Polysilazane Precursor Used for Formation of Oxidized Insulator

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Abstract. We report SiO_2 film formation using Polysilazane precursor treated with remote oxygen plasma and high pressure H_2O vapor heating. Polysilazane precursor films with a thickness of 130 nm were formed on silicon substrates by spin coating method. They were annealed at 350℃ in remote oxygen plasma at a pressure of $2.0\text{x}10^{-2}$ Pa and a $13.56\text{x}10^{6}$ Hz radio frequency power of 300 W for 3h followed by $1.3\text{x}10^{6}$ Pa-H_2O vapor at 260℃ for 3h. Polysilazane films were entirely oxidized by high pressure H_2O vapor heat treatment, and the density of Si-H bonding in Polysilazane films was effectively removed by the combination of high pressure H_2O vapor heat treatment with remote oxygen plasma treatment. While MOS capacitors fabricated only by high pressure H_2O vapor heat treatment had a high fixed oxide charge density of 2.3×10^{12} cm^{-2} and a density of interface trap of 5.4×10^{11} $cm^{-2}eV^{-1}$, remote oxygen plasma treatment followed by high pressure H_2O vapor heat treatment was reduce them to 1.6×10^{11} cm^{-2}, 4.6×10^{10} $cm^{-2}eV^{-1}$, respectively. The combination of high pressure H_2O vapor heat treatment with remote oxygen plasma treatment was effective to form SiO_2 film using Polysilazane precursor.

Introduction

The formation of good quality of SiO_2 films and SiO_2/Si interface at low temperatures is important for device fabrication. We have reported that improvement in SiO_2 film and SiO_2/Si interface was achieved by high pressure H_2O vapor heat treatment [1-2]. Polysilazane precursor have a possibility of gate insulator formation at low temperature because SiO_2 film was fabricated by annealing at 450℃ in air. In this study, we report SiO_2 films formation using Polysilazane precursor treated with remote oxygen plasma and high pressure H_2O vapor heating. Structural properties of SiO_2 films are reported with analysis using Fourier transform infrared spectrometry (FTIR). Electrical properties of SiO_2 films and SiO_2/Si interface are also reported using C-V measurement. We show a possibility of SiO_2 films with good electrical properties for gate insulator using the present method.

Experimental

SiO_2 films with a thickness of 130 nm were formed by spin coating method on P-type single crystalline silicon substrates. Remote oxygen plasma treatment was carried out with a flow of gases of Oxygen (O_2) 2 sccm at a pressure of $1.0\text{x}10^{-2}$ Pa and 13.56 MHz radio frequency (RF) power of 300W for 3 h with the temperature of 130℃, 260℃, 350℃, respectively. The samples were subsequently heated at 260℃ with $1.3x10^6$ Pa-H_2O vapor for 3 h. Optical absorption spectra of SiO_2 films were measured using Fourier transform infrared spectrometry (FTIR) to investigate absorption ratio of Si-O, Si-H and Si-O-H bondings. In order to investigate the electrical properties, Metal-Oxide-Semiconductor (MOS) capacitors were fabricated. Aluminum electrodes were formed on the SiO_2 films with the area of 0.01 cm^2 just after remote oxygen plasma treatment. The sample was subsequently heated at 260℃ with $1.3x10^6$ Pa-H_2O vapor for 3h. Capacitance responses at a frequency of 1 MHz were measured.

Results and Discussion

Figure 1 shows optical absorption spectra measured for samples of Polysilazane precursor film as-spin coated (1), remote oxygen plasma treatment at 350℃ (2), remote oxygen plasma treatment at 350℃ followed by high pressure H_2O vapor heat treatment (3). We focused on optical absorption peak corresponding to the Si-O vibration mode around 1080 cm^{-1}, the Si-H vibration mode around 2300 cm^{-1} and the Si-O-H vibration mode around 3500 cm^{-1}. The arrows indicate those wave numbers. Optical absorption peaks corresponding to the Si-N vibration mode around 875 cm^{-1} and the N-H vibration mode around 1175 cm^{-1} were observed in the spectrum of as-spin coated [10]. These are the composition of Polysilazane precursor. The intensities of Si-N and N-H peak were reduced by remote oxygen plasma treatment. On the other hand, the intensity of Si-O peak was slightly increased by remote oxygen plasma treatment. This means that Polysilazane precursor films were slightly oxidized by remote oxygen plasma treatment. The intensities of Si-N and N-H peak were completely reduced, and the intensity of Si-O peak was markedly increased by high pressure H_2O vapor heat treatment after remote oxygen plasma treatment and its line shape became similar to that of thermally grown SiO_2 films. These results indicate that oxidization of Polysilazane precursor films were effectively achieved by high pressure H_2O vapor heat treatment. The intensity of Si-H peak was reduced by remote oxygen plasma treatment, and it was completely reduced by high pressure H_2O vapor heat treatment. Hydrogen was effectively removed during those oxidation processes. Si-O-H peak was slightly increased by high pressure H_2O vapor heat treatment. We estimated total absorbance of optical absorption peaks by integrating from 900 to 1300cm^{-1} corresponding to Si-O bonding, from 2100 to 2500cm^{-1} corresponding to Si-H bonding and from 2900 to 3900cm^{-1} corresponding to Si-O-H bonding.

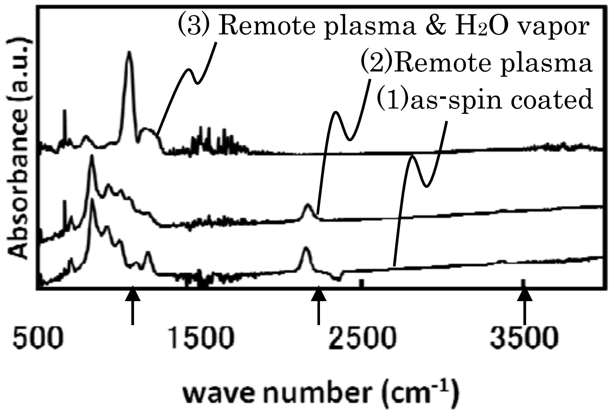

Fig.1: optical absorption spectra measured by FTIR for as-spin coated (1), remote oxygen plasma treatment at 350℃ with the RF power of 300 W for 3 h (2), remote oxygen plasma treatment at 350℃ with the RF power of 300 W for 3 h followed by $1.3x10^6$Pa-H_2O vapor heat treatment at 260℃ for 3h (3). The arrows indicate optical absorption peak corresponding to Si-O (1080cm^{-1}), Si-H (2100cm^{-1}) and Si-O-H (3500cm^{-1}) vibration mode.

Figure 2 shows total absorbance of optical absorption peaks corresponding to Si-O bonding (a), Si-H bonding (b) and Si-O-H bonding (c) as a function of heating temperature for remote oxygen plasma treatment. Total absorbance of optical absorption peaks corresponding to Si-O bondings treated by remote oxygen plasma treatment at 350℃ followed by high pressure H_2O vapor heat treatment was determined to be 100. As-spin coated sample had an intensity of Si-O peak of 23 as shown in Figure.2 (a). Polysilazane intrinsically has no oxygen atoms. There is a possibility of that the total absorbance included optical absorption due to Si-N bonding. The total absorbance of optical absorption peaks corresponding to Si-O bonding was increased to 44.5 by remote oxygen plasma treatment at 350℃. This means that oxygen radicals oxidized Polysilazane precursor. Moreover, it was markedly increased to 100 by remote oxygen plasma treatment 350 ℃ followed by high pressure H_2O vapor heat treatment. This result indicates that high pressure H_2O vapor heat treatment entirely oxidized Polysilazane precursor. As-spin coated sample had a total absorbance of optical absorption peaks corresponding to Si-H bonding of 22 as shown in Fig.2 (b). It was reduced to 9.4 by remote oxygen plasma treatment at 350℃, and markedly reduced to 0.07 by remote oxygen plasma treatment at 350℃ followed by high pressure H_2O vapor heat treatment. These results indicate that the Si-H bondings in Polysilazane precursor was effectively removed by the combination of high pressure H_2O vapor heat treatment with remote oxygen plasma treatment. As-spin coated sample had a total absorbance of optical absorption peaks corresponding to Si-O-H bonding of 2.8 as shown in Fig.2 (c). There was no oxygen atom in Polysilazane precursor and the total absorbance of optical absorption peaks corresponding to Si-O-H bonding was small. It was reduced to 1.1 by remote oxygen plasma treatment at 350℃. This result indicates that remote oxygen plasma treatment did not induce the formation of Si-O-H bonding. As shown in Figure 2 (b) and (c), remote oxygen plasma treatment effectively removed the Si-H bondings and did not form the Si-O-H bonding. On the other hand, the total absorbance of optical absorption peaks corresponding to Si-O-H bonding was increased to 3.7 by remote oxygen plasma treatment at 350℃ followed by high pressure H_2O vapor heat treatment. This result indicates that high pressure H_2O vapor heat treatment induced hydroxyl to form the Si-O-H bondings in Polysilazane precursor.

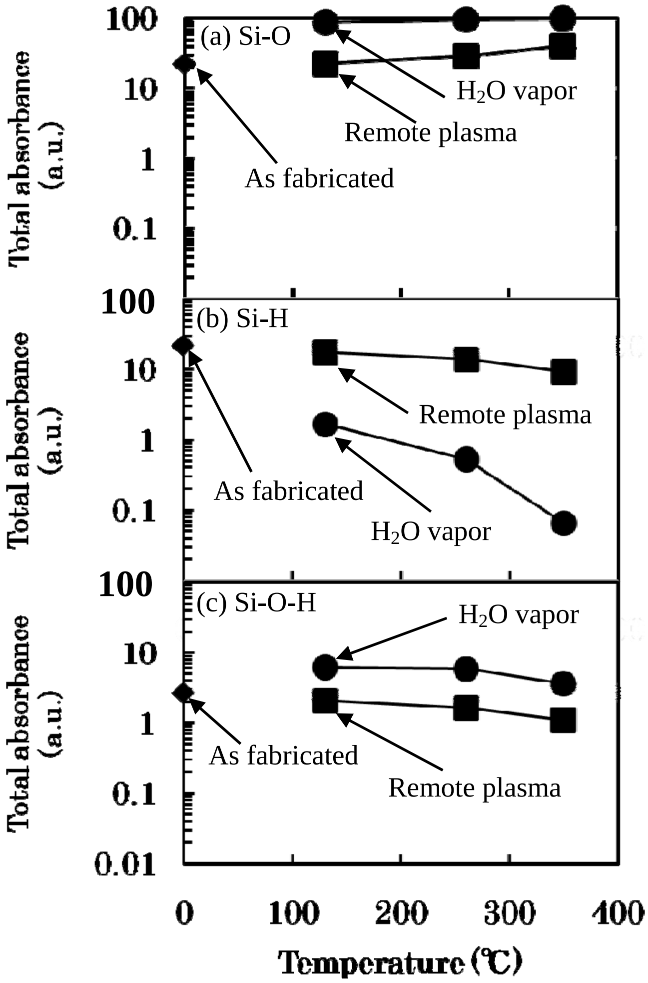

Fig.2: Total absorption corresponding to the intensity of Si-O peak (a), the intensity of Si-H peak (b) and the intensity of Si-O-H peak (c) as a function of heating temperature for remote oxygen plasma treatment.

Figure.3 shows the fixed oxide charge and the interface trap states as a function of heating temperature for remote oxygen plasma treatment. We could not measure the capacitance responses for the sample fabricated by remote oxygen plasma treatement. We thought that it was not enough to oxidize Polysilazane precursor, because the sample had a small intensity of

Si-O peak in FTIR optical absorption spectrum. The SiO_2 films formed by high pressure H_2O vapor heat treatment had a high fixed oxide charge of $2.3\times10^{12}cm^{-2}$ and a high interface trap states of $5.4\times10^{11}cm^{-2}eV^{-1}$. Remote oxygen plasma treatment at 350℃ followed by high pressure H_2O vapor heat treatment reduced them to $1.6\times10^{11}cm^{-2}$, $4.6\times10^{10}cm^{-2}eV^{-1}$, respectively. Remote oxygen plasma treatment reduced the fixed oxide charge density and the interface trap states with increasing the heating temperature. These results indicate that remote oxygen plasma treatment at 350℃ effectively reduced the defects of SiO_2 films and SiO_2/Si interface. It reduced Si-H bondings as shown in Fig. 2(b). We thought that the low hydrogen content is required to form SiO_2 films with low defect densities.

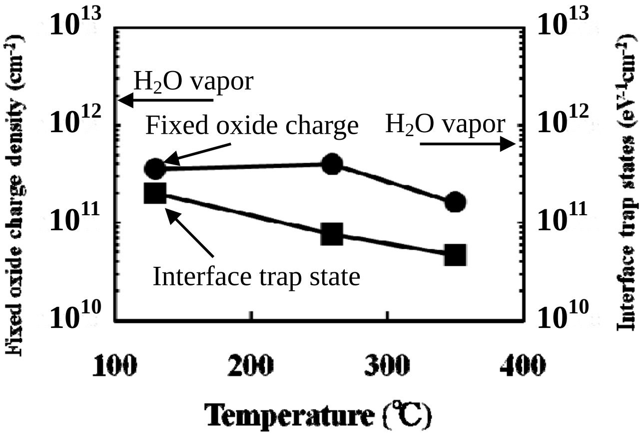

Fig.3: The fixed oxide charge density and the interface trap state as a function of heating temperature for remote oxygen plasma treatment. The arrows indicate that the fixed oxide charge density and the interface trap state for SiO_2 films fabricated by 1.3×10^6 Pa-H_2O vapor heat treatment at 260℃ for 3h.

Summary

We investigated SiO_2 films formation using Polysilazane precursor treated by remote oxygen plasma and high pressure H_2O vapor heating. The total absorbance of optical absorption corresponding to Si-O bonding after remote oxygen plasma treatment at 350℃ followed by high pressure H_2O vapor heat treatment was determined to be 100. As-spin coated samples had a total absorbance of optical absorption corresponding to Si-O bonding of 22. It was increased to 44.5 by remote oxygen plasma treatment at 350℃, and markedly increased to 100 by remote oxygen plasma treatment at 350℃ followed by high pressure H_2O vapor heat treatment. High pressure H_2O vapor heat treatment entirely oxidized Polysilazane precursor. As-spin coated sample had a total absorbance of optical absorption corresponding to Si-H bonding of 22. It was reduced to 9.4 by remote oxygen plasma treatment, and further reduced to 0.07 by remote oxygen plasma treatment at 350℃ followed by high pressure H_2O vapor heat treatment. The Si-H bonding in Polysilazane precursor was effectively removed by the combination of high pressure H_2O vapor heat treatment with remote oxygen plasma treatment. On the other hand, the present combination treatment slightly increased the total absorbance of optical absorption corresponding to Si-O-H bonding from 2.8 to 3.7. While the MOS capacitor fabricated by high pressure H_2O vapor heat treatment had a high fixed oxide charge density of 2.3×10^{12} cm^{-2} and a density of interface trap of 5.4×10^{11} $cm^{-2}eV^{-1}$, remote oxygen plasma treatment at 350℃ followed by high pressure H_2O vapor heat treatment reduced them to 1.6×10^{11} cm^{-2} and 4.6×10^{10} $cm^{-2}eV^{-1}$, respectively. From these results, the combination of high pressure H_2O vapor heat treatment with remote oxygen plasma treatment improved electrical properties of SiO_2 films and SiO_2/Si interface.

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