

Structural Inhomogeneity of Thermally Grown SiO₂ Films Evaluated with Transmission Infrared Spectroscopy

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A depth profile of thermally grown silicon dioxide films is evaluated with chemical etching and infrared spectroscopy. A drastic decrease of the peak wave number and an increase of full width at half maximum of the infrared absorption spectra are observed as the SiO₂ film grown at 1000°C is etched back to less than 5 nm. This is a direct evidence for the existence of the "interfacial transition layer" as predicted by the bond strain gradient model. Different susceptibility of the interfacial and bulk oxides to thermal relaxation is considered to cause the interfacial transition layer. On the other hand, the inhomogeneity observed in the bulk oxide is not fully explained by the model which emphasizes inhomogeneous thermal annealing time after an oxide growth in the direction perpendicular to the Si/SiO₂ interface. It is demonstrated that the existence of an underlying oxide layer has a significant effect on strain relaxation of the SiO₂ overlayer.

1 Introduction

Recent advances in VLSI technology have led to demand for highly reliable gate oxide films for MOS devices. It is necessary to understand the quality of thermally grown SiO₂ films from both electrical and structural points of view. The structural properties of thermally grown SiO₂ films are, however, less well understood than the electric characteristics although there are pioneering works on structural properties using infrared spectroscopy [1-6]. The objectives of this study are to evaluate structural inhomogeneity of thermally grown SiO₂ films in the direction perpendicular to the Si/SiO₂ interface, and to investigate the origin of the inhomogeneity. A depth profile of thermally grown SiO₂ films is measured by using chemical etching and transmission infrared spectroscopy.

2 Experimental

The starting substrates were p-type 2-5 Ω cm (100) FZ wafers. Thermal oxidation was carried out in a dry O₂ ambient or N₂ diluted 3.3 % O₂ ambient at 800 °C and 1000 °C to thicknesses in the range of 94~146 nm. After the SiO₂ film on the back side of the wafer was etched off, the oxide film on the front side was chemically etched in an NH₄F/HF solution. Samples with different oxide thicknesses down to 1.3 nm were prepared.

Infrared absorption spectra were measured with FT-IR (Fourier Transform Infrared Spectroscopy) in a transmission configuration where the incident beam was normal to the samples. The peak wave num-

ber and full width at half maximum (FWHM) of the absorption band due to the Si-O-Si stretching vibration were evaluated as a function of the residual oxide thickness. Since the transmission infrared spectra of SiO₂ films can be measured in a wide range of thickness (1 nm ~ 1 μm), it is possible to systematically evaluate the depth profile of SiO₂ films from the interfacial oxide to the bulk oxide.

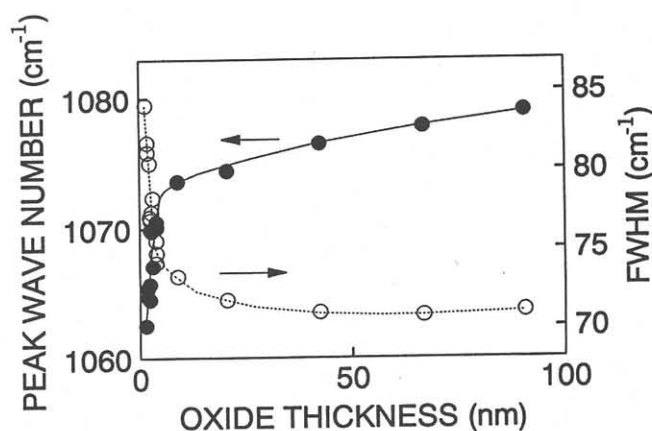


Figure 1: Peak wave number(●) and full width at half maximum (○) of the absorption band due to Si-O-Si stretching vibration vs. remaining oxide thickness for N₂ diluted 3.3 % O₂ oxidation at 1000 °C.

3 Results

Figure 1 shows the peak wave number and FWHM as a function of the residual oxide thickness for an SiO₂ film grown at 1000 °C in N₂ diluted 3.3 % O₂ ambient. The peak wave number drastically decreases as the oxide film is etched back to less than 5 nm. The FWHM is observed to increase in accordance with the decrease of the peak wave number.

Figure 2 shows the dependence of the peak wave number on oxidation conditions. The oxides grown at 1000 °C have a sharp fall-off of the peak wave number within 5 nm from the Si/SiO₂ interface, whereas the oxide grown at 800 °C does not show such a conspicuous fall-off near the interface. The peak wave number shows no dependence on the oxidation conditions for $t_{\text{ox}} < 2$ nm.

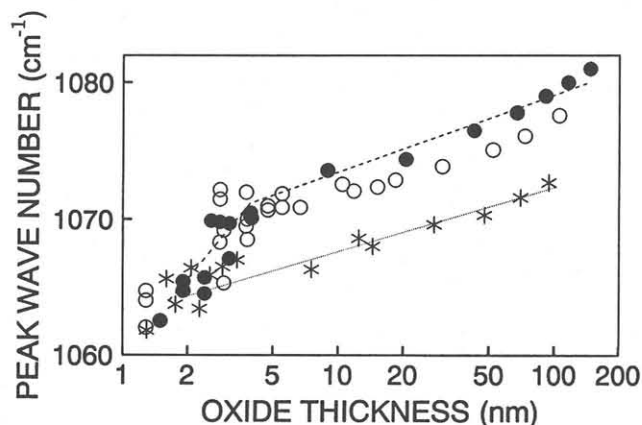


Figure 2: Peak wave number vs. residual oxide thickness for various oxidation conditions. ●: N₂ diluted 3.3 % O₂ oxidation at 1000 °C, ○: dry O₂ oxidation at 1000 °C, and *: dry O₂ oxidation at 800 °C.

4 Discussion

4.1 Interfacial Oxide Region

The behaviors of the peak wave number and FWHM in the interfacial oxide region ($t_{\text{ox}} < 5$ nm) as shown in Fig. 1 indicate the decrease of the average Si-O-Si bond angle [3] and the broadening of the bond angle distribution, respectively. This means that the bond strain increases as the Si/SiO₂ interface approaches. The result provides a direct evidence for the bond-strain-gradient (BSG) model [7] which was inferred from XPS results [8]. A similar red-shift in the infrared absorption peak due to LO phonon mode has recently been reported by Yamazaki *et al.*, using FT-IR-ATR measurements [9]. Our result shows a clear downward shift of the absorption peak due to TO phonon mode, with a simple transmission FT-IR method.

The drastic decrease of the peak wave number in the interfacial oxide region is, however, observed only for the SiO₂ films grown at a high temperature

(1000 °C), as shown in Fig. 2. This result is considered to be due to different susceptibility of the interfacial and bulk oxides to strain relaxation. The interfacial oxide is prevented from strain relaxation in a wide range of process temperature because of the constraints on atomic bonding configuration originating from the Si/SiO₂ interface [4,5]. The bulk oxide goes through thermal relaxation at a high temperature, typically above 950 °C [10]. Therefore, the SiO₂ films grown at 1000 °C have a strained interfacial oxide and a relaxed bulk oxide, thereby producing the "interfacial transition layer" with a large strain gradient. On the other hand, the SiO₂ films grown at 800 °C have strained layers throughout the oxide, thus showing little distinction between the interfacial oxide and the bulk oxide.

4.2 Bulk Oxide Region

4.2.1 Inhomogeneous thermal history within SiO₂ film

There is a continuous increase of the peak wave number extending into the bulk oxide region (See Fig. 2). This increase has been attributed to inhomogeneous thermal annealing time after an oxide growth [4]. It is deduced from the model that the peak wave number should be equal for homogeneous thermal annealing, irrespective of the SiO₂ film thickness. In order to examine this point, the following experiment was carried out. The SiO₂ films were grown at 800 °C to various thicknesses. They were subsequently annealed together in Ar ambient at 1000 °C. The thermal budget during these processes is considered to be equivalent for all the SiO₂ films because the annealing at 1000 °C is the dominant thermal process. As shown in Fig. 3, the peak wave number of the annealed oxides increases as the oxide thickness becomes larger. This result is not consistent with the implication of the inhomogeneous annealing model [4].

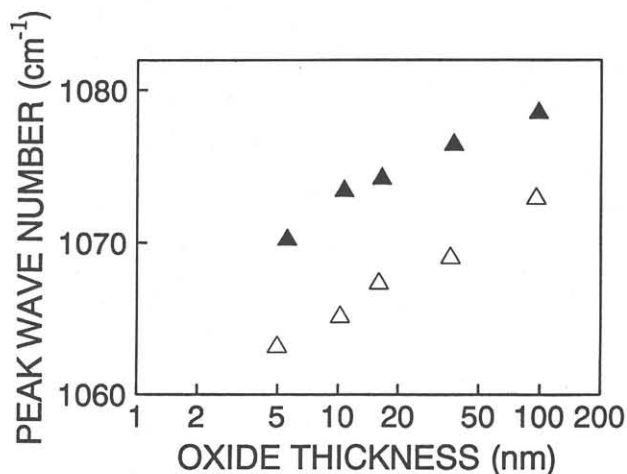


Figure 3: Change of peak wave number due to annealing. Thermally grown oxides in dry O₂ at 800 °C (△) were subsequently annealed in Ar at 1000 °C for 23 hours (▲).

4.2.2 Role of underlying oxide layer in strain relaxation

In order to clarify the origin of the inhomogeneity of the bulk oxide, an experiment using a two-step oxidation was carried out. Figure 4 shows the experimental setup. The first oxidation was carried out at 1000 °C, followed by the second oxidation at 800 °C (sample A). To confirm the negligible thermal budget to the first oxide layer during the second oxidation, the equivalent thermal budget as the sample A was applied to sample B by annealing in an inert gas. The peak wave number of the sample B did not change during the annealing (See the row of sample B in Table 1). Therefore, no thermal strain relaxation of the first oxide layer is considered to take place during the second oxidation of the sample A.

The peak wave number of the first oxide layer in the sample A was evaluated before and after the second oxidation (See the row of sample A in Table 1). The evaluation after the second oxidation was carried out by making a subtraction between the absorbance spectra of the sample A with and without the first oxide layer. The result in Table 1 shows a significant increase of the peak wave number for the first oxide layer of the sample A. Since the strain relaxation due to the thermal budget is negligible, the increase of the peak wave number is considered to originate from the growth of the second oxide layer.

The result described above indicates that the strain relaxation due to the underlying oxide layer is one of the main factors contributing to the inhomogeneity of the bulk oxide.

Table 1: Peak wave number of the first oxide layer grown at 1000 °C (shaded area in Fig. 4).

	As grown at 1000 °C	After 800 °C processes
Sample A	1074.3 cm ⁻¹	1080.3 cm ⁻¹
Sample B	1074.1 cm ⁻¹	1074.1 cm ⁻¹

5 Conclusions

- (1) The peak wave number shifts downward and FWHM broadens as SiO₂ films thermally grown at 1000°C are etched back to less than 5 nm. This is a direct evidence for the existence of “interfacial transition layer,” as predicted by the bond strain gradient model.
- (2) Different susceptibility of the interfacial oxide and the bulk oxide to thermal relaxation is considered to bring about the transition layer.
- (3) The inhomogeneity of the bulk oxide is not fully explained by considering only the inhomogeneous thermal history within the SiO₂ film. It was demonstrated that the growth of an underlying oxide layer has a significant effect on strain relaxation of the SiO₂ overlayer.

Acknowledgments

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References

[1] I. W. Boyd and J. I. B. Wilson, Appl. Phys. Lett. **50**, 320 (1987).
[2] I. W. Boyd and J. I. B. Wilson, J. Appl. Phys. **62**, 3195 (1987).
[3] G. Lucovsky, M. J. Manitini, J. K. Srivastava, and E. A. Irene, J. Vac. Sci. Technol. **B5**, 530 (1987).
[4] J. T. Fitch, C. H. Bjorkman, G. Lucovsky, F. H. Pollak and X. Yin, J. Vac. Sci. Technol. **B7**, 775 (1989).
[5] J. T. Fitch, G. Lucovsky, E. Kobeda and E. A. Irene, J. Vac. Sci. Technol. **B7**, 153 (1989).
[6] C. H. Bjorkman, J. T. Fitch, and G. Lucovsky, Appl. Phys. Lett. **56**, 1983 (1990).
[7] F. J. Grunthaner, P. J. Grunthaner, and J. Maserjian, IEEE Trans. Nucl. Sci. **NS-29**, 1462 (1982).
[8] F. J. Grunthaner and J. Maserjian, in *The Physics of SiO₂ and Its Interfaces*, edited by S. T. Pantelides (Pergamon Press, New York, 1978), pp.389-95.
[9] T. Yamazaki, S. Miyazaki, C. H. Bjorkman, M. Fukuda and M. Hirose, Mat. Res. Soc. Symposium Proc. (1994), to be published.
[10] E. A. Irene, E. Tierney, and J. Angilello, J. Electrochem. Soc. **129**, 2594 (1982).

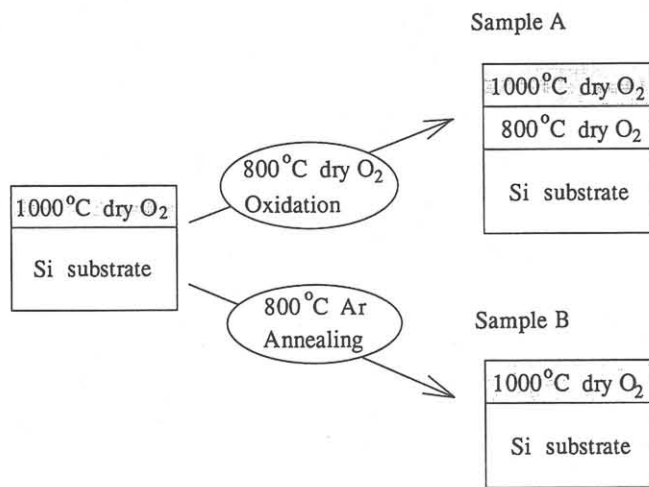


Figure 4: Schematic diagram of two-step oxidation experiment. Thermal oxide was grown in dry O₂ ambient at 1000°C to a thickness of 54 nm. Subsequent oxidation was carried out at 800°C for 67 hours, increasing the oxide thickness by 82 nm (sample A). The equivalent thermal budget was applied to sample B through annealing in Ar at 800 °C for 67 hours.