Effect of Silicon Wafer *In Situ* Cleaning on the Chemical Structure of Ultrathin Silicon Oxide Film

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The effect of silicon wafer *in situ* cleaning on the chemical structures of thermally grown silicon oxide films was studied by X-ray photoelectron spectroscopy and scanning tunneling microscopy. After the silicon wafer *in situ* cleaning was performed by the decomposition of native oxides in high vacuum, the nearly 1.6-nm-thick thermal oxides were formed in dry oxygen at 800°C. If the heating time for the decomposition of native oxides was too short, intermediate states transformed from native oxides were found to remain on the surface of the oxide films. On the other hand, if the heating time was too long, the amount of intermediate states at the interface was found to increase as a result of the increase in interface roughness. The optimum condition for *in situ* cleaning is heating at 900°C for 30 minutes in high vacuum.

KEYWORDS: *in situ* cleaning, X-ray photoelectron spectroscopy, scanning tunneling microscopy, interface roughness, native oxide

§1. Introduction

In order to form ultrathin silicon oxide films of high quality, the thickness of native oxide formed before thermal oxidation should be minimized or the structure of native oxides should be transformed to defect-free oxides before thermal oxidation. The procedure to achieve the latter has not been found yet. On the other hand, several studies have been performed on the former, as described in the following. The decomposition of native oxides in high vacuum was first studied by Ishizaka and Shiraki[1] in order to obtain a contamination-free clean silicon surface at relatively low temperature. In their studies, a mixed solution of HCl, H_2O_2 and H_2O was used to form native oxides. This silicon wafer cleaning procedure is usually called Shiraki's method. The decomposition temperatures of various native oxides formed during wet chemical treatments were studied by Kobayashi *et al.** by measuring SiO, which was produced as a result of the thermal desorption of native oxides. It is the purpose of the present paper to investigate the effect of decomposition of native oxides in high vacuum on the chemical structure of thermal oxides formed after the decomposition by measuring chemical structures of thermal oxides and interface roughness.

§2. Experimental

The silicon wafers used for the present study are 3 Ωcm p-type (100)-oriented CZ silicon wafers. The native oxides used for silicon wafer *in situ* cleaning at 800 and 900°C were formed in a solution with a composition of $HCl:H_2O_2:H_2O=1:1:4$ maintained at 90°C after perfor-

ming modified Radio Cooperation of America (RCA) cleaning,[2] while those used for *in situ* cleaning at 850°C were formed in several mixed solutions of HCl, H_2O_2 and H_2O maintained at 90°C after performing modified RCA cleaning.[2] After these native oxides were heated in high vacuum, silicon oxides with a thickness of nearly 1.6 nm were formed by the ultraclean oxidation method[3] at 800°C. Here, the base pressure of an oxidation furnace is below 6.7×10^{-7} Pa. Heating times at 900°C were 10, 20, 30 and 60 minutes, and that at 850 and 800°C was 30 minutes. The thermal oxide, which was formed at 800°C by the ultraclean oxidation method[3] after removing 200-nm-thick thermal oxide by advanced Buffered Hydrogen Fluoride (HF 3.7 wt.%, NH_4F 20 wt.%),[4,5] was used as a reference in order to distinguish the effect of thermal decomposition of native oxide on the chemical structures of thermal oxide from the influence of other effects. Here, 200-nm-thick thermal oxide was formed in dry oxygen at 1000°C.

Angle-resolved Si2p, O1s and C1s spectra were measured at take-off angles of 2, 10 and 90 degrees with an acceptance angle of 3.3 degrees using ESCA-300 (Scienta Instruments AB) furnished with a monochromatized Al Kα radiation source. The roughness at the silicon oxide/silicon interface was measured by wide-coverage-type scanning tunneling microscope, SAM3100, manufactured by Seiko Instruments Inc., after one-minute etching of thermal oxides in advanced BHF (HF 0.17 wt.%, NH_4F 17 wt.%)[4,5] followed by three minutes of cleaning in deionized water.

§3. Experimental Results and Discussion

Figures 1(a), 1(b) and 1(c) show $Si2p_{3/2}$ photoelectron spectra measured at photoelectron take-off angles of 90, 10 and 2 degrees, respectively. Here, $Si2p_{1/2}$ spectra were removed.[6] Spectra a were measured for 1.5-nm-thick

*Y. Kobayashi, Y. Shinoda and Y. Sugii: Extended Abstracts 21st Conf. Solid State Devices and Materials, Tokyo, 1989 (Business Center for Academic Societies, Tokyo, 1989) p. 401.
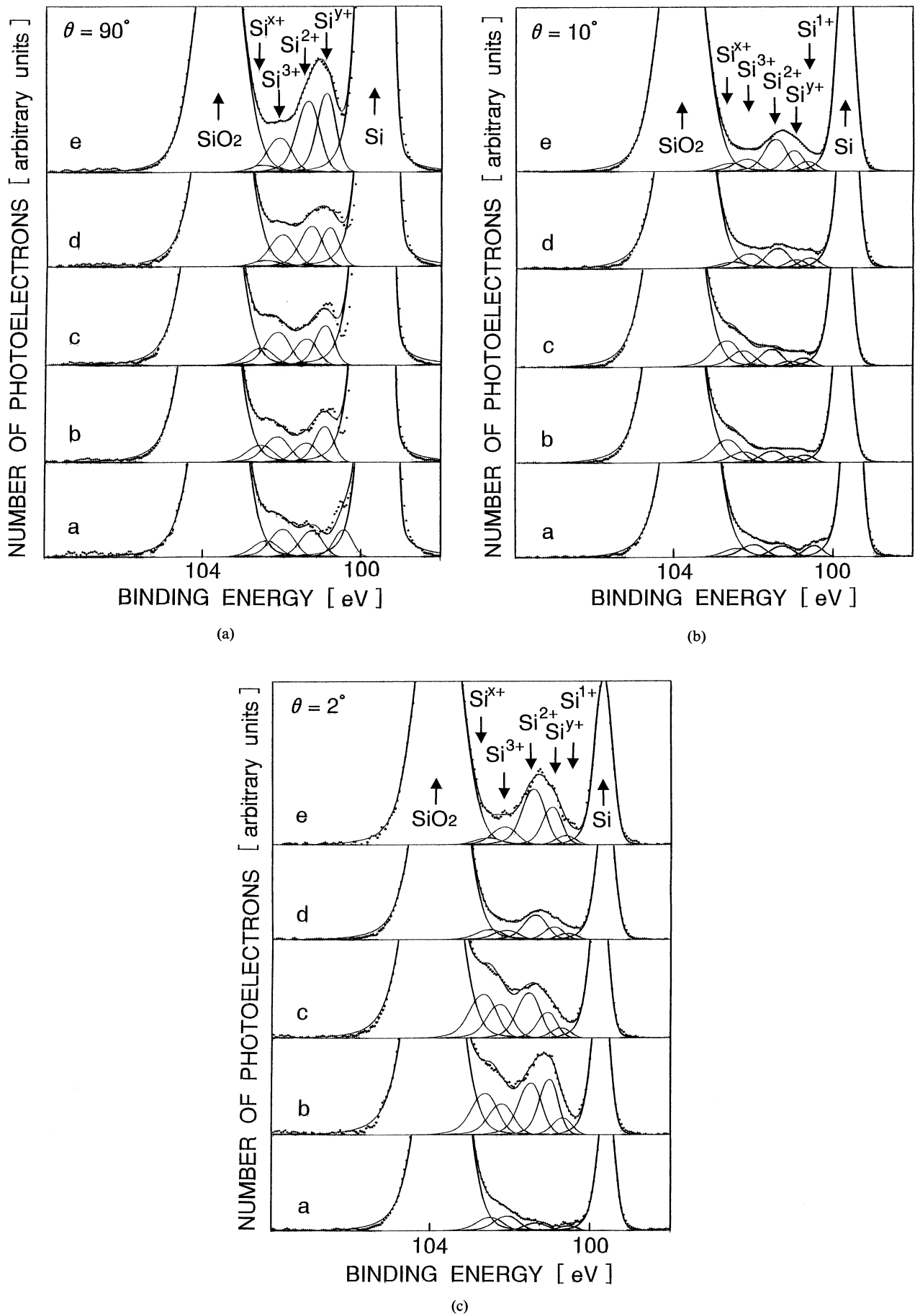
(a)

(b)

(c)

Fig. 1. Si2p$_{3/2}$ spectrum a is measured for 1.5-nm-thick thermal oxide grown without *in situ* cleaning. Si2p$_{3/2}$ spectra b, c, d and e are measured for nearly 1.6-nm-thick thermal oxides grown after *in situ* cleaning with heating times of 10, 20, 30 and 60 minutes, respectively.

thermal oxide film after removing 200-nm-thick thermal oxide film formed in dry oxygen at 1000°C by advanced BHF,[4,5)] and are used as reference spectra. Spectra b, c, d and e in these figures were measured for thermal oxides formed after heating native oxide in high vacuum at 900°C for 10, 20, 30 and 60 minutes, respectively. Thickness of thermal oxide film which exhibits the Si2p photoelectron spectrum denoted by b, c, d and e in Fig. 1 is 1.6, 1.5, 1.6 and 1.8 nm, respectively. In order to show the effect of heating time on the amount of intermediate states, whose binding energy is between that of silicon in the silicon substrate and that of silicon in silicon dioxide, the spectral intensities for silicon in silicon dioxide are adjusted to be equal to each other. Furthermore, it should be noted that the spectra measured at a photoelectron take-off angle of 90 degrees include the spectra from the interface, while the spectra measured at a take-off angle of 2 degrees include the spectra mostly from the surface. This is because the effective escape depth of photoelectrons from silicon dioxide at photoelectron take-off angles of 90, 10 and 2 degrees is 3.4, 0.58 and 0.12 nm, respectively. The escape depth of Si 2p photoelectrons excited by Al Kα radiation from silicon dioxide[7)] was determined as 3.4 nm from the oxide film thickness dependence of (NO/NS). Here, NO and NS are the spectral intensities of silicon in silicon dioxide and silicon in silicon substrate, respectively.

In Fig. 1, the intermediate states are shown to consist of five peaks whose chemical shifts and Full Width Half Maximums (FWHM) are shown in Table I. According to this table, FWHM increases with increase in chemical shift. Such a dependence of FWHM on chemical shift was previously found by Himpsel et al.[8)] A peak assigned by Si^{1+}, Si^{2+} and Si^{3+} has almost the same binding energy as that reported by Himpsel et al.[8)] and can be correlated with the bonding configurations shown in (a), (b) and (c), respectively, in Fig. 2. A peak assigned by Si^{x+} has the same binding energy as that reported by Sugiyama et al.[9)] and can be correlated with the intermediate state located in the oxide film having the bonding configuration shown by (d) in Fig. 2. A peak assigned by Si^{y+} is tentatively correlated with the intermediate state located at the interface whose bonding configuration is shown by (e) in Fig. 2. This is because the binding energy of this intermediate state calculated using the concept of local electronegativity[10,11)] and the values of electronegativities[12)] listed in Table II is 1.33 eV and is quite close to that measured for a photoelectron take-off angle of 90 degrees. On the other hand, if the intermediate state whose bonding configuration is shown by (e) in Fig. 2 is located in the oxide film, the calculated binding energy of this intermediate state is 2.35 eV. Because such a state is not included in the Si 2p photoelectron spectra shown in Fig. 1, the intermediate state Si^{y+} observed for the take-off angle of 2 degrees implies the existence of a silicon cluster near the surface of the oxide film which produces the intermediate states located in the oxide film having the bonding configuration shown by (e) in Fig. 2. Furthermore, because the binding energy of the intermediate state at the interface whose bonding configuration is shown by (f) in Fig. 2 is 2.14 eV, this state is not included in the Si 2p

Table I. Chemical shift and FWHM of deconvoluted spectra.

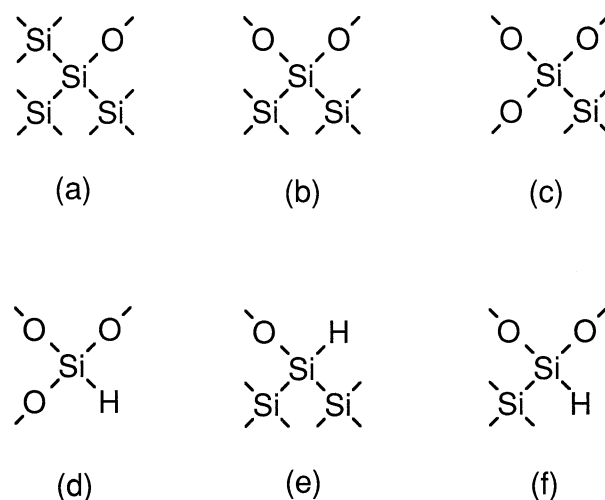| Intermediate state	Si^{1+}	Si^{2+}	Si^{3+}	Si^{x+}	Si^{y+}
Chemical shift (eV)	0.95	1.75	2.48	2.90	1.29
FWHM (eV)	0.58	0.69	0.76	0.81	0.58

Fig. 2. Possible bonding configurations near the interface region.

Table II. Values of electronegativity.

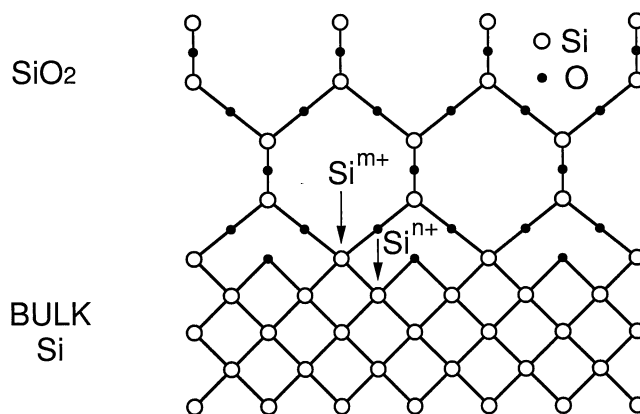| Element	Electronegativity
Si	2.84
H	3.55
O	5.21

Fig. 3. Possible bonding configurations near the interface region of oxide film formed on (100) surface.

photoelectron spectra shown in Fig. 1.

Moreover, because there are some discrepancies in Fig. 1(a) between the observed spectra and the calculated spectra consisting of these five peaks, intermediate states assigned as Si^{m+} and Si^{n+} in Fig. 3, whose existence in the interface region on the (001) surface was pointed out by Harman et al.,[13)] can possibly be contained in the ob-

served spectra. This is because the binding energy of Si^{m+} and Si^{n+} calculated based on the concept of local electronegativity[10,11] and the values of electronegativities[12] listed in Table II are 1.96 eV and 1.16 eV, respectively, and are close to those of Si^{2+} and Si^{y+} observed at the photoelectron take-off angle of 90 degrees, respectively.

In Fig. 4 the spectral intensity, NI, for silicon in intermediate states divided by NO is shown as a function of heating time with the photoelectron take-off angle as a parameter. When heating time was less than 20 minutes, the native oxides were not decomposed completely, and the various intermediate states remained on the surface of the thermal oxides, as can be seen in Fig. 1. On the other hand, when heating time was 60 minutes, the amount of intermediate states at the interface and that on the surface were large. As discussed in a later section, the anomalously large amount of intermediate states in this case can be correlated with the large interface roughness shown by the STM profile in Fig. 5(e). As can be seen in Fig. 1, the intermediate states which are correlated with this interface roughness mainly arise from two components, that is, Si^{2+} and Si^{y+}. When native oxide was heated at 900°C for 30 minutes, for all photoelectron take-off angles, the normalized amount of intermediate state NI/NO was comparable to that obtained for thermal oxide without *in situ* cleaning, listed in Table III. The optimum conditions of *in situ* cleaning determined from the amount of intermediate states are heating native oxide in high vacuum at 900°C for 30 minutes. Here, as can be seen from the STM profile in Fig. 5(d), the nearly periodically undulating interface with inclination of 2.3
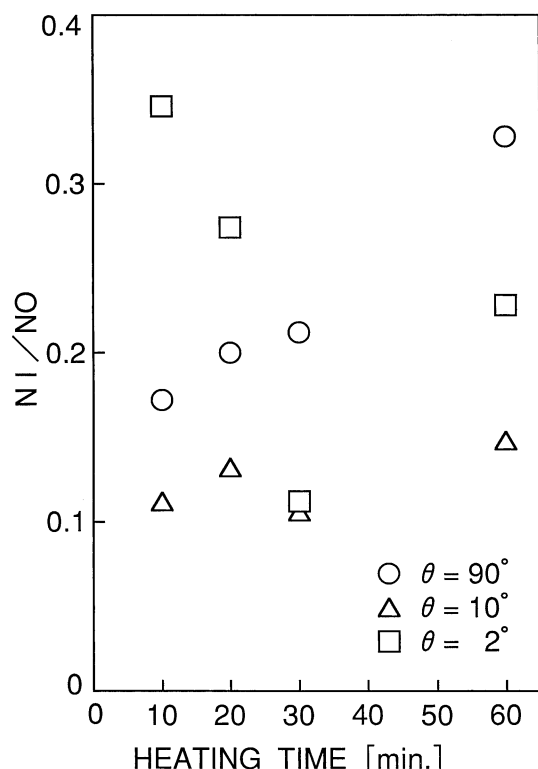
degrees in this case does not contribute appreciably to the production of intermediate states.

The STM profiles in Figs. 5(a) to 5(e) correspond to
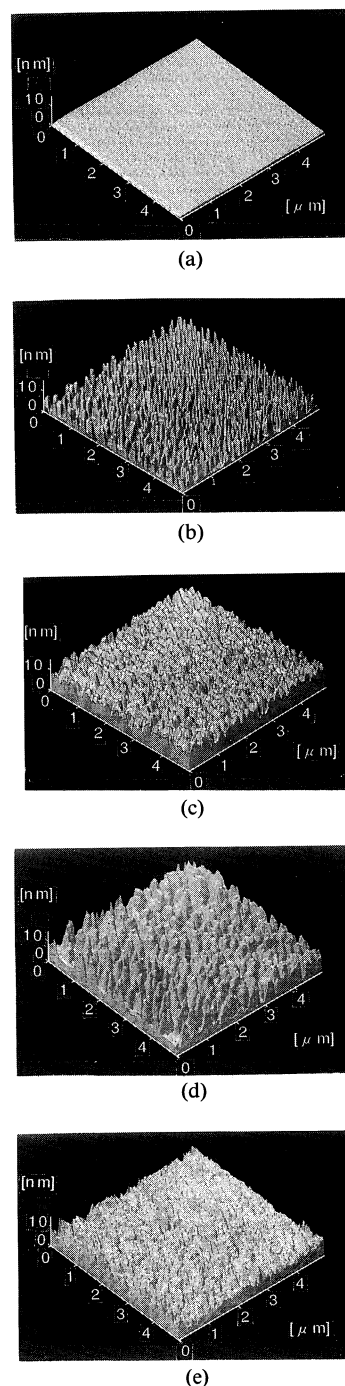

(a)

(b)

(c)

(d)

(e)

Fig. 5. STM profile a is measured for 1.5-nm-thick thermal oxide grown without *In Situ* cleaning. STM profiles b, c, d and e are measured for nearly 1.6-nm-thick thermal oxides grown after *In Situ* cleaning with heating times of 10, 20, 30 and 60 minutes, respectively.

Fig. 4. Si2p$_{3/2}$ spectral intensity NI for silicon in intermediate states divided by that NO for silicon in silicon dioxide is shown as a function of heating time with photolelectron take-off angle as a parameter.

Table III. NI/NO for thermal oxide without *in-situ* cleaning.

take-off angle (degrees)	NI/NO
90	0.172
10	0.078
2	0.079

spectra a, b, c, d and e in Fig. 1, respectively. In Fig. 6, the relationship between NI/NO for a photoelectron take-off angle of 90 degrees and the interface roughness R_{max} is shown. Here, R_{max} is defined by the difference in height from the maximum peak to the minimum valley over the area of 5 μm × 5 μm on the wafer in Fig. 5. The greatest amount of intermediate states in this figure corresponds to the STM profile in Fig. 5(e). The value of interface roughness R_{max} in this case is not so different from that for the STM profile in Fig. 5(d). However, the nonperiodically undulating interface in this case produces large amounts of intermediate states. It should be noted that the value of 0.172 in Table III is close to the calculated value of 0.16 for NI/NO of 1.5-nm-thick thermal oxide film with an atomically flat interface. Therefore, the STM profile in Fig. 5(a) implies that the interface formed without in situ cleaning is almost atomically flat.

The interface roughness produced after heating native oxide, which was formed on the (100) surface in a solution with a composition of $HCl:H_2O_2:H_2O=1:1:1$ maintained at 90°C after performing modified RCA cleaning[2] in high vacuum at 850°C for 30 minutes, was found to be comparable to that shown in Fig. 5(b). This means that 30 minutes is not sufficient for the decomposition of native oxides at this temperature. This result is also reasonable from the fact that heating time of 30 minutes is optimum for the decomposition of native oxides at a higher temperature of 900°C. The interface roughness produced after heating native oxide in high vacuum at 800°C for 30 minutes is less than that shown in Fig. 5(d).

However, in this case, appreciable amounts of intermediate states were found to remain on the surface of oxide film. This implies that the native oxide was not decomposed completely in this case.

Furthermore, it was found that the increase in interface roughness results in the increase of optical absorption below the fundamental optical absorption edge of fused quartz. Optical absorption spectrum a in Fig. 7 was measured for 1.8-nm-thick thermal oxide films whose $Si2p_{3/2}$ spectrum is shown in Fig. 1(e). The spectrum b in Fig. 7 obtained for 1.4-nm-thick thermal oxide film which was prepared by chemical etching of 4.5-nm-thick thermal oxide film grown without in situ cleaning. Therefore, the anomalous increase in optical absorption produced by in situ cleaning can be correlated with the increase in intermediate states in the oxide film. The method of determing the absorption spectra is described elsewhere.[14,15]

Considering the decomposition mechanism of silicon oxide presented by Offenberg et al.,[16] the possible mechanisms of producing surface roughness are as follows. 1) If the native oxide is not uniform, it will be decomposed nonuniformly. Bare silicon surface appearing as a result of this decomposition will react with O_2 and H_2O remaining in the vacuum chamber to produce SiO. 2) Even if the native oxide is uniform, oxygen in the wafer is distributed nonuniformly and reacts with surface silicon to form SiO. These two mechanisms are expected to result in nonuniform etching of the silicon surface and may also be applicable to studies by Ohkura et al.*
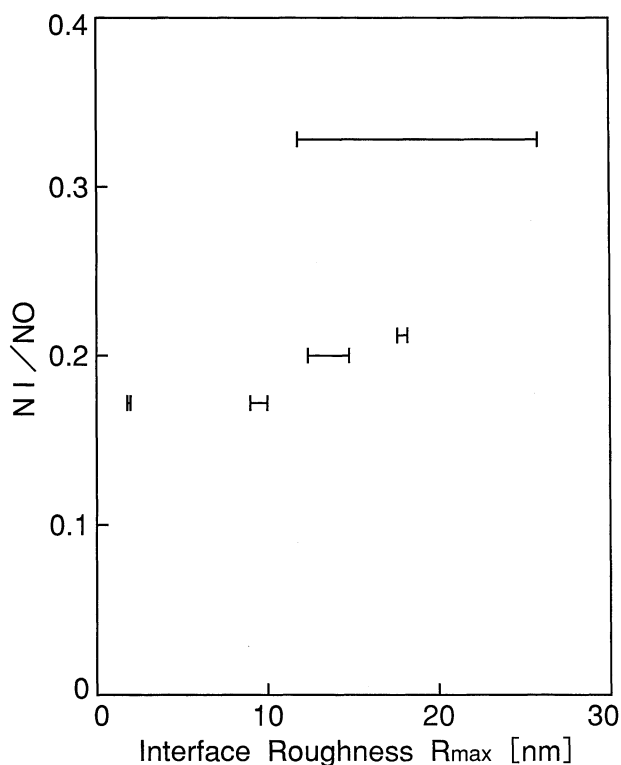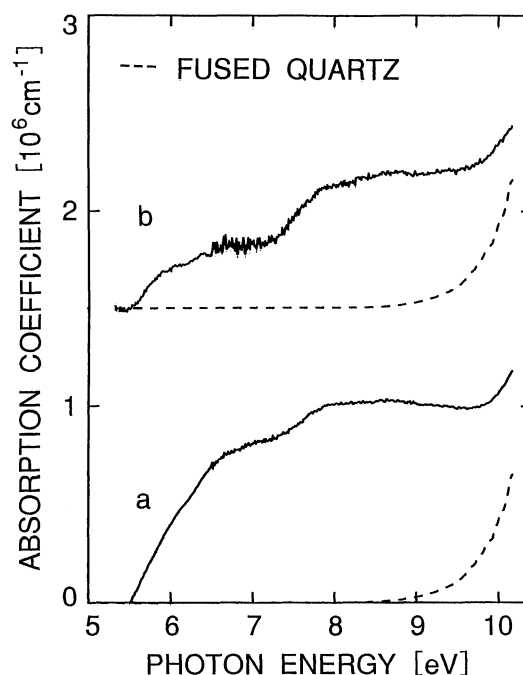

Fig. 6. Amount of intermediate states determined from Fig. 1 are shown as a function of interface roughness defined by the difference in height between the maximum peak and the minimum valley on the wafer.

Fig. 7. Optical absorption spectrum a was measured for oxide whose $Si2p_{3/2}$ is shown in spectrum e in Fig. 1. Spectrum b was measured for oxide which was prepared by chemical etching of 4.5-nm-thick thermal oxide film grown without In Situ cleaning.

*A. Ohkura, H. Oku, K. Matsumoto and T. Ohmi: Extended Abstracts 1991 Intern. Conf. Solid State Devices and Materials, Yokohama, 1991 (Business Center for Academic Societies Japan, Tokyo, 1991) p. 207.

§4. Conclusions

The chemical structures and interface roughness of ultrathin thermal oxides formed after heating native oxides in high vacuum were investigated by X-ray photoelectron spectroscopy and scanning tunneling microscopy. When heating time was too short, the native oxide was not decomposed completely. On the other hand, when heating time was too long, the amounts of intermediate states increased as a result of increase in interface roughness. When native oxide was heated at 900°C for 30 minutes, the normalized amount of intermediate states was comparable to that for thermal oxide without *in situ* cleaning. Therefore, the optimum condition of *in situ* cleaning determined from the amount of intermediate states is heating native oxide at 900°C for 30 minutes. Furthermore, the interface roughness was found to produce the increase in optical absorption.

Acknowledgement

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