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Improvement of SiO_2 Properties by Heating Treatment in High Pressure H_2O Vapor

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Properties of SiO_2 and SiO_2/Si interfaces formed by plasma chemical vapor deposition were improved by heating at 270°C in high pressure H_2O vapor. The treatment reduced the fixed oxide charge density from 2.5×10^{12} cm^{-2} (initial) to 8×10^{10} cm^{-2} as the H_2O vapor pressure increased to 54 bar. The peak frequency of the absorption band caused by the Si-O antisymmetric stretching vibration mode was increased to 1078 cm^{-1} for treatment with 54 bar H_2O vapor, while it was 1062 cm^{-1} before the treatment. The full width at half-maximum of the absorption band was reduced to 65 cm^{-1}.

KEYWORDS: plasma CVD, fixed oxide charge, interface trap state, hydrolysis, thermally relaxed state

SiO_2 formation at a low temperature is important for many applications. A low temperature process, especially below 350°C, can allow us to use inexpensive glass substrates in fabricating thin film transistors (TFTs).[1,2] It is suitable for application to large flat liquid crystal display panels. Moreover, surface passivation with SiO_2 films is important for fabrication of solar cells with a long carrier lifetime. A low temperature process for SiO_2 formation can reduce the production cost of solar cells. In general, SiO_2 films formed at a low temperature do not have a Si-O bonding network in the complete thermally relaxed state, which thermally grown oxide films have.[3] There can be defects associated with a weak bond network between silicon and oxygen atoms. Moreover, plasma processes may cause serious damage to the films and at SiO_2/Si interfaces as well as during the film formation because of high energy charged species in plasma. The plasma damage can result in formation of defects in the SiO_2 films and at the SiO_2/Si interfaces. We previously reported on a method of heating in H_2O vapor at 300°C with a H_2O partial pressure of 50–100 Torr (0.07–0.13 bar) to reduce the defects.[4–6] The densities of the fixed oxide charge and the interface trap states can be reduced by this treatment. An increase in the average bonding angle of Si-O-Si from 137.8 degrees to 141.0 degrees was achieved by the treatment. However, it was still far from the thermally relaxed state; the average bonding angle of Si-O-Si was lower than that of thermally grown oxide films and it was difficult to reduce very high densities of the fixed oxide charge, higher than 10^{12}cm^{-2}, to a low enough level, $\sim 10^{11}$cm^{-2}, at below 350°C in the H_2O vapor.

Here we report on improvement of properties of SiO_2 films and SiO_2/Si interfaces by heating at 270°C in high pressure H_2O vapor. Reduction of the densities of the fixed oxide charge and the interface trap states in metal-oxide-semiconductor (MOS) capacitors is described. Optical absorption in the infrared region shows that the present treatment makes the Si-O bonding network similar to that of thermally grown silicon oxide films, which is in a thermally relaxed state.

Three types of SiO_2 films were formed on p-type silicon substrate at 250°C by 13.56-MHz-radio-frequency-remote-plasma-chemical-vapor deposition (rf-RPCVD) with two metal mesh plates between the substrate and a top rf electrode for control of the plasma density near the substrate.[7] SiO_2 films 120 nm thick with very high densities of the fixed oxide charge and interface trap states were fabricated by application -30 V to the metal mesh facing the substrate and with O_2 and SiH_4 gas flow rates of 3 sccm each. The other two types of SiO_2 films with lower defect densities were fabricated with no bias voltage applied to the metal mesh and O_2/SiH_4 gas flow rates of 4 sccm/3 sccm and 5 sccm/3 sccm (lowest initial defect case), respectively. The samples were then placed into a pressure-proof stainless-steel chamber with a volume of 60 cm^3 using a metal seal. Pure water 0.02 cm^3–5 cm^3 was also placed into 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.

After the heating, the thickness and the refractive index of the SiO_2 films were measured by 632.8-nm-photoellipsometry. For Al gate MOS capacitors, 100-nm-thick Al electrodes were evaporated on the SiO_2 surface as well as the rear Si surface. After the evaporation, the samples were heated to 300°C in dry air in order to realize the ohmic contact characteristic of the Si/Al interface. The densities of the fixed oxide charge and the interface trap states were determined from capacitance vs voltage (C–V) characteristics at a frequency of 1 MHz. Optical absorption spectra in the infrared range of the SiO_2 films were measured using a Fourier transform infrared (FTIR) spectrometer.

Figure 1 shows the normalized thickness of the SiO_2 films as a function of the amount of H_2O placed into the chamber after the heat treatment. There was no appreciable change in the SiO_2 thickness with the H_2O amount up to 1 cm^3. On the other hand, the thickness decreased to 80 nm as the H_2O amount was increased to 5 cm^3. The H_2O vapor pressure reached the saturation pressure of 54 bar at 270°C when the H_2O amount was 1.2 cm^3. These results show that the SiO_2 is etched by H_2O at the saturation vapor pressure. There was no change in the refractive index with an initial value of 1.466 for the treatment with an H_2O amount of up to 1 cm^3, while it decreased to 1.460 as the H_2O amount was increased from 1 cm^3 to 5 cm^3.

Figure 2(a) shows the fixed oxide charge density as a function of H_2O amount for the heat treatment. For the highest initial defect density case, the fixed oxide charge density was gradually reduced from 2.5×10^{12} cm^{-2} (ini-

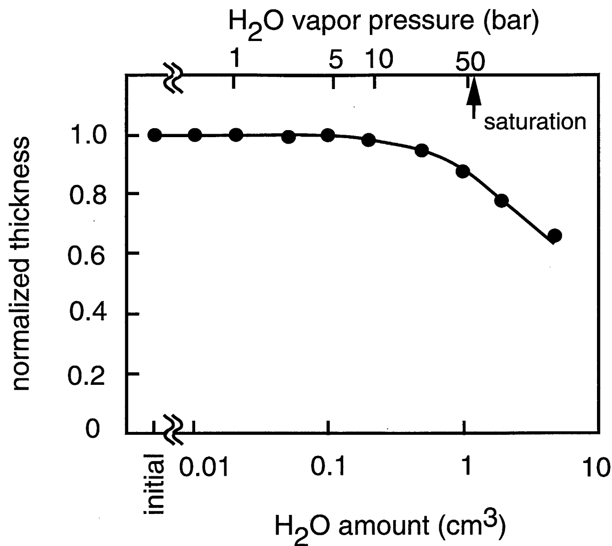

Fig. 1. Normalized thickness of SiO_2 films as a function of the amount of H_2O which was placed into the chamber for the heat treatment at 270°C for 3 h. The H_2O vapor pressure is indicated by the upper horizontal axis. The initial thickness was 120 nm.

tial) to 8×10^{10} cm^{-2} as the H_2O amount was increased to 5 cm^3. For other samples with the lower initial defect densities, the fixed oxide charge density was reduced to $\sim 5 \times 10^{10}$ cm^{-2} by the treatment with only 0.2 cm^3 of H_2O. The density of interface trap states was also reduced by the treatment, as shown in Fig. 2(b). The density of interface trap states was reduced to less than 10^{11} cm^{-2}·eV^{-1} by the treatment with more than 0.5 cm^3 of H_2O for the sample with the highest initial interface trap density. For the other two samples, it reached a level of 10^{10} cm^{-2}·eV^{-1} order for the treatment with up to 0.2 cm^3 of H_2O. The results in Fig. 2 show that the heat treatment in high pressure H_2O vapor effectively reduces the densities of the fixed oxide charge and the interface trap states in SiO_2 and at SiO_2/Si interfaces even if these densities are initially very high. Plasma processing can cause distribution of these defect densities in a wafer, especially a large wafer, because of fluctuation of the plasma density. The present method can be used to reduce the defect densities and their distribution, which is an advantage for reducing the threshold voltage and for achieving uniform carrier mobility for TFTs.

Figure 3 shows the peak wavenumber of the optical absorption band caused by the Si-O antisymmetric stretching vibration mode and the full width at half maximum (FWHM) of the absorption band as functions of the amount of H_2O for the sample with the highest initial densities of the fixed oxide charge and the interface trap states. Before the treatment, the sample had a low peak wavenumber (1062 cm^{-1}) and a large FWHM (81 cm^{-1}). This means that the average bonding angle between silicon and oxygen atoms (Si-O-Si) was low and the bonding angles were widely distributed. According to the central force model,[3,8] the average bonding angle was 139.0 degrees. The peak wavenumber increased to 1078 cm^{-1} as the H_2O amount was increased to 5 cm^3. The FWHM was reduced to 65 cm^{-1} by the treatment with 5 cm^3 of H_2O, as shown in Fig. 3. These values are very close to

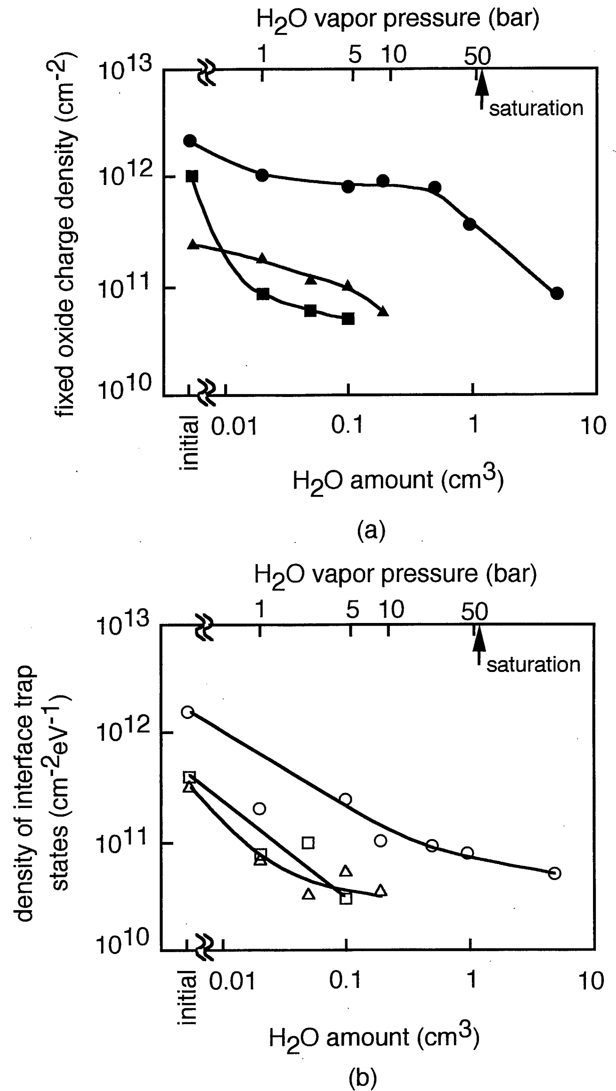

Fig. 2. The fixed oxide charge density (N_f) (a), and the interface trap density (D_{it}) (b), as functions of the H_2O amount (the H_2O vapor pressure) for MOS capacitors. Initial values are also presented in the figure.

those for thermally oxidized silicon films. The results in Fig. 3 show that the SiO_2 films fabricated by the plasma CVD at 250°C have an open network structure and are susceptible to heating in H_2O vapor. The water placed in the chamber is evaporated by the heating to 270°C. A reaction occurs between H_2O gas and SiO_2 (hydrolysis). Si-O bonds, especially weak ones with a low bonding angle may 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 more stable Si-O bonds with a larger bonding angle would be formed during the heat treatment. That H_2O hydrolysis rate increases with increasing H_2O pressure and particularly high when the pressure reachs the saturation pressure of 54 bar at 270°C. The Si-O-Si bonding angle increased to 143.9 degrees as estimated from the peak wavenumber 1078 cm^{-1} for the 5 cm^3-H_2O heat treatment. These results suggest that the heat treatment with high pressure H_2O vapor makes SiO_2 films a more uniform network with a larger Si-O-Si average bonding angle, which

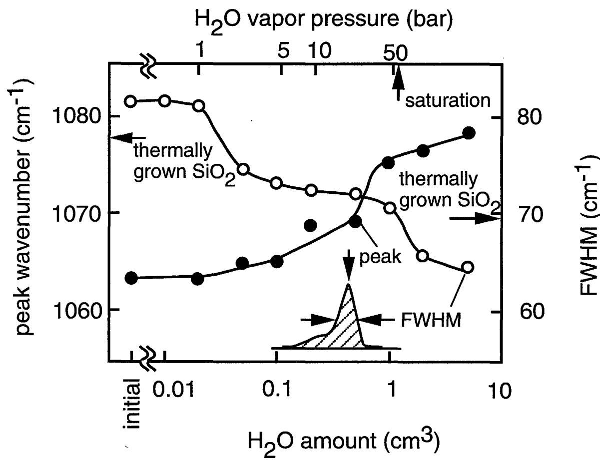

Fig. 3. The peak wavenumber of SiO optical absorption band associated with the antisymmetric stretching vibration mode and the full width at half maximum (FWHM) of the band as functions of the H_2O amount (the H_2O vapor pressure) for the SiO_2 film with the highest initial N_f and D_{it} shown in Fig. 2. The peak wavenumber of the SiO optical absorption band and its FWHM for a 100 nm thick thermally grown oxide film formed at 1000°C in dry atmosphere are also presented.

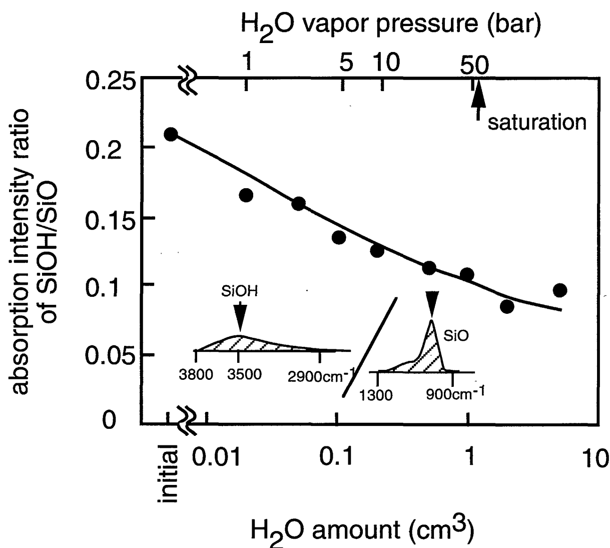

Fig. 4. The intensity ratio of SiOH absorption to SiO absorption as a function of the H_2O amount (the H_2O vapor pressure). The absortion intensity was determined by integration of the spectral intensity from 2900 cm^{-1} to 3800 cm^{-1} for SiOH, and 900 cm^{-1} to 1300 cm^{-1} for SiO.

is similar to the thermally relaxed state that thermally grown oxide films exhibit. Figure 4 shows the absorption intensity of the Si-O-H vibration mode at around 3500 cm^{-1} divided by the absorption intensity of the Si-O vibration mode as a function of the H_2O amount. The intensity decreased as the H_2O amount was increased. The number of Si-O-H bonds was reduced. This result shows that the H_2O hydrolysis is a catalytic process and effective for reduction of the Si-O-H bond density.

In summary, the heating treatment with high pressure H_2O vapor at 270°C was developed for improvement of properties of SiO_2 and SiO_2/Si interfaces formed by plasma CVD. The treatment reduced the fixed oxide charge density from 2.5×10^{12} cm^{-2} (initial) to 8×10^{10} cm^{-2} with a saturation H_2O vapor pressure of 54 bar for an Al-gate MOS capacitor. The peak frequency of the absorption band caused by the Si-O antisymmetric stretching vibration mode was increased to 1078 cm^{-1} by treatment with a 54 bar H_2O vapor, whereas it was 1062 cm^{-1} initially. The FWHM of the absorption band was reduced from 81 cm^{-1} to 65 cm^{-1}. The density of the Si-O-H bonds was also reduced. These results indicate that this treatment makes SiO_2 films stable Si-O bonding networks similar to thermally relaxed states of thermally grown oxide films.

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