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Heat treatment in high pressure H_2O vapor used for improvement of Si—O bonding network near SiO_2/Si interface

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Abstract

Heat treatment with H_2O vapor at a pressure of 5.4×10^6 Pa at 270°C was applied to annealing thin thermally grown SiO_2 and plasma oxidized layers to improve the Si—O bonding network near the SiO_2/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 SiO_2 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 SiO_2/Si interfaces was achieved at low temperature by the heat treatment.

Keywords: Heat treatment; Interfaces; Silicon oxide; Water

1. Introduction

Improvement of properties of SiO_2 and SiO_2/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 SiO_2 is a stable and reliable material. It has been known however that there is structural inhomogeneity in depth direction for thermally grown SiO_2 formed in dry O_2 [3,4]. The average bonding angle of Si—O—Si is low compared with that of bulk SiO_2 and there is broadening of the angle distribution near the SiO_2/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 SiO_2 layer on the silicon surface at a low temperature [6]. SiO_2 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 SiO_2/Si interfaces.

This paper reports improvement in Si—O bonding networks of thermally grown SiO_2 layers near SiO_2/Si interfaces and thin plasma oxidized SiO_2 layers by the heat treatment with high pressure H_2O 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 SiO_2 layers near the SiO_2/Si interfaces are discussed.

2. Experimental

Samples of thermally grown SiO_2 were fabricated by two fabrication steps. (1) Sample 1: at first, thermally grown SiO_2 layers with a thickness of 96 nm were 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 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 cm^3 using a metal seal. Water (2 cm^3) 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 H_2O as well as air inside the chamber. H_2O was evaporated by heating and the pressure in the chamber increased up to 5.4×10^6 Pa (saturation pressure at 270°C). These annealing conditions were determined in a previous report on the heat treatment with a high pressure H_2O vapor of SiO_2 films formed by plasma enhanced chemical vapor deposition (PECVD) [7]. (2) Sample 2: thermally grown

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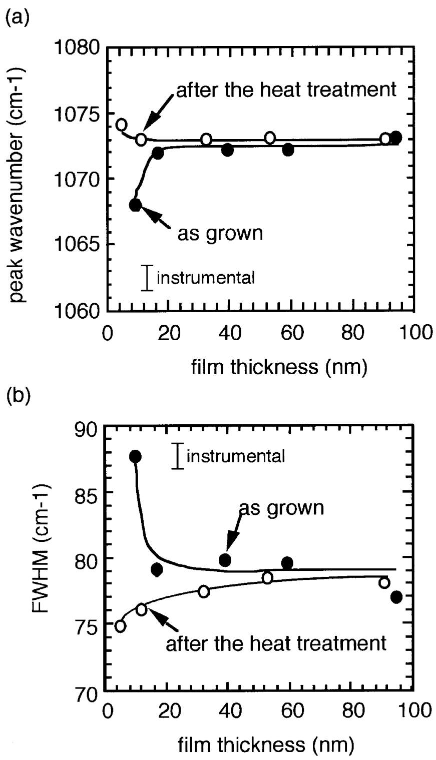

Fig. 1. Peak wavenumber of the absorption band caused by the SiO antisymmetric stretching vibration mode (a) and FWHM of the absorption band (b) as functions of the SiO_2 film thickness for the thermally grown SiO_2 samples with different thicknesses before and after the heat treatment at 270°C with 5.4×10^6Pa H_2O vapor for 3 h.

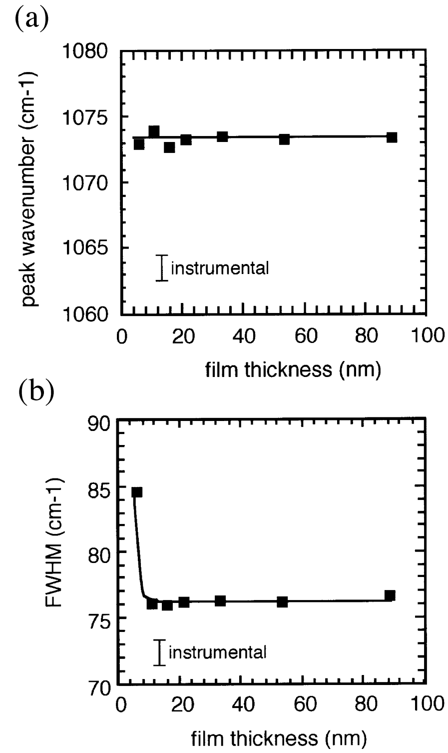

Fig. 2. Peak wavenumber of the absorption band caused by the SiO antisymmetric stretching vibration mode (a) and FWHM of the absorption band (b) as functions of the SiO_2 film thickness for the thermally grown SiO_2 samples. The SiO_2 layers were etched to different thicknesses after the heat treatment at 270°C with 5.4×10^6 Pa H_2O vapor for 3 h of 96-nm thick SiO_2 layers.

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_2O 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_2O 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_2O gas was introduced with flow rate of 50 sccm and a resulting pressure of 1.3×10^2 Pa. N_2O 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_2O 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 thickness 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_2O 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-

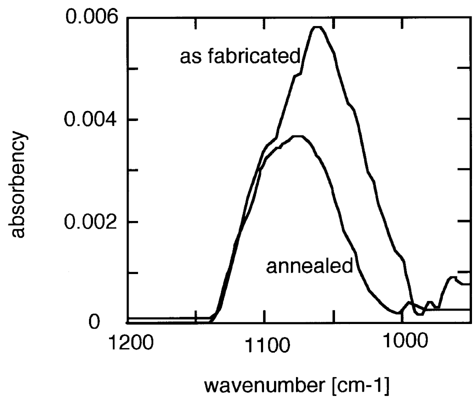

Fig. 3. Changes in the absorption spectra caused by the SiO antisymmetric stretching vibration mode by the heat treatment at 270°C with 5.4×10^6 Pa H_2O vapor for 3 h for SiO_2 layers formed using N_2O plasma at 300°C for 1 h with a radio frequency power of 50 W and a gas pressure of 1 Torr.

ment as the film thickness decreased from 10 to 6 nm in contrast to the case prior to the treatment.

Fig. 2 shows the peak wave number of the absorption band caused by the SiO antisymmetric stretching vibration mode (a) and FWHM of the absorption band as functions of the film thickness of the thermally grown SiO_2 when the SiO_2 films were etched to different thicknesses after the heat treatment of 96-nm thick SiO_2 films (sample 2). There was no decrease in the peak wave number in the film thickness between 6 and 90 nm, as shown in Fig. 2a. On the other hand. the FWHM of the SiO absorption band increased from 76 to 84 cm^{-1} as the film thickness decreased from 12 to 6 nm.

The 3-nm thick SiO_2 layers formed by N_2O plasma oxidation gave a broad SiO absorption band with a peak wave number of 1060 cm^{-1} and FWHM of 86 cm^{-1} as shown in Fig. 3. The heat treatment with 5.4×10^6 Pa H_2O vapor at 270°C for 3 h increased the peak wave number of the SiO absorption band to 1078 cm^{-1} and reduced the FWHM to 73 cm^{-1}. No SiOH absorption band was detected for samples of thermally grown SiO_2 and plasma oxidized SiO_2 before and after the heat treatment.

Measurement of the optical absorption band caused by SiO antisymmetric stretching vibration modes revealed that the heat treatment with high pressure H_2O vapor at 270°C improved the SiO bonding network near the SiO_2/Si interfaces. From the peak wave number of SiO absorption band, the average bonding angle of Si—O—Si was estimated using the central force model [5]. The relation between the SiO bonding stretching wavenumber ν and the average bonding angle θ is given as, $\nu = \nu_0 \sin\theta$, where $\nu_0 = 1134$ cm^{-1}. A peak wavenumber of 1068 cm^{-1} of the SiO absorption band gave an average bonding angle of $140.7 \pm 0.3°$ for 8-nm thick-thermally grown SiO_2 before the heat treatment, shown in Fig. 1a. The error of the average bonding angle is simply derived from the measurement resolution of the peak wavenumber, ± 1 cm^{-1}. The heat treatment with the high pressure H_2O vapor increased the peak wave number of SiO absorption band to 1073 and 1074 cm^{-1} for 4 and 10-nm thick SiO_2 films, respectively, as shown in Fig. 1a. This resulted in the fact that the average bonding angle was increased to $142.3 \pm 0.3°$ and $142.5 \pm 0.3°$, respectively. which were almost the same as that of the bulk SiO_2 region (16~96 nm thickness). The thickness averaged strain ε_{av} in the oxide film is given as $\varepsilon_{av} = 1 - \nu/\nu_1$, where $\nu_1 = 1078.5$ cm^{-1} according to Fitch et al.'s report [8]. The heat treatment with the high pressure H_2O vapor at 270°C reduced the thickness averaged strain 4 nm near the SiO_2/Si interfaces from $9.7 \pm 1.0 \times 10^{-3}$ (initial) to $4.2 \pm 1.0 \times 10^{-3}$ which was almost the same as the thickness averaged strain in thick SiO_2 films (16~96 nm thickness) of $5.1 \pm 1.0 \times 10^{-3}$. Although Yasuda et al. reported the reduction of the bonding strain near the SiO_2/Si interfaces by heat treatment at 800°C in O_2 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 H_2O and SiO_2 under the high pressure H_2O. Si—O bonds, especially weak ones with a low bonding angle would be broken by H_2O 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 H_2O 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 SiO_2, 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 SiO_2, 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 SiO_2 sample, as shown in Fig. 1b. For the thick SiO_2 case, the heat treatment for 3 h would not result in enough H_2O reaching the SiO_2/Si interface by diffusing to cause the oxidation reaction with H_2O 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 N_2O gases; the average bonding angle increased from $138.4 \pm 0.3°$ to $143.8 \pm 0.3°$ 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 SiO_2 and plasma oxidized SiO_2 layers were annealed with high pressure H_2O vapor, 5.4×10^6 Pa, at 270°C for 3 h using a pressure proof chamber. The thermally grown SiO_2 films had a low average bonding angle of Si—O—Si, 140.7 ± 0.3°, with a broad bonding angle distribution near the SiO_2/Si interfaces for the as-grown case. The heat treatment made the average bonding angle near the interface increase to 142.5 ± 0.3°, which was almost the same as that of the bulk SiO_2. The distribution of the bonding angle was reduced by the heat treatment. These results mean that the reaction of SiO_2 with H_2O vapor under high pressure results in strain relaxation at the SiO_2/Si interface at 270°C. The thickness averaged strain 4 nm near the SiO_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_2 films of $5.1 \pm 1.0 \times 10^{-3}$. The strain relaxation at the SiO_2/Si interface at low temperature probably resulted from the hydrolysis reaction between H_2O and SiO_2 under high pressure H_2O.

The increase of the Si—O—Si average bonding angle from 138.4 ± 0.3° to 143.8 ± 0.3° 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_2 layers

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