

Effect of Preoxide on the Structure of Thermal Oxide

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It is found from X-ray photoelectron spectroscopy study on the chemical structure of silicon dioxide, whose thickness is in the range of 1.2 nm to 8.6 nm, that the oxidation-induced chemical shift depends mainly on the distance, and that 0.4- and 0.6-nm-thick preoxide, which is formed in dry oxygen at 300°C, modifies the structure of oxide near the surface.

KEYWORDS: silicon oxide, preoxide, chemical structure, depth profiling, X-ray photoelectron spectroscopy

1. Introduction

The control of oxide formation on an atomic scale must be important for the formation of high-quality SiO₂/Si interfaces for future metal-oxide-semiconductor (MOS) technology. Because the formation of native oxide can be suppressed by terminating the silicon surface with hydrogen atoms,¹⁾ the hydrogen-terminated silicon surface, which is abbreviated in the following as the H-Si surface, must be used instead of a clean silicon surface for the control of oxide formation on an atomic scale. Furthermore, the 0.4-nm-thick oxide film formed on the H-Si(100) surface, which was obtained by the treatment in dilute HF solution, in dry oxygen at atmospheric pressure and 300°C, and is called preoxide in the following, is stable in ultradry argon even at atmospheric pressure and 900°C, and the thermal oxide formed in dry oxygen at 900°C through this preoxide has high electrical insulating performance.²⁾ Therefore, 0.4-nm-thick preoxide can stabilize the silicon surface at high temperatures. It is the purpose of the present paper to clarify the mechanism of stabilization of oxide structures by the preoxide.

2. Experimental Details

Thicknesses of oxide films used in the present study were controlled precisely by using ultraclean argon, the amount of moisture in which was less than 5 ppb at the inlet of the oxidation system, and ultraclean oxygen gases. These films are hereafter called ultraclean oxides. Wafers used in the present study were Czochralski-grown p-Si(100) with a resistivity of 2.5–3.5 Ω cm. In order to decrease atomic step densities on initial silicon surfaces,³⁾ nearly 200-nm-thick thermal oxide films were formed in dry oxygen at 1000°C on Si(100) surfaces. After the chemical cleaning, the thermal oxide films were removed by the treatment in dilute HF solution followed by a rinse in deionized water for 10 min. The H-Si surfaces thus obtained were heated up to 300°C in the ultraclean argon gas at the rate of 50°C/min, and were then oxidized at 300°C in the ultraclean oxygen gas to form the preoxides with thicknesses of 0.4 nm and 0.6 nm. After raising the temperature of preoxides up to 800°C in the ultraclean argon gas, oxidation was performed through these preoxides at 800°C in the ultraclean oxygen gas to form ultraclean

oxides, with thickness in the range of 1.3 nm to 7.1 nm. Oxides of another kind, with thickness in the range of 1.2 nm to 8.6 nm, were formed in conventional furnace at 800°C and are hereafter called conventional oxides. The maximum thickness of oxide grown during wafer loading into a conventional furnace is nearly 1.2 nm.

In order to measure structural change in depth direction nondestructively, angle-resolved Si 2*p* photoelectron spectra were measured for as-grown oxides. In order to confirm the effect of preoxides on the chemical structures in the depth direction, the changes in Si 2*p* photoelectron spectra produced by chemical etching were measured. Photoelectron spectra excited by monochromatic AlK α radiation were measured at photoelectron take-off angles of 15, 30 and 90° with an acceptance angle of 3.3°, using ESCA-300 manufactured by Scienta instruments AB.⁴⁾ The area used for XPS study was 6 mm × 0.5 mm for photoelectron take-off angle of 90°. Other experimental details were described elsewhere.⁵⁾

After removing the extremely small background signal based on Tougaard's method⁶⁾ from the observed spectrum, the spectrum is decomposed into Si 2*p*_{1/2} and Si 2*p*_{3/2} spin-orbit partner lines. In this decomposition, it is assumed that the spin-orbit splitting of the Si 2*p* photoelectron spectrum is 0.60 eV, and the Si 2*p*_{1/2} to Si 2*p*_{3/2} intensity ratio is 0.5.⁷⁾ It is also assumed that the intermediate oxidation states consist only of Si¹⁺, Si²⁺, and Si³⁺.⁷⁾ The oxide film thicknesses were determined from the ratio of Si 2*p* spectral intensity for silicon oxide to that for silicon substrate. Here, 2.7 nm and 3.4 nm are the escape depths of Si 2*p* photoelectron in Si and SiO₂, respectively.⁸⁾

3. Experimental Results and Discussion

Figures 1 and 2 show the changes in chemical shift of Si⁴⁺ spectrum measured at photoelectron take-off angles of 15, 30 and 90° as a function of oxide film thickness for three kinds of as-grown oxides and for three kinds of chemically etched oxides. Here, the three kinds of oxides are conventionally grown oxide, ultraclean oxide formed through 0.4-nm-thick preoxide and ultraclean oxide formed through 0.6-nm-thick preoxide. According to these figures, the dependence of the chemical shift of Si⁴⁺ on the oxide film thickness

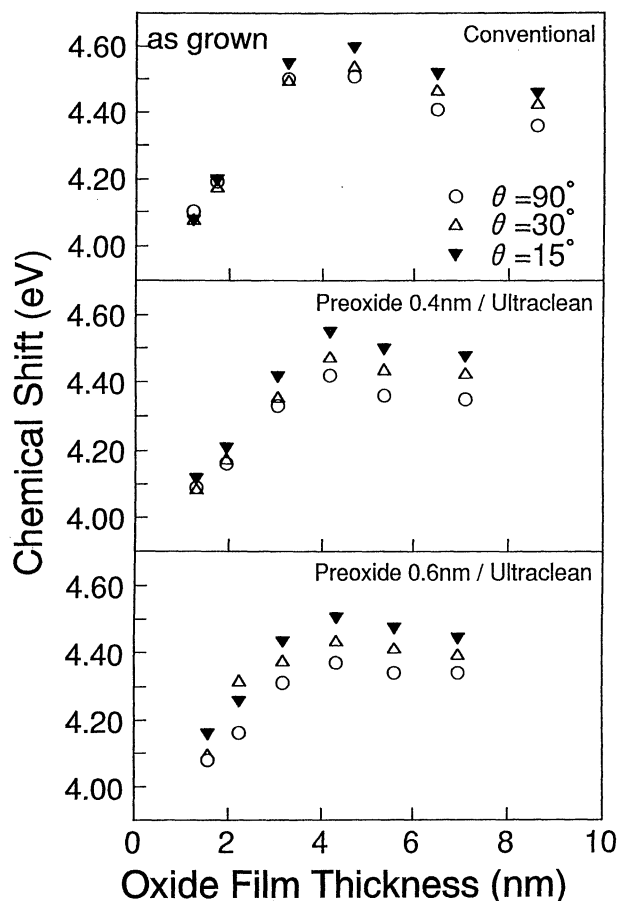


Fig. 1. Observed dependence of chemical shift on oxide film thickness for as-grown conventional oxide, as-grown ultraclean oxide formed through 0.4-nm-thick preoxide and as-grown ultraclean oxide formed through 0.6-nm-thick preoxide.

for as-grown oxides roughly agrees with that for chemically etched oxides. In the following, the dependence of the chemical shift of the Si^{4+} spectrum on the oxide film thickness for as-grown oxides was analyzed as a typical example. According to Fig. 1, the chemical shifts for the three kinds of oxide films increase with increase in the oxide film thicknesses from 1 nm to 4 nm, assume maximum values at the oxide film thickness of nearly 4 nm, and decrease with further increase in the oxide film thickness.

According to the previous studies, the chemical shift is weakly affected by the changes in Si–O–Si bond angles near the interface.⁹⁾ By considering the case where the chemical shifts are only related with the charge transfer from a certain atom to its neighboring atoms,^{10,11)} the chemical shifts are assumed to depend only on the distance from the SiO_2/Si interface.¹²⁾ In addition, a full width at half maximum (FWHM) is assumed to depend only on the distance from the SiO_2/Si interface. Furthermore, Si 2*p* photoelectron spectra measured at a photoelectron take-off angle of 90° must arise not only from the surface, but also from the interface, while the spectra measured at a photoelectron take-off angle of 15° must arise mostly from the surface. Since the effective escape depths of photoelectrons from silicon dioxide at photoelectron take-off angles of 90, 30

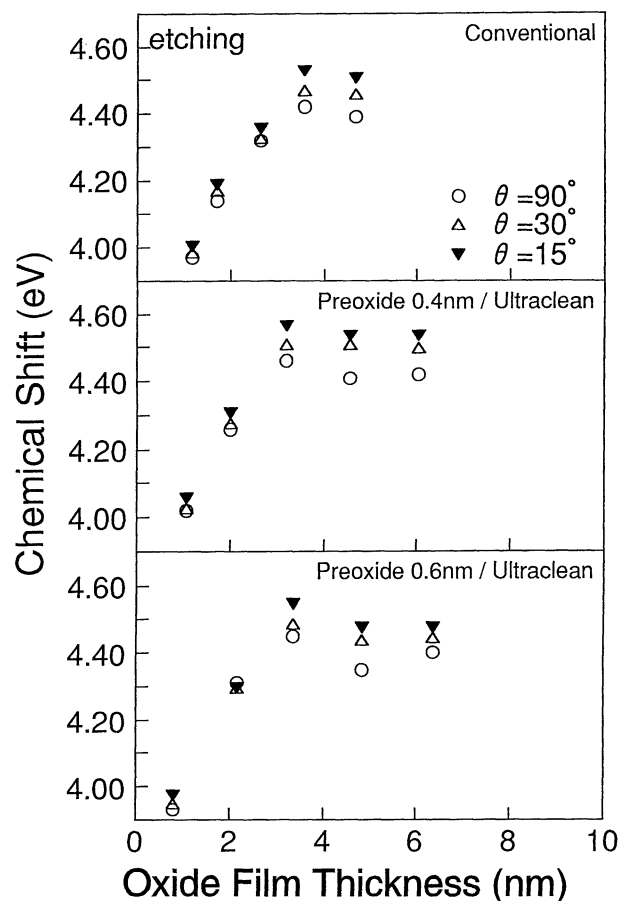


Fig. 2. Observed dependence of chemical shift on oxide film thickness for chemically etched conventional oxide, chemically etched ultraclean oxide formed through 0.4-nm-thick preoxide and chemically etched ultraclean oxide formed through 0.6-nm-thick preoxide.

and 15° are 3.4, 1.7 and 0.87 nm, respectively. Therefore, the chemical shift of the Si^{4+} spectrum measured at photoelectron take-off angle of 15° must be equal to that for oxide close to the surface. In our calculation of the dependence of chemical shift on oxide film thickness, chemical shifts and FWHMs measured at photoelectron take-off angle of 15° are assumed to be equal to those for oxides close to the surface. Calculated and observed data are shown in Fig. 3 with the three curves corresponding to the three take-off angles of photoelectrons. The calculated curves roughly agree with observed data.

Figure 4 shows the FWHM of the Si^{4+} spectrum as a function of oxide film thickness for as-grown oxides. According to this figure, the values of FWHM for the three kinds of oxide films increase with increase in thickness up to the oxide film thickness of 4 nm, assume maximum values at the oxide film thickness of nearly 4 nm, and then decrease with further increase in oxide film thickness. The values of FWHM for ultraclean oxides are smaller than those for conventional oxide over the whole thickness range studied. Here, small FWHM must imply a homogeneous oxide network.

If the chemical shifts and FWHM of Si^{4+} are as-

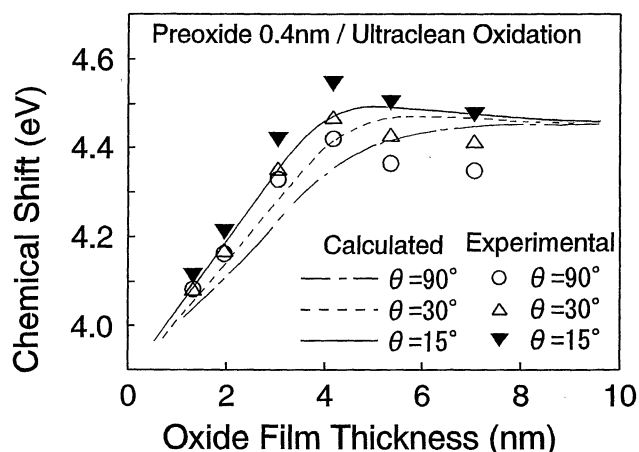


Fig. 3. Observed and calculated dependence of chemical shift on oxide film thickness for as-grown ultraclean oxide formed through 0.4-nm-thick preoxide.

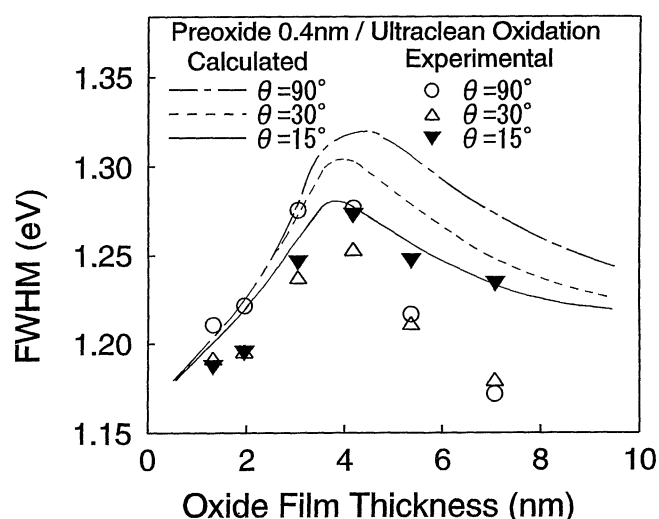


Fig. 5. Observed and calculated dependence of FWHM on oxide film thickness for as-grown ultraclean oxide formed through 0.4-nm-thick preoxide.

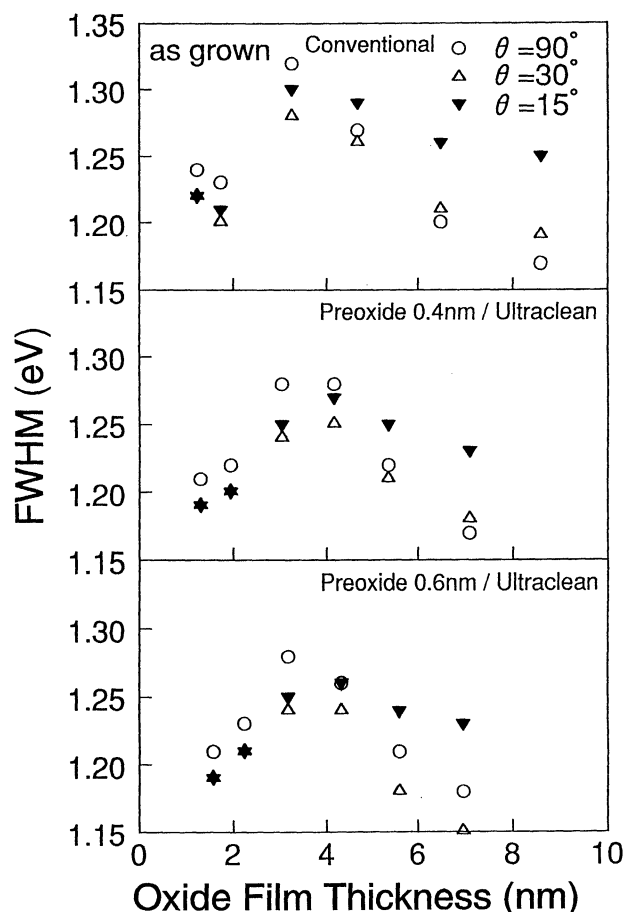


Fig. 4. Observed dependence of FWHM on oxide film thickness for as-grown conventional oxide, ultraclean oxide formed through 0.4-nm-thick preoxide and ultraclean oxide formed through 0.6-nm-thick preoxide.

sumed to depend only on the distance from the SiO_2/Si interface, and the chemical shifts and the FWHM values measured at photoelectron take-off angle of 15° are equal to those for oxides close to the surface, the three curves shown in Fig. 5 are obtained. From this figure, the calculated curves of FWHM do not agree with observed results especially for oxide film thickness larger than 4 nm. In order to explain these dis-

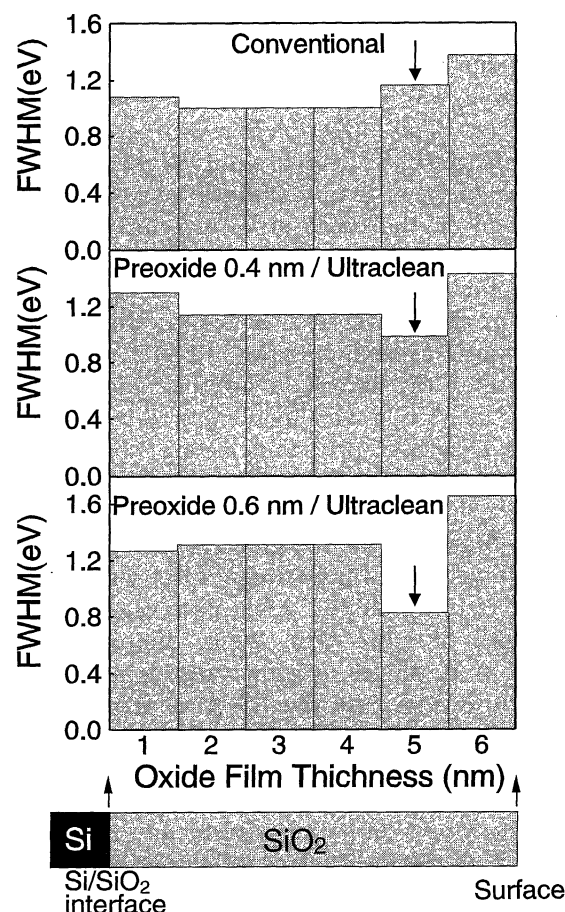


Fig. 6. Calculated changes in FWHM for 6-nm-thick oxide in the depth direction for as-grown conventional oxide, as-grown ultraclean oxide formed through 0.4-nm-thick preoxide and as-grown ultraclean oxide formed through 0.6-nm-thick preoxide.

crepancies, the dependences of FWHM of Si^{4+} on oxide film thickness shown in Fig. 6 are considered. In this case, the calculated curves shown in Fig. 7 are obtained, which roughly agree with observed results. Figure 6 indicates that for oxides formed through 0.4-

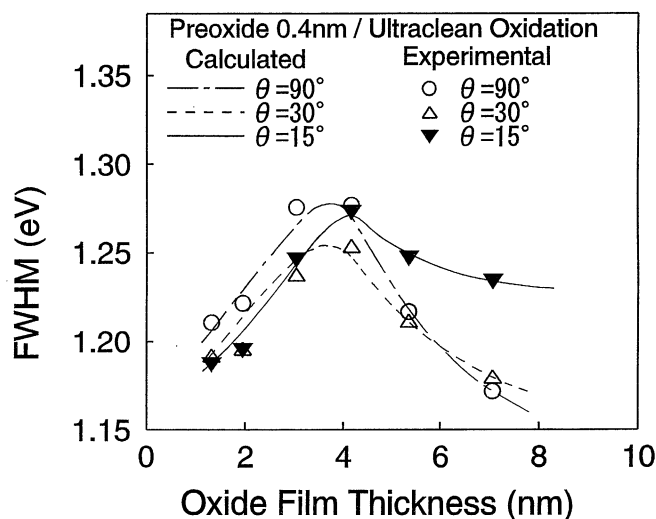


Fig. 7. Observed and calculated dependence of FWHM on oxide film thickness for as-grown ultraclean oxide formed through 0.4-nm-thick preoxide assuming dependence of FWHM on oxide film thickness shown in Fig. 6.

and 0.6-nm-thick preoxides, FWHM of Si^{4+} decreases near the surface, while for an oxide formed without preoxidation, FWHM of Si^{4+} does not decrease near the surface. This difference must be due to the preoxide because the decrease in FWHM near the surface is larger when the preoxide is thicker. The effect of preoxide on the oxide structure must be present even for oxide films with thickness less than 4 nm, but is not appreciable in contrast to the effect of the interface on the oxide structure. However, when the oxide film thickness exceeds 4 nm as a result of oxidation, the effect of the interface on the oxide structure becomes small while the effect of preoxide on the oxide structure becomes appreciable. Here, 4 nm must be related with the thickness of the structural transition layer.^{11,13)}

Figure 8 shows that the changes in FWHM due to chemical etching differ between as-grown oxides and chemically etched oxides. After removal of oxide film to a depth of more than 2 nm, almost the same FWHMs as those for as-grown oxides are obtained. Therefore, in this case the effect of preoxide on the oxide structure is eliminated.

4. Conclusions

The following results were obtained from the chemical structural changes in the depth direction of the conventional oxide and the ultraclean oxide, which was formed through 0.4- and 0.6-nm-thick preoxides, studied by X-ray photoelectron spectroscopy. The chemical shifts for as-grown and chemically etched oxides depend mainly on the distance from the SiO_2/Si interface. The effect of preoxide on the oxide structures becomes appreciable when the oxide film thickness exceeds 4 nm. In this case the preoxide leads to the decrease in FWHM near the surface, implying the production of homogeneous oxide film near the surface.

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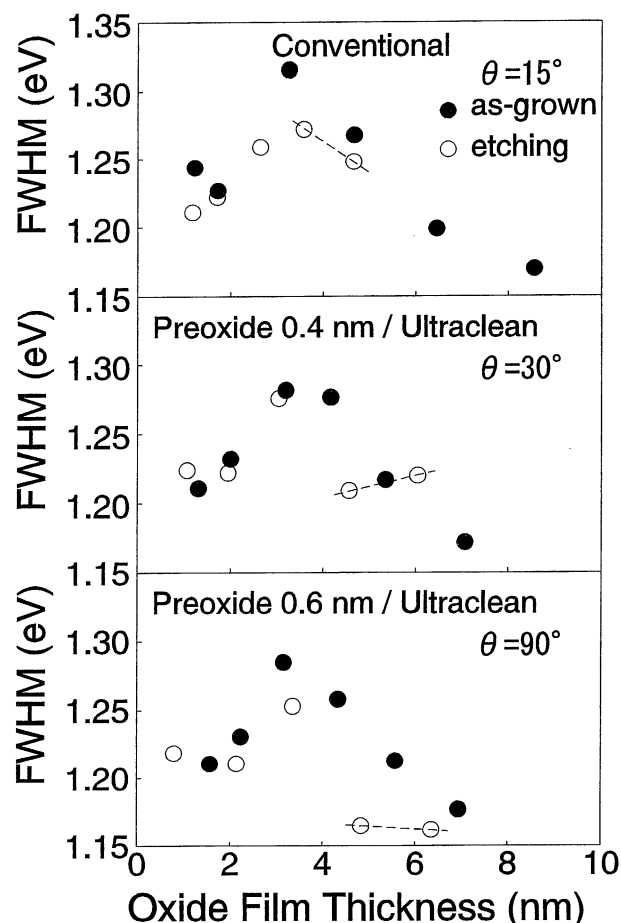


Fig. 8. Observed dependence of FWHM on oxide film thickness for as-grown and chemically etched oxides.

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