Improvement of SiO$_2$ Properties and Silicon Surface Passivation by Heat Treatment with High-Pressure H$_2$O Vapor

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Heat treatment with high-pressure H$_2$O vapor was applied to improve the properties of SiO$_x$ ($x < 2$) films formed by vacuum evaporation, for passivation of the silicon surface. Heat treatment at 340–420 °C changed SiO$_x$ films into SiO$_2$ films with an Si–O–Si bonding network similar to that of thermally grown SiO$_2$ films. The densities of interface trap states and fixed positive charges were reduced to 6.5×10^{10} cm^{-2}eV^{-1} and 2.5×10^{11} cm^{-2}, respectively, after heat treatment at 340 °C with 2.4×10^6 -Pa–H$_2$O vapor for 3 h. The heat treatment reduced the recombination velocity for the electron minority carriers from 1200 cm/s (as fabricated) to 140 cm/s.

Although conventional solar cell passivation using thermal oxides requires temperatures between 850 °C and 1050 °C, many methods have been developed to establish low-cost, simple fabrication technologies. For example, plasma-enhanced chemical vapor deposition (PECVD) has become a promising technology for low temperature passivation of solar cells.[1–3] Substrate temperatures during PECVD typically range between 250 °C and 350 °C. Recombination velocities lower than 100 cm/s have been reported for passivation using silicon oxide or silicon nitride films prepared by PECVD. Hydrogenation using hydrogen plasma or hydrogen radicals has also been widely investigated for the reduction of defects at the interface between insulator and silicon.[4–6] We have reported simple heat treatment at approximately 300 °C with high-pressure H$_2$O vapor, which improves the bulk properties of SiO$_2$ fabricated by PECVD, as well as SiO$_2$/single-crystalline Si interface properties.[7,8] Heat treatment markedly reduces the density of the fixed oxide charges in SiO$_2$ films as well as the density of trap states of SiO$_2$/Si, and reduces bonding strain at the SiO$_2$/Si interfaces. In this paper, we propose a simple passivation method of the silicon surface using high-pressure H$_2$O vapor annealing and SiO$_x$-film evaporation. SiO$_x$ ($x < 2$) films are formed on silicon surfaces at room temperature by vacuum evaporation.[9] Although they are defective, heat treatment with high-pressure H$_2$O vapor oxidizes SiO$_x$ films and improves the SiO$_x$/Si interfaces. Increase in the minority carrier lifetime and decrease in the recombination velocity after the annealing are reported.

SiO$_x$ films were formed on the silicon surface using a thermal evaporation method. A powder of SiO with a purity of 99.99 % was put in a Ta boat connected to electrodes placed in a vacuum chamber. A silicon substrate was placed above the boat. There was a shutter between the boat and the sample. The chamber was evacuated to a pressure of 3×10^{-6} Torr. With the shutter closed, a voltage was applied to the Ta boat in order to heat it to just below the evaporation threshold for the desorption of gases adsorbed in the SiO powder, such as H$_2$O as well as H$_2$. After the pressure decreased to less than 1×10^{-5} Torr, the applied voltage was increased to realize a deposition rate of 40 nm/min. The shutter was then opened and the SiO evaporation initiated. The substrate temperature increased from room temperature to about 50 °C owing to radiation emitted from the heated Ta boat.

For heat treatment with high-pressure H$_2$O vapor, samples were placed in a pressure-proof stainless-steel chamber with a volume of 60 cm^3 using a metal seal.[7] Pure water was also put into the chamber. The samples were heated by placing the chamber on a heater plate. The H$_2$O evaporated during heating and the gas pressure increased. Optical absorption spectra of SiO$_x$ films were measured using Fourier transform infrared spectrometry (FTIR) to investigate Si–O–Si bonding states. In order to investigate the electrical properties of the SiO$_2$/Si interface, metal-oxide-semiconductor (MOS) capacitors were fabricated on p-type Si with an orientation of (100) and a resistivity of 10 Ωcm^{-1}. Al was evaporated in vacuum and 100-nm-thick Al gate electrodes were formed at room temperature on the SiO$_x$ films just after deposition or after heat treatment with high-pressure H$_2$O vapor. Capacitance responses at a frequency of 1 MHz were measured. The effective lifetime of excess minority carriers was also investigated for p-type Si with an orientation of (100) and a resistivity of 5000 Ωcm, by measuring the decay in the reflectivity of a 14-GHz-microwave-probe when the excess minority carriers were induced by 200-ns-pulsed-laser irradiation with a wavelength of 940 nm, in order to estimate the recombination velocity at the silicon surface coated with 100-nm-thick SiO$_x$ films.[10,11]

Figure 1 shows the peak wave number of the optical absorption band caused by the Si–O–Si antisymmetric stretching vibration mode and the full-width at half maximum (FWHM) of the absorption band as functions of the heating temperature for sample heated with 1 cm^3 of pure water for 3 h. The spectra of the optical absorption coefficient at wave numbers between 800 cm^{-1} and 1300 cm^{-1} before and after heat treatment are shown in the inset. The absorption coefficient was obtained from measurements of transmissivity and reflectivity of the samples, using the simple equation of $T = (1 - R)\exp(-\alpha x d)$, where T is the transmissivity, R is the reflectivity, d is the film thickness and α is the optical absorption coefficient. Because SiO$_x$ films were etched by heat treatment with high-pressure H$_2$O vapor,[7] we carefully measured the film thickness after heat treatment. Before heat treatment, the as-deposited 250-nm-thick SiO$_x$ films showed a broad absorption band with a low peak wave number (1010 cm^{-1}) and a large the FWHM (160 cm^{-1}), as shown by curve (a) in the inset. The peak wave number increased to 1076 cm^{-1} and FWHM decreased to 75 cm^{-1} as the heat-
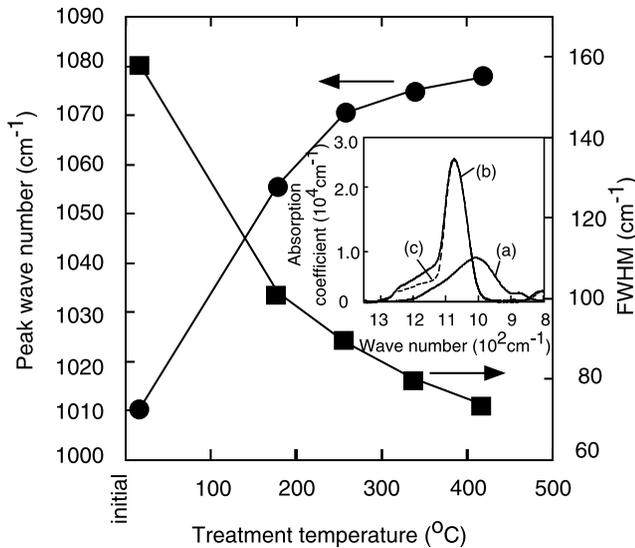
Fig. 1. The peak wave number of the optical absorption band caused by the Si–O–Si antisymmetric stretching vibration mode and its full-width at half maximum (FWHM) of the absorption band as functions of the heating temperature when SiO_x samples were heated with 1-cm^3 of pure water for 3 h. Inset shows optical absorption coefficient per unit film thickness for SiO_x samples as-deposited (a) and annealed at 340 °C (b). Dashed curve (c) is the spectrum of thermally grown SiO_2 at 1000 °C, which was drawn with a maximum absorbance coincident with that of SiO_x annealed at 340 °C.
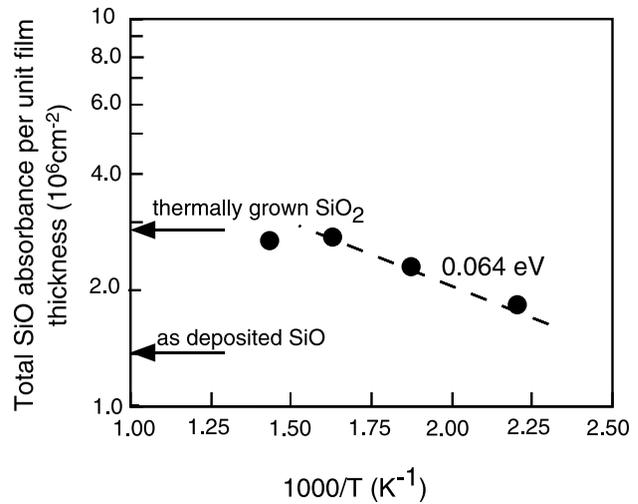
Fig. 2. The total optical absorbance caused by the Si–O–Si antisymmetric stretching vibration mode per unit film thickness, which was obtained by integration of the absorption coefficient from of 850 cm^{-1} to 1300 cm^{-1} as a function of the reciprocal annealing temperature. Because 1 cm^3 of pure water was used under every annealing condition, the H_2O pressure was 1.4×10^6 Pa, 4.1×10^6 Pa, 4.7×10^6 Pa and 5.3×10^6 Pa for annealing temperatures of 180 °C, 270 °C, 340 °C and 420 °C, respectively. The total optical absorbances per unit film thickness of as-deposited SiO_x and thermally grown SiO_2 are also shown.

Fig. 3. The densities of fixed positive charges and interface trap states as functions of H_2O-vapor pressure. The SiO_x samples were annealed at 340 °C for 3 h. The experimental errors were 3×10^{10} cm^{-2} and 5×10^{10} cm^{-2}eV^{-1} for minimum densities of fixed positive charges and interface trap states, respectively.

ing temperature increased from 180 °C to 420 °C for high-pressure H_2O vapor annealing. The spectral line shape was markedly changed and became almost the same as that of thermally grown SiO_2 films after heat treatment at temperatures of 340 °C and 420 °C, as shown by curves (b) and (c) in the inset. These optical changes mean that the annealed films had an Si–O–Si bonding network similar to that of thermally grown SiO_2 films. Figure 2 shows a total optical absorbance per unit film thickness, which was obtained by integration of the absorption coefficient from 850 cm^{-1} to 1300 cm^{-1}, which corresponds to the volume density of Si–O bonds in the films, as a reciprocal function of annealing temperature. The initial SiO_x films had a low total opticl absorbance per unit film thickness of 1.35×10^6 cm^{-2}, which is 0.49 times that of thermally grown SiO_2 films, because thermally evaporated SiO_x films had many oxygen defects. The total optical absorbance per unit film thickness increased as the annealing temperature increased. The activation energy of increase in the total optical absorbance per unit film thickness was 0.064 eV, as shown in Fig. 2. This low activation energy means that the SiO_x films can be easily oxidized by the heat treatment with high-pressure H_2O vapor. The total optical absorbance per unit film thickness had a maximum value of 2.61×10^6 cm^{-2} when SiO_x film was annealed at 340 °C. It was 0.94 times that of thermally grown SiO_2 films. Because the absorption spectral line shape resulting from the Si–O–Si antisymmetric stretching vibration mode after annealing at 340 °C was almost the same as that of thermally grown SiO_2 films, we hypothesize the existence of voids in the film, which reduce the average volume density of Si–O bonds. The thermal evaporation would not result in films as dense as thermally grown films. The total optical absorbance per unit film thickness for annealing at 420 °C was lower than that for an-

nealing at 340 °C. Annealing at 420 °C would cause substantial etching of Si–O bonds, especially weak bonds in the films, so that the density of voids would increase and the density of Si–O bonds would decrease.
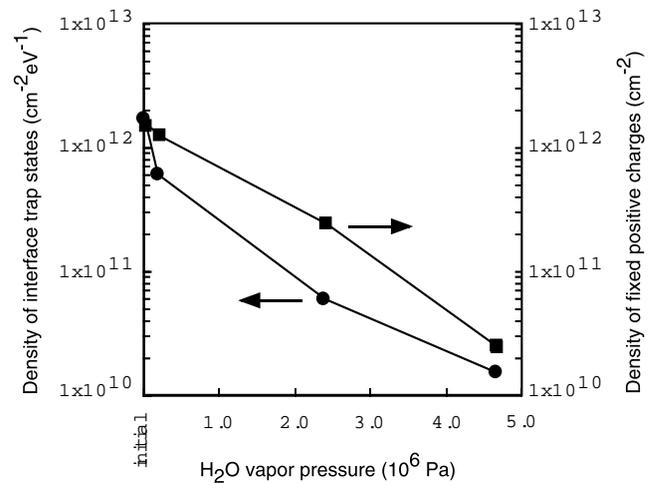
Figure 3 shows the densities of interface trap states and fixed positive charges as functions of H_2O vapor pressure, obtained from the data of capacitance vs voltage applied to the MOS capacitors when the sample was annealed at 340 °C for 3 h. The density of fixed positive charges was markedly reduced from 1.6×10^{12} cm^{-2} to 5.6×10^{10} cm^{-2} because the number of Si dangling bonds caused by oxygen defects was reduced through oxidization in high-pressure H_2O vapor, so that the density of positive-charge-trapped states, for example
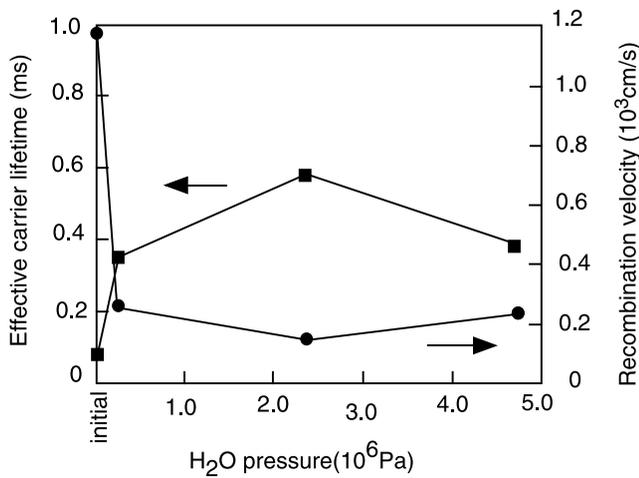
Fig. 4.   The effective lifetime of electron excess minority carriers for p-type CZ silicon with a resistivity of 5000 Ωcm, whose surfaces were coated with SiO_x film, and the recombination velocity estimated from the effective lifetime as functions of H_2O-vapor pressure. The samples were annealed at 340 °C for 3 h. The experimental error of the maximum carrier lifetime was 50 μs so that the experimental error of the recombination velocity was 15 cm/s.

the E' center, was reduced. Although the density of interface trap states was high at 1.7×10^{12} cm^{-2}eV^{-1} for as-deposited samples, it was reduced to 1.5×10^{10} cm^{-2}eV^{-1} as H_2O-vapor pressure was increased to 4.7×10^6 Pa. This result means that the Si dangling bonds at SiO_2/Si interfaces were effectively reduced in number through low- temperature annealing with high-pressure H_2O vapor. The effective lifetime of electron-excess minority carriers for p-type CZ silicon, whose surface was coated with SiO_x films, was increased by heat treatment with high-pressure H_2O vapor. The sample coated with as-deposited SiO_x films had a low lifetime of 80 μs, as shown in Fig. 4, although it had a long lifetime of 2.8 ms when both bare surfaces were passivated with ethyl-alcohol liquid containing 3 weight % iodine.[12] This means that there was a high density of trap states for electron minority carriers at the interfaces of as-deposited SiO_x/Si. Heat treatment with high-pressure H_2O vapor increased the lifetime of the minority carriers. The maximum lifetime was 580 μs, which was obtained after 2.4×10^6 Pa–H_2O-vapor heat treatment, as shown in Fig. 4. The maximum lifetime gave the minimum carrier recombination velocity of 140 cm/s, although the recombination velocity was high, 1200 cm/s, for the case of as-deposited SiO_x/Si, as shown in Fig. 4. An interesting result is that heat treatment with high-pressure H_2O vapor reduced the carrier recombination velocity as well as the density of fixed positive charges. The field effect passivation caused by positive charges fixed in insulators is well known.[13] A high density of positive charges can cause an increase in the density of minority electron carriers at SiO_2/Si interfaces and reduce their recombination velocity. The reduction in the density of

fixed positive charges means that the reduction in the recombination velocity results not from field effect passivation, but mainly from reduction in the density of the carrier trap states at the SiO_2/Si interfaces.

A simple method for passivation of the silicon surface was proposed. SiO_x ($x < 2$) films were formed on silicon surfaces at room temperature by vacuum evaporation. Although they are defective and their Si–O bonding network was far different from that of thermally grown SiO_2 films, heat treatment with high-pressure H_2O vapor oxidized SiO_x films and changed film properties so that they became similar to those of thermally grown SiO_2 films. The peak wave number of the optical absorption band caused by the Si–O–Si antisymmetric stretching vibration mode was increased from 1010 cm^{-1} (initial) to 1076 cm^{-1} after heat treatment at 420 °C with 4.7×10^6 Pa H_2O vapor for 3 h, and the FWHM of the absorption band was reduced from 160 cm^{-1} to 75 cm^{-1}. The volume density of Si–O bonds was increased with a thermal activation energy of 0.064 eV. The densities of interface trap states and fixed positive charges were reduced to 6.5×10^{10} cm^{-2}eV^{-1} and 2.5×10^{11} cm^{-2}, respectively, after heat treatment at 340 °C with 2.4×10^6 -Pa–H_2O vapor for 3 h. The effective lifetime of electron-excess minority carriers for p-type CZ silicon was increased from 80 μs to 580 μs after the heat treatment. This means that the recombination velocity was reduced from 1200 cm/s (as fabricated) to 140 cm/s. These results suggest that the present method will be useful for fabricating solar cells at a low temperature and at low cost.

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