Heat treatment in high pressure H₂O vapor used for improvement of Si—O bonding network near SiO₂/Si interface

Toshiyuki Sameshima*, Keiji Sakamoto, Mitsuru Satoh
Tokyo A&T University, 22416, Nakamachi, Koganei, Tokyo 1848588, Japan

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Abstract

Heat treatment with H₂O vapor at a pressure of 5.4 × 10⁶ Pa at 270°C was applied to annealing thin thermally grown SiO₂ and plasma oxidized layers to improve the Si—O bonding network near the SiO₂/Si interfaces. The heat treatment increased the Si—O—Si average bonding angle from 140.7 ± 0.3° to 142.5 ± 0.3°C near the interfaces for thermally grown SiO₂ formed in dry oxygen at 1000°C and reduced the distribution of the angle. The increase of the Si—O—Si average bonding angle from 140.7 ± 0.3° to 143.8 ± 0.3° and the narrowing of the angle distribution were also observed for the 3-nm-thick plasma oxidized films. These results show that strain relaxation at the SiO₂/Si interfaces was achieved at low temperature by the heat treatment. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Improvement of properties of SiO₂ and SiO₂/Si interfaces at a low temperature is important for device fabrication, for example, as the gate insulator for thin film transistors [1,2], the surface passivation layer for solar cells and the intermediate layer for integrated circuits. Thermally grown SiO₂ is a stable and reliable material. It has been known however that there is structural inhomogeneity in depth direction for thermally grown SiO₂ formed in dry O₂ [3,4]. The average bonding angle of Si—O—Si is low compared with that of bulk SiO₂ and there is broadening of the angle distribution near the SiO₂/Si interface associated with high bonding strain. This means the Si—O bonding networks near the interface is not in the complete thermally relaxed state [5]. There can be defects associated with the weak bond network between silicon and oxygen atoms. Plasma oxidation is attractive for formation of thin SiO₂ layer on the silicon surface at a low temperature [6]. SiO₂ layers are formed with oxygen atoms incorporating into silicon with high ion energies. It is far from a thermal equilibrium process. There can be a high strain and defects at SiO₂/Si interfaces.

This paper reports improvement in Si—O bonding networks of thermally grown SiO₂ layers near SiO₂/Si interfaces and thin plasma oxidized SiO₂ layers by the heat treatment with high pressure H₂O vapor at a temperature of 270°C. Changes in optical absorption spectra associated with SiO antisymmetric stretching vibration are presented. The Si—O—Si bonding angle and strain relaxation of these SiO₂ layers near the SiO₂/Si interfaces are discussed.

2. Experimental

Samples of thermally grown SiO₂ were fabricated by two fabrication steps. (1) Sample 1: at first, thermally grown SiO₂ layers with a thickness of 96 nm were formed at 1000°C in dry O₂ using p-type silicon substrates with a resistivity of 0.1 Ω m. The SiO₂ layers were etched to different thicknesses between 9 and 96 nm using an etching solution of 1.5% HF diluted with pure water. The samples were placed into a pressure-proof stainless-steel chamber with a volume of 60 cm³ using a metal seal. Water (2 cm³) was also placed in the chamber. The chamber was then placed on a resistive heater for heating the sample at 270°C for 3 h with the H₂O as well as air inside the chamber. H₂O was evaporated by heating and the pressure in the chamber increased up to 5.4 × 10⁶ Pa (saturation pressure at 270°C). These annealing conditions were determined in a previous report on the heat treatment with a high pressure H₂O vapor of SiO₂ films formed by plasma enhanced chemical vapor deposition (PECVD) [7]. (2) Sample 2: thermally grown...
SiO$_2$ layers with a thickness of 96 nm were also formed at 1000°C in dry O$_2$ using p-type silicon substrates with a resistivity of 0.1 Ω m. The SiO$_2$ layers were then heated with the high pressure H$_2$O vapor. The annealing condition was same in the case of sample 1. After annealing, the SiO$_2$ layers were etched to different thicknesses between 6 and 90 nm. Optical absorption spectra in the infrared range of the SiO$_2$ films were measured using a Fourier transform infrared (FTIR) spectrometer.

Plasma oxidized SiO$_2$ layers were formed on p-type silicon substrates with resistivity of 0.1 Ω m by N$_2$O plasma treatment. The silicon substrate were put in a chamber for the plasma treatment and placed on a resistive heater plate whose surface made of a stainless steel was biased at zero voltage. After the evacuation of the chamber, the samples were heated at 300°C. N$_2$O gas was introduced with flow rate of 50 sccm and a resulting pressure of 1.3 × 10$^2$ Pa. N$_2$O plasma was produced by applying radio frequency (13.56 MHz) voltage to an electrode facing the sample 0.04 m apart with a power of 50 W for 1 h. Plasma oxidized SiO$_2$ layers with a thickness of 3 nm were formed. The film thickness was determined by measurement of the intensity of the optical absorption band caused by SiO antisymmetric stretching vibration. The sampler were annealed at 270°C for 3 h with 5.4 × 10$^6$ Pa H$_2$O vapor.

3. Results and discussion

Fig. 1 shows the peak wave number of the absorption band caused by the SiO antisymmetric stretching vibration mode (a) and the full width at half-maximum (FWHM) of the absorption band (b) as functions of the SiO$_2$ film thickness for the thermally grown SiO$_2$ samples with different thicknesses before and after the heat treatment described as for sample 1. Before the heat treatment (as-grown SiO$_2$), the peak wave number was reduced from 1073 to 1068 cm$^{-1}$ as the film thickness decreased from 16 to 9 nm, while the peak wave number almost leveled off for the film thickness between 96 and 16 nm. On the other hand, the FWHM increased from 79 to 88 cm$^{-1}$ as the film thickness decreased from 16 to 9 nm. These results mean that there is an inhomogeniety of the Si–O bonding network near the SiO$_2$/Si interfaces because of bonding strain [4]. The film thickness was slightly reduced because of etching SiO$_2$ with high pressure H$_2$O vapor [7]. The heat treatment caused a change in the spectra of the SiO absorption band. There was no decrease in the peak wave number for the film thickness between 6 and 91 nm, as shown in Fig. 1a. Moreover, after the heat treatment, the FWHM of the Si–O absorption band was slightly reduced from 78 to 75 cm$^{-1}$ by the heat treat-
The relation between the SiO absorption band and the peak wavenumber of SiO antisymmetric stretching vibration modes revealed that the heat treatment with high pressure H₂O vapor at 270°C increased the peak wavenumber of 1078 cm⁻¹ for 4 and 10-nm thick SiO₂ films, respectively, as shown in Fig. 1a. This resulted in the fact that the average bonding angle was increased to 142.3 ± 0.3° and 142.5 ± 0.3°, respectively, which were almost the same as that of the bulk SiO₂ region (16°–96 nm thickness). The thickness averaged strain ε_n in the oxide film is given as ε_n = 1 − υ/ν_1, where ν_1 = 1078.5 cm⁻¹ according to Fitch et al.’s report [8].

The heat treatment with the high pressure H₂O vapor at 270°C reduced the thickness averaged strain 4 nm near the SiO₂/Si interfaces from 9.7 ± 1.0 × 10⁻³ (initial) to 4.2 ± 1.0 × 10⁻³ which was almost the same as the thickness averaged strain in thick SiO₂ films (16°–96 nm thickness) of 5.1 ± 1.0 × 10⁻³. Although Yasuda et al. reported the reduction of the bonding strain near the SiO₂/Si interfaces by heat treatment at 800°C in O₂ atmosphere [3], the strain relaxation was achieved at the much lower temperature of 270°C by the present heat treatment. Moreover, the heat treatment of thin oxidized layers resulted in narrowing of the band width of the SiO absorption, as shown in Fig. 1, which means the homogenization of the Si–O–Si bonding angle distribution. Although, the mechanism of the strain relaxation by the low temperature treatment is not clear yet, the authors believe that hydrolysis reaction occurs between H₂O and SiO₂ under the high pressure H₂O, Si–O bonds, especially weak ones with a low bonding angle would be broken by H₂O incorporation into the film, resulting in Si–O–H bond formation [9]. Every two sets of Si–O–H bonds would be then combined and H₂O is released. More stable Si–O bonds with a larger bonding angle would be finally formed during the heat treatment.

The strain relaxation was also achieved for the case of heat treatment of 96-nm thick SiO₂, as shown in Fig. 2a. However, FWHM of the SiO absorption band slightly increased near the interface shown in Fig. 2b, although the degree of increase in FWHM was reduced compared with that of as-grown SiO₂, as shown in Fig. 1b. Homogenization of the Si–O–Si bonding angle distribution was not achieved compared with the case of the heat treatment of the thin SiO₂ sample, as shown in Fig. 1b. For the thick SiO₂ case, the heat treatment for 3 h would not result in enough H₂O reaching the SiO₂/Si interface by diffusing to cause the oxidation reaction with H₂O in the present conditions.

The change in optical absorption band shown in Fig. 3 revealed that the heat treatment resulted in a change in the bonding network of Si–O–Si formed by plasma oxidation with N₂O gases; the average bonding angle increased from 138.4 ± 0.3° to 143.8 ± 0.3° and the distribution of the angle was reduced. The present heat method will be useful for improvement of the properties of thin oxide films at low temperature.

4. Summary

Thermally grown SiO₂ and plasma oxidized SiO₂ layers
were annealed with high pressure H\textsubscript{2}O vapor, \(5.4 \times 10^6\) Pa, at 270\(^\circ\)C for 3 h using a pressure proof chamber. The thermally grown SiO\textsubscript{2} films had a low average bonding angle of Si–O–Si, 140.7 \(\pm\) 0.3\(^\circ\), with a broad bonding angle distribution near the SiO\textsubscript{2}/Si interfaces for the as-grown case. The heat treatment made the average bonding angle near the interface increase to 142.5 \(\pm\) 0.3\(^\circ\), which was almost the same as that of the bulk SiO\textsubscript{2}. The distribution of the bonding angle was reduced by the heat treatment. These results mean that the reaction of SiO\textsubscript{2} with H\textsubscript{2}O vapor under high pressure results in strain relaxation at the SiO\textsubscript{2}/Si interface at 270\(^\circ\)C. The thickness averaged strain 4 nm near the SiO\textsubscript{2}/Si interfaces was reduced from \(9.7 \pm 1.0 \times 10^{-3}\) (as-grown) to \(4.2 \pm 1.0 \times 10^{-3}\), which was almost the same as the thickness averaged strain in thick SiO\textsubscript{2} films of \(5.1 \pm 1.0 \times 10^{-3}\). The strain relaxation at the SiO\textsubscript{2}/Si interface at low temperature probably resulted from the hydrolysis reaction between H\textsubscript{2}O and SiO\textsubscript{2} under high pressure H\textsubscript{2}O.

The increase of the Si–O–Si average bonding angle from 138.4 \(\pm\) 0.3\(^\circ\) to 143.8 \(\pm\) 0.3\(^\circ\) and the narrowing of the angle distribution were also observed in the case of the heat treatment of the 3-nm thick plasma oxidized SiO\textsubscript{2} layers.

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References