Thickness-Deconvolved Structural Properties of Thermally Grown Silicon Dioxide Film

Kenji ISHIKAWA, Hiroki OGAWA, Sumiko OSHIDA, Kaina SUZUKI and Shuzo FUJIMURA

Process development division C850, Fujitsu Limited 1015 Kamikodanaka, Nakahara-ku, Kawasaki 211, Japan

We have studied structural and optical properties of thermally grown silicon dioxide (SiO₂) films. These properties were examined by incrementally etching back the oxide films and performing infrared reflection absorption spectroscopy (IR-RAS) measurement at each thickness. We have divided the oxide into incremental layers and calculated the dielectric function of the each layers. This study shows that interfacial layer, whose structure differ from that of bulk oxide, with thickness below 1nm exists at the Si-SiO₂ interface. In addition, farther from the interface, transverse optical mode frequency shifts in wave number to a higher value.

1. INTRODUCTION

In gate oxide fabrication of silicon metal-oxide-semiconductor devices, the evaluation of the chemophysical oxide structure is required in order to assess the influence of film formation method on device performance. As device dimensions shrink, gate oxide thicknesses reach under 5nm and the oxide structure is probably different in this region. In previous publications^{1,2)}, the frequency of infrared (IR) transmittance absorption peak due to the transverse optical resonance (TO) mode arising from Si-O bond-stretching vibration vary as a function of the film thickness. They divided incrementally the oxide film into several layers and calculated the thickness-deconvolved data for each layers by requiring that average value for the layers added together must fall on curve fitted to the data averaged over the film thickness. These studies did not consider peak frequency shift due to an existence of structural and optical different layer, however. Previous work³⁾ has shown that the spectra of the oxide film with thickness below 3nm differ from that of the bulk oxide due to the Si-SiO2 interfacial layer with thickness below 1nm. In this study, to avoid the effect of interfacial layer and to deconvolute the structural properties, we calculated the dielectric function of the each layers.

2. EXPERIMENTAL

Substrate material used was Si<111> wafers of 0.01Ω cm and $1k\Omega$ cm resistivity, respectively. Following wet cleaning, the samples were oxidized in a standard furnace at 950°C. The loading to the furnace were performed in an argon ambient at room temperature to prevent any unintentional oxide.

The wafers were then wet-chemically etched back in 5nm increments using a 1vol% diluted hydrogen fluoride (HF) solution ranging in thickness from 80nm to 5nm, and 0.2vol% HF in 0.5nm increments ranging in thickness from 5nm to 0nm. In order to stop etching immediately, the samples were rinsed in deionized water for short time. At

the last step, the samples exposed hydrophobic surface of silicon and are used as proper reference of IR measurement. IR reflection absorption spectroscopy (RAS) measurements were then performed at each thickness using a Fourier transform infrared spectrometer (JEOL JIR-6500), a mercury cadmium telluride (MCT) detector cooled liquid nitrogen, a wire grid polarizer and an RAS kit (Spectra-tech FT-80). The RAS spectra has taken with p-polarized light at 80° incidence under a dry nitrogen ambient. The spectral resolution was 8cm⁻¹ and 500 scans were carried out to obtain a spectrum. Reflectance spectra of oxide films were produced by calculation of the ratio of oxide spectra and the reference spectra. Absolute reflectance spectra were obtained from referred to a spectrum of gold mirror with no dispersion and highly reflection coefficient, above 95%.

Thickness measurements of films ranging in thickness from 80nm to 5nm were performed by ellipsometer (Rudolf Research Auto-EL3). In the case of thin film with thickness below 5nm, we used value of height of TO mode.

The results of the RAS measurements described above are shown in Fig. 1.

3. ANALYSIS

In order to deconvolute the structural and optical properties of the each layers, we divided the SiO_2 film into several incremental layers (Fig. 2) and calculated the dielectric function of the each layers by requiring that the calculated spectra



Fig. 1 Actual RAS spectra of thermally grown oxide films at each thickness below 3nm.

for the first n layers must fall on curves fitted to the actual spectra of the first n layers thickness. In previous work, the dielectric function of the oxide was calculated numerically by two RAS spectra taken at 70° and 80° incidence.⁴) In the case

of n layers or of thin layer, this method tends to make an error in calculation, however. In this study, in order to minimize the error, we used a model of the dielectric function following the Gauss model⁵⁾

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_{j=1}^{n} \frac{1}{\sqrt{2\pi} \sigma_{j}} \int_{0}^{\infty} exp\left(-\frac{(\omega' - \omega_{o}^{(j)})^{2}}{2\sigma_{j}^{2}}\right) \frac{\omega_{p}^{(j)^{2}}}{\omega'^{2} - \omega^{2} - i \omega \omega_{\tau}^{(j)}} d\omega'$$

$$= \varepsilon_{\infty} + \sum_{j=1}^{n} \frac{i \sqrt{\pi} \omega_{p}^{(j)^{2}}}{2\sqrt{2} a_{j} \sigma_{j}} \left[exp\left(-\frac{(a_{j} - \omega_{o}^{(j)})^{2}}{2\sigma_{j}^{2}}\right) erfc\left(\frac{(a_{j} - \omega_{o}^{(j)})}{i\sigma_{j}}\right) + exp\left(-\frac{(a_{j} + \omega_{o}^{(j)})^{2}}{2\sigma_{j}^{2}}\right) erfc\left(\frac{(a_{j} + \omega_{o}^{(j)})}{i\sigma_{j}}\right) \right]$$
(1)

where ω is frequency, ω_o is the resonance frequency, ω_p is the plasma frequency, ω_τ is the damping frequency, σ is the gaussian width, ε_{∞} is the high frequency dielectric constant, j is mode number and $a = \sqrt{\omega^2 - i \omega \omega_{\tau}^{(j)}}$, Im(a) > 0.

To calculate the reflectance, we apply the matrix formalism⁶), to the system air/pile of the layers/Si (Fig. 2a) and the reflectance R and transmittance T of this system are given by

$$\eta_{r} = \sqrt{\varepsilon_{r} - \varepsilon_{0} \sin^{2}\theta} / \varepsilon_{r}$$

$$\delta_{r} = 2 \pi d_{r} \sqrt{\varepsilon_{r} - \varepsilon_{0} \sin^{2}\theta}$$

$$M_{r} = \begin{pmatrix} \cos \delta_{r} & -i \sin \delta_{r} / \eta_{r} \\ -i \sin \delta_{r} \eta_{r} & \cos \delta_{r} \end{pmatrix}$$

$$\begin{pmatrix} B \\ C \end{pmatrix} = \prod_{r=1}^{n} M_{r} \begin{pmatrix} 1 \\ \eta_{r} \end{pmatrix}$$

$$R = \left| (\eta_{r} B - C) / (\eta_{r} B + C) \right|^{2}$$
(2)

$$T = 4 \eta_0 \eta_m / |\eta_r B + C|^2$$
(3)

where θ is incident angle and d is the layer thickness. r denote the layer number. In the case of 0.01 Ω cm substrate, we first calculated the actual dielectric function of silicon substrate since concentration of doped impurity is the order of 10^{18} cm⁻² and then the reflectance R_t calculated using eqn. (2). In the case of $1k\Omega$ cm substrate, we must consider the



Fig. 2 Schematic diagram of a) n layers stratified model for RAS spectra simulations nad b) internal multiple reflection of silicon substrate.

incoherent multiple internal reflections of substrate. The reflectance R_t is given by

$$R_{t} = R_{0} + T_{0}AR_{3}AT_{1} + \cdots$$
$$= R_{0} + \frac{T_{0}T_{1}A^{2}R_{3}}{1 - R_{1}A^{2}R_{3}}$$
(4)

where R and T are reflectance and transmittance for the single-reflection represented in eqns. 2 and 3. (Fig. 2b) We used literal value for the index of refraction for silicon.⁷) The single-transmitted attenuation A through substrate is obtained by⁸)

$$A^{2} = (r_{0} - r_{s}) / (r_{0} - r_{0}^{2} (2 - r_{s}))$$
(5)

where r_s is the actual absolute reflectance of bare silicon



Fig. 3 Actual RAS spectrum (dotted) of oxide film with thickness of 1.2 nm and calculated spectrum (solid) using the Gauss model and the n layers stratified model.



Fig. 4 Real (solid) and imaginary (dotted) part of the dielectric function of thickness-deconvolved oxide layer ranging in thickness from 1nm to 1.2 nm.



Fig. 5 RAS spectra of actual ((dotted), dotted line in Fig. 3) of oxide film of 1 nm and simulated (solid) of thickness-deconvolved oxide layer ranging in thickness from 1nm to 1.2 nm.



Fig. 6 Calculated RAS spectra of thickness-deconvolved oxide layer ranging in thickness from 1nm to 1.2 nm ((dotted), solid line in fig. 5) and from 14nm to 20 nm (solid).

substrate and r_0 is the calculated reflectance for the system air/Si.

The results of this analysis performed on the actual spectra of the oxide are shown in Fig. 3. For example, the dielectric function of the layer is plotted in Fig. 4.

4. DISCUSSION

We have compared the thickness-deconvolved data for the each layers. As shown in Fig. 5, the properties of a layer with thickness of 1nm (dotted) are much different from that of a layer ranging in thickness from 1nm to 1.2nm (solid). As shown in Fig. 6, the properties of the layer ranging in thickness from 1nm to 1.2nm (dotted, (solid in Fig.5)) roughly correspond that of a layer from 14nm to 20nm (solid). It is to note that the interfacial layer is very narrow and have been used to be overestimate.

As shown in Fig. 7, farther from the interface, the TO mode frequency for the layers ranging in thickness from 1nm to 80nm shifts slightly in wave number higher values. This tendency provide to be in agreement with the previous publications^{1,2,9}. It has been reported to provide more accurate fitting to the TO mode to divide resonance mode into two



Fig. 7 TO mode frequency for layers versus distance from the Si-SiO₂ interface.

parts¹⁰). There is a possibility of disagreement with TO frequency.

5. CONCLUSIONS

We have studied structural and optical properties of thermally grown oxide films. These properties were examined by incrementally etching back the SiO₂ films and performing IR-RAS measurement at each thickness. We have divided the oxide into incremental layers and calculated the dielectric function of the each layers. This study shows that interfacial layer with thickness below 1nm, whose structure differ from that of bulk oxide, place at the Si-SiO₂ interface and that frequency of TO mode shifts in wave number higher value farther from the interface.

References

- C. H. Björkman, J. T. Fitch, G. Lucovsky: Mat. Res. Soc. Symp. Proc. <u>146</u> (1989) 197.
- C. E. Shearon Jr., C. H. Björkman, G. Lucovsky: "The Physics and Chemistry of SiO₂ and the Si-SiO₂ Interface 2" edited by C. R. Helms, B. E. Deal (Plenum Press, New York, 1993) p. 99.
- K. Ishikawa, H. Ogawa, C. Inomata, S. Fujimura: Ext. Abst. Intern. Conf. Solid State Dev. Mater., Yokohama (1994) p. 850.
- K. Ishikawa, H. Ogawa, C. Inomata, S. Fujimura: Mat. Res. Soc. Symp. Proc. <u>318</u> (1993) 425.
- 5) R. Brendel, D. Bormann: J. Appl. Phys. 71, (1992) 1.
- H. A. Macleod: Thin Film Optical Filters 2nd ed. (Adam Hiiger, London 1986).
- D. F. Edwards: Handbook of Optical Constants of Solids ed. by E. D. Palik (1985) p. 547.
- S. Fujimura, K. Ishikawa, H. Mori: The Physics and Chemistry of SiO₂ and the Si-SiO₂ Interface 2 edited by C. R. Helms, B. E. Deal (Plenum Press, New York, 1993) p. 91.
- N. Yasuda, A. Toriumi: Ext. Abst. Intern. Conf. Solid State Dev. Mater., Yokohama (1994) p. 841.
- M. L. Naiman, C. T. Kirk, R. J. Aucoin, F. L. Terry, P. W. Wyatt: J. Electrochem. Soc. <u>131</u> (1984) 637.