. Suzuki et al.: Jpn. J. Appl. Phys. 25(1986)544.
- 11) P. J. Grunthaner et al.: J. Appl. Phys. 61(1987)629.
- 12) G. Hollinger and F. J. Himpsel: Appl. Phys. Lett. 44(1984)93.
- 13) W. Braun and H. Kuhlbeck: Surf. Sci. 180(1987)279.
- 14) G. Hollinger et al.: Phil. Mag. B55(1987)735.
- 15) A. Iqbal and C. W. Bates, Jr. : Appl. Phys. Lett. 47(1985)1064.
- 16) M. Hirose and T. Hayashi: reported at Spring Meeting, ECS, 1988, Abstr.204.
- 17) H. Yamagishi et al.: to be published in Jpn. J. Appl. Phys. (1988).
- 18) E. A. Irene et al.: J. Electrochem. Soc. 129 (1982) 2594.
- 19) T. Hattori et al.: reported at Spring Meeting, ECS, 1988, Abstr. 234.