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# Nondestructive Measurements of Si-SiO<sub>2</sub> Interface Structures Studied by Using X-Ray Excited Si KLL Auger Electron Spectra

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The increase in the probing depth to nearly 20 nm is realized for silicon oxide by using X-ray excited Si KLL Auger electron spectra. The conistent analytical results with those obtained by using Mg K $\alpha$  radiation excited Si 2p photoelectron spectra were obtained. These consistent analytical results verify the assumption that in the thickness range studied, the distribution of the intermediate oxidation states in the oxide film is almost independent on the oxide film thickness. This assumption is also confirmed from the depth profiling studies by using chemical etching.

## §1. Introduction

As a result of extreme decrease in the dimensions of metal-oxide-semiconductor field-effect transistor in recent year, the electronic states in  $\operatorname{Si-SiO}_2$  interfacial transition layer and those in amorphous SiO<sub>2</sub> network play a vital role in device operation.<sup>2</sup> Because of this, the chemical and physical structures of Si-SiO<sub>2</sub> interface and SiO, have been studied extensively by using various surface sensitive techniques. The existence of abrupt interface,<sup>2)</sup> the existence of disordered silicon layers next to the interface,<sup>3)</sup> the existence of intermediate oxidation states of silicon,<sup>4)</sup> structural changes in amorphous  $SiO_2$  net-work near the interface,<sup>5)</sup> structural origin of the interface electronic states<sup>6)</sup> were found from these techniques. It was also clarified from the electron microscopic observation that the interface is not flat in the atomic scale.<sup>7)</sup>

The dependence of  $\text{Si-SiO}_2$  interface structures on crystal orientation were found from the nondestructive measurements of Mg Ka radiation excited Si 2p photoelectron spectra.<sup>8)</sup> In this case, however, the interface structures were difficult to detect for the oxide film thickness of more than 10 nm. It is the purpose of the present paper to show the increase in the probing depth to nearly 20 nm by using X-ray excited Si KLL Auger electron spectra.<sup>9)</sup> The new method of background signal subtraction was developed in

order to obtain the consistent analytical results with those obtained by using Mg K $\alpha$  radiation excited Si 2p photoelectron spectra.

 Experimental Details and Analytical Procedures

Measurements were made on 6-8  $\Omega$ cm <100> oriented boron doped silicon wafers having area of 16 mm<sup>2</sup>. The wet oxides were grown on these wafers at 1000 °C to the thickness of 200 nm. After etching these initial oxides, thinner oxides were successively grown at 800°C in dry oxygen. The Si KLL Auger electron spectra excited by Ag La or Au Ma radiation were measured by using microcomputer controlled modified Shimadzu ESCA spectrometer. The spectral intensities were measured with the energy spacing of nearly 0.0417 eV. Under the present experimental conditions, the value of full width at half maximum (FWHM) of Au 4f 7/2 spectrum is 1.12 eV.

Fig. 1(a) and 1(b) shows some of Si KLL Auger electron spectra and Si 2p photoelectron spectra, respectively. The thickness of dioxide films in Fig. 1 was determined from the integrated intensity ratio of electrons emitted from the oxidized silicon to those from substrate silicon. The values of electron escape depth in silicon dioxide and silicon substrate used here are determined by the conventional method, <sup>10)</sup> and are 3.7 and 3.3 nm for Si KLL Auger electrons, and 2.8 and 2.4 nm for Mg Ka radiation excited Si 2p photoelectrons, respectively.

These spectra can be separated into three spectra originating from Si in silicon substrate, Si in silicon dioxide, and Si in intermediate oxidation states,  $\text{SiO}_{x}(0 < x < 2)$ . By comparing the spectra obtained for the oxide films grown on (100) surface with those on (111) surface, it was confirmed that intermediate oxidation states consist of three states,  $\text{Si}_{2}^{0}$ , SiO, and  $\text{Si}_{2}^{0}_{3}$ .

In order to investigate the intermediate oxidation states in more details, the intermediate oxidation state spectrum is separated into three spectra by the least squares calculation with the assumption that the lineshapes of three separated spectra are the same with that for chemically etched silicon. Examples of these separations are shown in Figs. 1(a) and 1(b). The amount of oxygen-induced binding energy shift observed in Si KLL Auger electron spectra is nearly twice as large as that in Si 2p photoelectron spectra, which makes it easy to resolve the intermediate oxidation states.

In Figs. 2(a) and 2(b), the intensities NI of three intermedaite oxidation state spectra separated from those in Figs. 1(a) and 1(b) are shown as a function of dioxide film thickness. Here, the value of NI is normalized by the spectral intensity NS of substrate silicon.

The intermediate oxidation state distribution can be determined from Fig. 2 as explained in the following. If  $Si0_x$  is located only at the interface(Model I), the number of photoelectrons originating from silicon substrate and that from SiO, decrease with the same rate because of the inelastic scattering in the oxide film. In such case, the values of (NI/NS) are independent on the dioxide film thickness. On the other hand, if  $SiO_{v}$  is distributed in the oxide film near the interface and the amount of SiO, decreases exponentially with approaching to the surface of the oxide film(Model II), the values of (NI/NS) are shown to increase with increasing dioxide film thickness. The values of (NI/NS) obtained experimentally can be explained by the combination of these two models. Namely,

$$(NI/NS) = C + B[exp(Ad) - 1]$$
(1)



Fig. 1. Ag La radiation excited Si KLL Auger electron spectra shown in (a) and Mg Ka radiation excited Si 2p photoelectron spectra in (b) for the oxide films formed at 800 °C on (100) surface. Examples of separations are shown by the dashed curves for 2.6 and 3.1 nm thick oxide films.

Here, d expresses the silicon dioxide film thickness. In this equation, the first and the second term is related with Model I and II, respectively.

#### §3. Discussions

Curves in Figs. 2(a) and 2(b) are calculated by considering the same intermediate oxidation state distribution in the oxide film and the difference in the electron escape depth for two cases. According to this figure, the almost consistent thickness dependence of (NI/NS) for SiO and Si203 are obtained for two cases for the oxide film thickness of less than 7 nm. In this thickness range, the value of (NI/NS) for SiO is weakly dependent on the dioxide film thickness, while that for Si203 is strongly dependent on the dioxide film thickness and decreases rapidly with decreasing dioxide film thickness. This indicates that SiO is mostly located at the interface, while Si203 is distributed in the oxide film near the interface, but not at the interface.

In the thickness range of more than 7 nm, the experimental value of (NI/NS) for SiO in Fig. 2(a) deviates from the calculated curve. If we assume that (NI/NS) for SiO is attributed mostly to the interface structure, the discrepancy between the calculated curve and the experimental value of (NI/NS) for SiO is found to decrease. However, such assumption is not supported by the depth profiling measurements described in the following.

In the analysis of the nondestructive measurements of Si 2p photoelectron spectral intensities, the chemical structure near the interface is assumed to be independent on the dioxide film thickness. In order to confirm this assumption, the dependence of (NI/NS) on the oxide film thickness were studied by the destructive measurements with the use of chemical etching.

The results are shown in Fig. 3 for the oxide films having starting oxide film thickness of 4.5, 9.3, and 16 nm, respectively, in addition to the values of (NI/NS) obtained for as-grown oxide films. According to this figure, almost the same thickness dependence of (NI/NS) are obtained for destructive and nondestructive measurements. This indicates that the chemical structures near the interface are weakly dependent on the dioxide film



Fig. 2. Oxide film thickness dependence of normalized spectral intensities for three intermediate oxidation states, Si<sub>2</sub>O, SiO, and Si<sub>2</sub>O<sub>3</sub> obtained from Si KLL Auger electron spectra shown in (a) and those obtained from Si 2p photoelectron spectra in (b).

thickness for the thickness range studied here.

### §4. Conclusion

The increase in probing depth to nealy 20 nm is realized for silicon oxide by using Ag La and Au Ma radiation excited Si KLL Auger electron spectra. The almost consistent analytical results were obtained for Mg Ka excited Si 2p photoelectron spectra and X-ray excited Si KLL Auger electron spectra. By using XPS measurements combined with chemical etching, it is confirmed that chemical structure near the interface is weakly dependent on the oxide film thickness discussed here.

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Fig. 3. Normalized intermediate oxidation state spectral intensities as a function of dioxide film thickness determined from the depth profiling measurements. The data in Fig. 2(b) are also shown.

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