

Invited

Si-SiO₂ Interface Structures of Ultrathin Oxides

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Based on the observation of crystal orientation dependence of Si 2p photoelectron spectra, the orientation dependence of interface structures and the distribution of intermediate oxidation states of silicon in the oxide film were determined. The effects of oxidation condition on the structures of interfacial transition layer and SiO₂ were also found.

§1. Introduction

As a result of extreme decrease in the dimensions of metal-oxide-semiconductor field-effect transistor in recent years, the electronic states in Si-SiO₂ interfacial transition layer and those in amorphous SiO₂ network play a vital role in device operation.¹⁾ Because of this, the chemical and physical structures of Si-SiO₂ interface and SiO₂ have been studied extensively by using various surface sensitive techniques. The existence of abrupt interface,²⁾ the existence of disordered silicon layers next to the interface,³⁾ the existence of intermediate oxidation states of silicon,⁴⁾ structural changes in amorphous SiO₂ network near the interface,⁵⁾ were found from these measurements. It was also clarified from the electron microscopic observation that the interface is not flat in the atomic scale.⁶⁾

In this report we concentrate primarily on describing the interface structures and the distribution of intermediate oxidation states of Si determined from the nondestructive measurements of Si 2p photoelectron spectra.⁷⁾

§2. Principles of Depth Profiling

If the distribution of intermediate oxides in the film is expressed by $f(y)$, X-ray excited Si 2p photoelectron spectral intensity, $NI(d)$, originating from this intermediate oxides can be given by the following equation:

$$NI(d) = K \int_{-t}^d f(y) \exp\left[-\int_y^d \frac{dz}{\Lambda(z)}\right] dy$$

Here, t is the thickness of the interfacial transition layer, $(t + y)$ is the distance from the interface, d is the thickness of SiO₂ layer, Λ is the electron escape depth, K is proportional to both X-ray intensity and photoelectric cross section.

If the amount of intermediate oxides in the film is small so that Λ is independent on y , $f(d)$ is given by the following equation:

$$f(d) = (1/K)[NI(d)/\Lambda] + (1/K)[\partial NI(d)/\partial d]$$

The appropriate distribution of intermediate oxides in the film can be found from the following considerations. If the intermediate oxides, SiO_x, is located only at the interface, number of photoelectrons NI , originating from Si in SiO_x, and NS , originating from Si substrate decrease with the same rate by the inelastic scattering in the film. Then, in such case the ratio (NI/NS) does not depend on d . On the other hand, if SiO_x is distributed uniformly in the film, the dependence of (NI/NS) on d should exhibit similar dependence with that for (NO/NS) , where NO is the photoelectron spectral intensity for Si in SiO₂.

In the conventional depth profiling studies, ion sputtering is used for the etching of the

film. However, it was found from the quantitative analysis of depth profiling measurement of Si 2p photoelectron spectra on ultrathin silicon oxide films that sputtering can not be used for the study of abrupt interface.⁸⁾ This is because the ion bombardment was found to produce intermediate oxides.⁹⁾

Because of this reason, two methods were examined in order to obtain the dependence of (NI/NS) on d . One method is destructive measurement of Si 2p photoelectron spectral intensities by decreasing thickness d with the use of chemical etching.⁵⁾ Another method is nondestructive measurement of Si 2p photoelectron spectral intensities for as-grown oxide films having various thickness prepared at the same oxidation condition and is based on the assumption that the interface structures do not depend on the oxide film thickness for the thickness range studied. The dependence of (NI/NS) on d obtained by two methods are almost equal to each other for the oxide film thickness of less than 10 nm. The preferential chemical etching seems to be negligible because of the almost constant etching rate.

In the following the distribution of intermediate oxides in the film are discussed mainly from the nondestructive measurements of Si 2p photoelectron spectra.⁷⁾

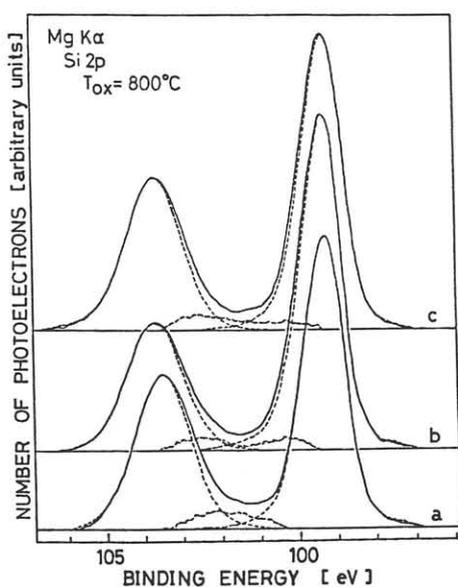


Fig. 1. Si 2p photoelectron spectra for three crystal orientations.

§3. Experimental Results and Discussions

3.1. Orientation Dependence of Interface Structure

The spectra a, b, and c shown by the solid lines in Fig. 1 are Mg K α radiation excited Si 2p photoelectron spectra obtained for the oxide films formed in dry oxygen at 800 °C on (100), (111), and (110) surface, respectively. The thickness of the silicon dioxide film for spectra a, b, and c is 2.4, 2.1, and 2.3 nm, respectively. These spectra can be separated into three spectra originating from Si in silicon substrate, Si in silicon dioxide, and Si in intermediate oxidation state. The spectra thus separated are shown by the dashed lines in Fig. 1. The difference for <100> and <111> is observed in the intermediate oxidation state spectra. Namely, the spectrum observed at around 101.3 eV in spectrum a is not observed in spectrum b, while the spectrum observed at around 100.3 eV in spectrum b is not observed in spectrum a. The spectrum observed at 101.3 eV and 100.3 eV agrees with previously assigned oxidation states, SiO and Si₂O, respectively.⁵⁾ The spectrum at around 102.6 eV is observed for three crystal orientations and agrees with previously assigned oxidation state, Si₂O₃.⁵⁾

3.2. Distribution of SiO_x in Depth Direction

In order to investigate the intermediate oxidation states in more details, the intermediate oxidation state spectra are separated by least squares calculations with the following assumptions: (1) the intermediate oxidation states consist of three oxidation states, Si₂O, SiO, and Si₂O₃; (2) the line shape of each spectrum is the same as that for chemically etched silicon. In Fig. 2 the values of (NI/NS) for three intermediate oxidation states are shown as a function of silicon dioxide film thickness for the oxide films formed at 1000 °C on (100) surface.

According to this figure, the value of (NI/NS) for SiO weakly depends on the oxide film thickness and approaches a constant value with decreasing thickness, while the value of (NI/NS) for Si₂O₃ strongly depends on the oxide film thickness such that the value of (NI/NS) exhibits rapid decrease with the decrease in the oxide

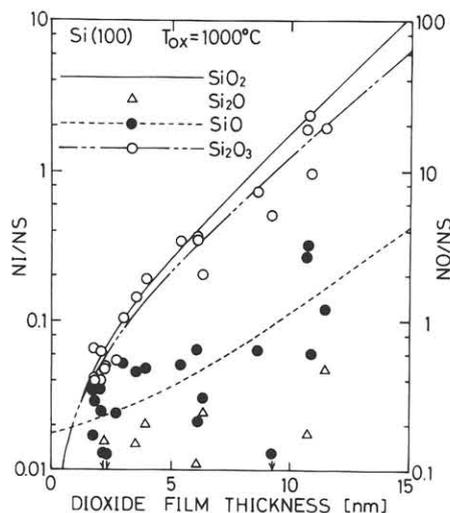


Fig. 2. Normalized intermediate spectral intensities as a function of dioxide film thickness obtained for as-grown oxide films.⁷⁾

film thickness in addition to the slightly weaker thickness dependence of (NO/NS).

Based on the considerations described in §2, SiO is located mostly at Si-SiO₂ interface, while Si₂O₃ is mostly located near the interface, but not at the interface. The amount of Si₂O₃ in the film is less than 10% of the amount of SiO₂. These distributions of SiO and Si₂O₃ in the oxide film can be also expected from the change in the binding energy of Si 2p core level for these intermediate oxides with the change in the oxide film thickness.¹⁰⁾

In the discussion above the interface structures are assumed to be independent on the oxide film thickness. This assumption is confirmed by the depth profiling measurements of Si 2p photoelectron spectral intensities as a function of depth by using chemical etching,¹¹⁾ and also by the measurements of Si KLL Auger electron spectra.¹¹⁾

3.3. Abruptness of Interface Structures

If the intermediate oxides are located only at Si-SiO₂ interface, the expression of (NI/NS) is given by $(n_i t / n_s \Lambda_s)$ for abrupt interface.¹⁰⁾ Here, t is the interface width, Λ_s is the electron escape depth in substrate silicon, and n_i and n_s is the atomic density of intermediate oxidation state-silicon in the interfacial transition layer and that of silicon in silicon sub-

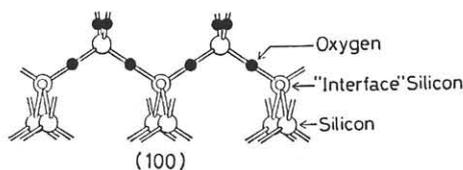


Fig. 3. Possible Si-SiO₂ interface structure

strate. Assuming $n_i \approx n_s$, $\Lambda_s = 2.41$ nm, and $t = 0.241$ nm, 0.1 is obtained for the value of (NI/NS). This is much larger than the extrapolated value, $(NI/NS)_i$, obtained for zero film thickness in Fig. 2. This indicates the existence of the abrupt interface consisting of SiO for the oxide films formed on (100) surface.

The same conclusions were obtained also for the oxide films formed on (111) and (110) surfaces. The possible interface structure for the oxide film formed on (100) surface is shown in Fig. 3.

It should be noted that the contribution of Si₂O₃ is usually overestimated in the estimation of the interface width because of the neglect of Si₂O₃ distribution in the oxide film.

3.4. Structure of SiO_x in the Oxide Film

The amount of SiO_x in the oxide film reaches nearly 10% of that of SiO₂ near the interface. Therefore, this observation is difficult to explain by the existence of dangling bonds, but will be explained by the existence of Si-Si bonds in the oxide film. The small amounts of SiO and Si₂O in the oxide film expected from Fig. 2 imply the existence of extremely small amount of silicon clusters in the oxide film.¹²⁾

3.5. Effect of Oxidation Condition on the Amount of SiO_x

Fig. 4 shows (NI/NS) as a function of silicon dioxide film thickness, for the oxide films prepared in dry oxygen with the oxidation temperature as a parameter. According to this figure, the change in oxidation temperature strongly affects the amounts of SiO and Si₂O₃ in the oxide film, while it weakly affects the amount of SiO at the interface. Therefore, the interface structure is slightly affected by the change in oxidation temperature.

The change in oxidation atmosphere from dry

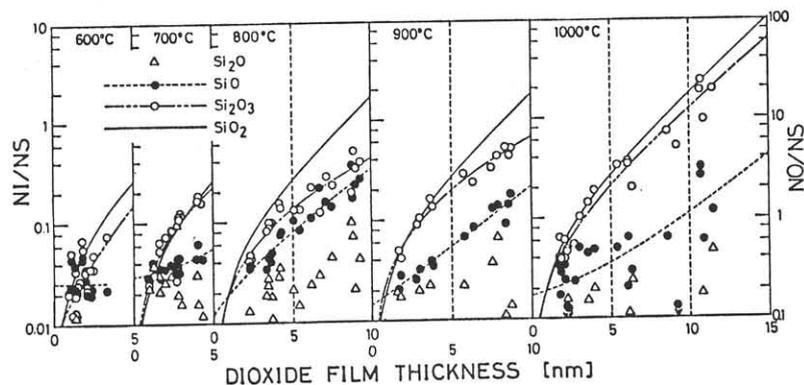


Fig. 4. Effect of oxidation temperature on the thickness dependence of normalized spectral intensities obtained for as-grown oxide films.

oxygen to wet argon was found to diminish the amount of Si_2O_3 in the oxide film. Also, the effect of oxidation temperature on the oxide films formed in wet argon was found to be different from that on the oxide films formed in dry oxygen.¹³⁾

§4. Summary

Based on the observation of the crystal orientation dependence of Si 2p photoelectron spectra for ultrathin oxide films, the orientation dependence of the interface structures and the possible existence of Si-Si bonds in the oxide film near the interface were found. The abruptness of the interface structures were also confirmed from the present study. The effect of oxidation conditions on the structures of interfacial transition layer and oxide film were also studied.

Acknowledgements

The authors are grateful to M. Ohno of Hitachi VLSI Engineering Co. Ltd. and to M. Ogino of Research and Development Center, Toshiba Corp. for supplying silicon wafers used in the present experiments. A part of this work was supported by the Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture of Japan.

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