Appl. Phys. A 69, 221–224 (1999) / Digital Object Identifier (DOI) 10.1007/s003399900071

Applied Physics A
Materials
Science & Processing

Defect reduction and surface passivation of SiO_2/Si by heat treatment with high-pressure H_2O vapor

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Received: 1 March 1999/Accepted: 28 March 1999/Published online: 24 June 1999

Abstract. Heat treatment with high-pressure H_2O vapor was applied to improve interface properties of SiO_2/Si and passivate the silicon surface. Heat treatment at 180–420 °C with high-pressure H_2O vapor changed SiO_x films, 150 nm thick formed at room temperature by thermal evaporation in vacuum, into SiO_2 films with a Si−O−Si bonding network similar to that of thermally grown SiO_2 films. Heat treatment at 130 °C with 2.8×10^5 Pa H_2O for 3 h reduced the recombination velocity for the electron minority carriers from 405 cm/s (as-fabricated 150-nm-thick SiO_x/Si) to 5 cm/s. Field-effect passivation was demonstrated by an additional deposition of defective SiO_x films on the SiO_2 films formed by heat treatment at 340 °C with high-pressure H_2O vapor. The SiO_x deposition reduced the recombination velocity from 100 cm/s to 48 cm/s.

PACS: 73.20.At; 73.50.Gr; 73.50.Pz; 78.20.Ci

Technologies of defect reduction and surface passivation are important for a variety of device fabrication. Many methods have been developed to establish low-cost and simple technologies. For example, hydrogenation using hydrogen plasma or hydrogen radical has been widely investigated for the reduction of defects in silicon as well as at interfaces between insulator and silicon [1–3]. Plasma-enhanced chemical vapor deposition (PECVD) has become a promising technology for low-temperature passivation by formation of insulators for solar cells [4–6]. 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. We recently reported on a simple heat treatment at approximately 300 °C with high-pressure H_2O vapor, which improved SiO_2 bulk properties fabricated by PECVD, as well as SiO_2/single-crystalline Si interface properties [7, 8]. The heat treatment 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 also reduces the bonding strain at the SiO_2/Si interfaces.

In this paper, we discuss surface passivation of silicon using heat treatment with high-pressure H_2O vapor. We report a remarkable reduction in the surface recombination velocity of excess electron minority carriers by SiO_x ($x < 2$) film formation on silicon surfaces followed by heat treatment with high-pressure H_2O vapor at temperatures from 130 °C to 340 °C.

1 Experimental

SiO_x films were formed on the silicon surface using a thermal evaporation of powders of SiO with a purity of 99.99% [9]. After preheating of a Ta boat, in which powder of SiO was placed, for gas desorption such as H_2O as well as H_2 adsorbed in the SiO powder, SiO_x film deposition was carried out at a rate of 40 nm/min. For heat treatment with high-pressure H_2O vapor, samples were placed into a pressure-proof stainless-steel chamber with a volume of 60 cm^3 using a metal seal [7]. Pure water was put into the chamber. The samples were then heated. The H_2O 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. The effective lifetime of excess minority carriers was investigated for *p*-type Si with an orientation of (100) and a resistivity of 5000 Ω cm, 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 150-nm-thick SiO_x films [10, 11].

2 Results and discussions

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 a sample heated with 0.5 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

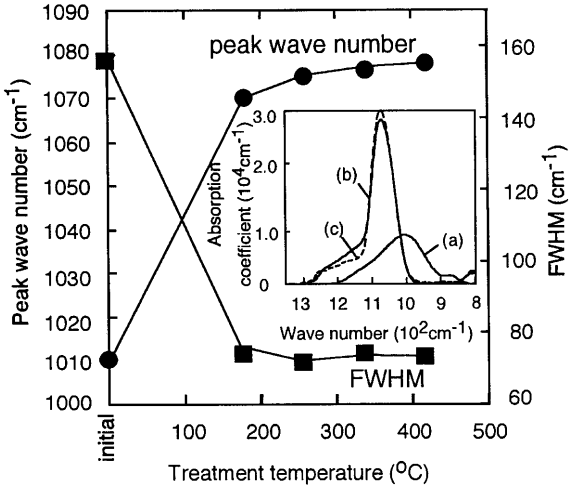

Fig. 1. The peak wave number of the optical absorption band caused by the Si−O−Si antisymmetric stretching vibration mode and its full-width at half maximum (FWHM) of the absorption band as functions of the heating temperature when SiO_x samples were heated with 0.5 cm^3 pure water for 3 h. *Inset* represents optical absorption coefficient for SiO_x samples as-deposited (a) and annealed at 340 °C (b). The *dashed curve* (c) is a spectrum of thermally grown SiO_2 at 1000 °C

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 $T = (1 - R)\exp(-\alpha d)$, 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_2O vapor at temperatures higher than 260 °C, we carefully measured the film thickness after heat treatment. Before heat treatment, the as-deposited 150-nm-thick SiO_x films showed a broad absorption band with a low peak wave number (1010 cm^{-1}) and a large FWHM (160 cm^{-1}), as shown by curve (a) in the inset. The peak wave number increased to 1078 cm^{-1} and FWHM decreased to 72 cm^{-1} as the heating 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, as shown by curves (b) and (c) in the inset. These changes in optical spectra mean that the annealed films had a Si−O−Si bonding network similar to that of thermally grown SiO_2 films. Total optical absorbance per unit film thickness 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, was 0.49 times that of thermally grown SiO_2 for as-deposited SiO_x films because of many dangling bonds of silicon in the film. The total optical absorbance per unit film thickness was markedly increased by heat treatment. It reached, at maximum, 0.96 times that of thermally grown SiO_2 films with a heat treatment at 340 °C. Since the absorption spectral line shape resulting from the Si−O−Si antisymmetric stretching vibration mode was almost the same as that of thermally grown SiO_2 films, after heat treatment, we hypothesize an existence of voids in the film, which reduces 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 annealing at 340 °C. Annealing at 420 °C would cause substantial breaking of Si−O bonds, especially weak bonds in the films, because the film etching was observed after heat treatment. The density of voids would increase and the density of Si−O bonds would decrease.

Figure 2 shows the effective lifetime of excess minority carriers (electrons) for *p*-type silicon wafers coated with SiO_x films as a function of the annealing temperature for a heat treatment with 0.5 cm^3 of H_2O vapor. The carrier recombination velocity was estimated:

$$1/\tau_{\text{eff}} = 1/\tau_{\text{b}} + S_{\text{f}}/D + S_{\text{r}}/D\,, \tag{1}$$

where τ_{eff} is the effective life time, τ_{b} is the bulk life time, D is the thickness of silicon wafers, and S_{f} and S_{r} are the recombination velocities at the front and rear surface, respectively [11]. Samples with a surface coated with as-deposited SiO_x films had a low lifetime $\tau_{\text{eff}} = 0.23$ ms, when the other surface was passivated with an ethyl-alcohol liquid containing 3 wt. % iodine, which realized surface passivation with a recombination velocity of ≈ 10 cm/s in our experimental system [12]. On the other hand, it had a long lifetime of $\tau_{\text{eff}} = 2.55$ ms when both bare surfaces were passivated with ethyl-alcohol liquid containing 3 wt. % iodine. This means that there was a high density of trap states for electron minority carriers at the interfaces of as-deposited SiO_x/Si. The effective lifetime of the electron minority carrier markedly increased to $\tau_{\text{eff}} = 2.9$ ms after heat treatments at 130 °C with 2.8×10^5 Pa, as shown in Fig. 2. Although the recombination velocity was high at 405 cm/s for the case of as-deposited SiO_x/Si, it reduced to 5 cm/s after the heat treatment at 130 °C. This result shows that heat treatment with high-pressure H_2O vapor improved the interface properties of SiO_x/Si. The effective carrier lifetime gradually

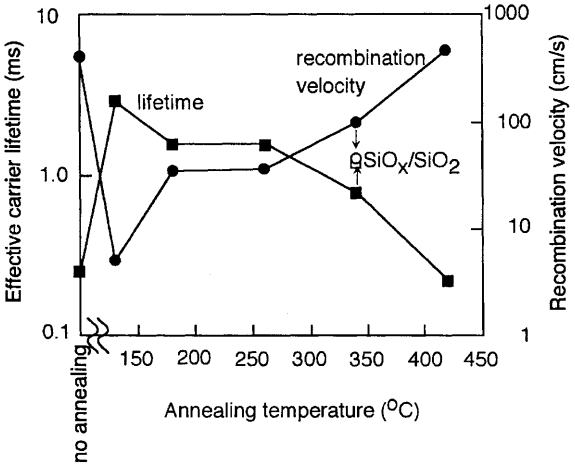

Fig. 2. The effective lifetime of excess minority carriers for *p*-type CZ silicon with a resistivity of 5000 Ω cm. The surface is coated with SiO_x films, and the minority carrier recombination velocity is estimated from the effective lifetime. The samples were heated for 3 h with 0.5 cm^3 H_2O. The H_2O vapor pressure was 2.8×10^5 Pa (saturation) at 130 °C, 2.1×10^6 Pa at 260 °C, 2.4×10^6 Pa at 340 °C, and 2.7×10^6 Pa at 420 °C, respectively. Open marks at 340 °C represent the effective carrier lifetime and the recombination velocity when samples annealed with 2.4×10^6 Pa H_2O vapor at 340 °C were coated with additional 150-nm-thick SiO_x films by thermal evaporation in vacuum at room temperature

decreased and the recombination velocity increased as the annealing temperature increased from 130 °C to 420 °C, as shown in Fig. 2. According to our previous studies [7, 13], the density of interface trap states and the density of fixed positive charges are reduced by heat treatment. For example, heat treatment with 2.5×10^6 Pa H_2O vapor at 270 °C for 3 h reduced the density of interface trap states from $2 \times 10^{12}\,cm^{-2}eV^{-1}$ (as fabricated) to $1 \times 10^{11}\,cm^{-2}eV^{-1}$, and also reduced the density of fixed positive charges from $2.5 \times 10^{12}\,cm^{-2}$ (as fabricated) to $5 \times 10^{11}\,cm^{-2}$. The densities of interface trap states and fixed positive charges were decreased as the heating temperature increased and the H_2O vapor pressure increased. Moreover, the degree of reduction in the density of interface trap was higher than that of reduction in the density of fixed positive charge states in heat treatment at low heating temperatures or low H_2O pressures. From these experimental results, we conclude that the reduction in the recombination velocity shown in Fig. 2 resulted from the reduction in the density of the carrier trap states at the SiO_2/Si interfaces, and that the lowest recombination velocity of 5 cm/s for 130 °C heat treatment resulted from field effect passivation caused by the residual density of fixed positive charges as well as from the reduction in the density of interface trap states at SiO_2/Si interfaces.

The field-effect passivation can be caused by positive charges fixed in insulators [14, 15]. Because thermally evaporated SiO_x films were defective and had a high density of fixed positive charges at around $2 \times 10^{12}\,cm^{-2}$, the high density of positive charges would cause an increase in the density of minority electron carriers at SiO_2/Si interfaces and reduce their recombination velocity if SiO_2/Si interfaces have good properties with a low density of trap states. In order to demonstrate field-effect passivation, additional SiO_x films, 150 nm thick, were evaporated on 150-nm-thick SiO_x films annealed at 340 °C for 3 h with 2.4×10^6 Pa H_2O vapor. The effective lifetime of excess minority carriers was increased from 0.8 ms to 1.3 ms and the recombination velocity decreased from 100 cm/s to 48 cm/s after the SiO deposition as shown in Fig. 2. This result shows that a high density of positive charge fixed in the top SiO_x film can cause an increase in the density of electron carrier at the underlying SiO_2/Si interfaces and increased the effective lifetime.

Figure 3 shows the effective lifetime (a) and the recombination velocity (b) as functions of the H_2O amount for heat treatment at temperatures of 130 °C, 260 °C, and 340 °C for 3 h. The effective lifetime increased and the recombination velocity decreased as the H_2O amount increased to 0.5 cm^3 for each annealing temperature case, as shown in Fig. 3. The maximum effective lifetime and the minimum recombination velocity were 2.9 ms and 5 cm/s after heat treatment at 130 °C with 2.8×10^5 Pa (saturation pressure), 1.5 ms and 35 cm/s after heat treatment at 260 °C and 2.1×10^6 Pa, and 0.78 ms and 100 cm/s after heat treatment at 340 °C and 2.4×10^6 Pa, respectively. These improvements in the effective lifetime and the recombination velocity were mainly caused by reduction of the density of interface trap states with increasing H_2O amount [13]. The lower recombination velocities achieved by heat treatment at lower temperature achieved probably resulted from the passivation induced by an electrical field due to the residual density of fixed positive charges after heat treatment at lower temperatures. Etching of SiO_x films was observed after heat treatment with an H_2O amount larger than 1.0 cm^3 at 260 °C and 340 °C. The thickness was reduced from 150 nm (initial) to 120 nm after heat treatment at 340 °C with 4.8×10^6 Pa H_2O vapor (1.0 cm^3 of H_2O). For those annealing cases, weak bonds of Si−O in the films would be broken and a substantial number of voids was probably formed so that the coverage ratio of the silicon surface with SiO_x would be reduced for heat treatment at high temperatures and with high pressures of H_2O vapor. We interpret that the reduction in the effective lifetime and the increase in the recombination velocity for heat treatments at 260 °C and 340 °C with the H_2O amount larger than 1.0 cm^3 shown in Fig. 3 were caused by reduction in the surface coverage ratio with SiO_2.

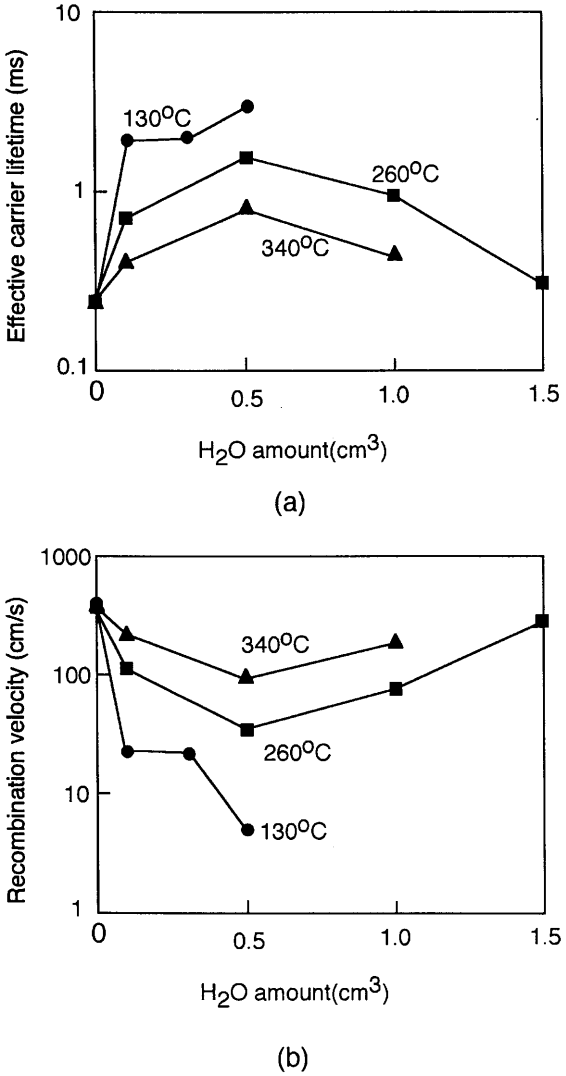

Fig. 3. Effective lifetime of excess minority carriers for *p*-type CZ silicon with a resistivity of 5000 Ω cm. The surface is coated with SiO_x films: the minority carrier recombination velocity is estimated from the effective lifetime. The samples were annealed at 130 °C, 260 °C, and 340 °C for 3 h

The optimum silicon surface passivation for SiO_x/Si was obtained by heat treatment conditions at temperatures of 130–260 °C with H_2O pressures 2.8×10^5–2.1×10^6 Pa and 0.5 cm^3 of H_2O within the 60 cm^3 chamber. The reduction in the density of interface trap states, the electrical field caused by the residual density of fixed positive charges, and

a high surface coverage resulted in the optimum silicon surface passivation.

3 Summary

A simple method for passivation of the silicon surface was demonstrated. SiO_x ($x < 2$) films 150 nm thick were formed on silicon surfaces at room temperature by thermal evaporation in vacuum. 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 the SiO_x films and changed their 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 increased from 1010 cm^{-1} (as deposited) to 1070–1078 cm^{-1} after heat treatment at 180–420 °C with 1.8×10^6–2.7×10^6 Pa H_2O vapor for 3 h. At the same time FWHM of the absorption band reduced from 160 cm^{-1} (as deposited) to 73–70 cm^{-1}. The effective lifetime of electron-excess minority carriers for *p*-type CZ silicon increased from 0.23 ms to 2.9 ms after the heat treatment for 3 h at 130 °C with a H_2O vapor pressure of 2.8×10^5 Pa. The recombination velocity was reduced from 405 cm/s (as fabricated) to 5 cm/s after the heat treatment at 130 °C probably because of a reduction in the density of interface trap states as well as electrical field effect caused by fixed oxide charges in the films. The field-effect passivation was demonstrated by an additional deposition of 150-nm-thick SiO_x films on the SiO_2 films annealed at 340 °C with high-pressure H_2O vapor. The SiO_x deposition reduced the recombination velocity from 100 cm/s to 48 cm/s because of the electric field caused by high density of positive charges fixed in the top SiO_x films.

Acknowledgements. The authors thank T. Mohri and Professor Saitoh for their support.

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