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# Passivation of $SiO_2$/Si Interfaces Using High-Pressure-$H_2O$-Vapor Heating

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High-pressure $H_2O$ vapor heating was used for the passivation of silicon surface. The thermally evaporated $SiO_x$ films formed on the silicon surface was oxidized and Si–O bonding density increased with an activation energy of 0.035 eV with increasing heating temperature upon heat treatment with $1.0 \times 10^6$ Pa $H_2O$ vapor. The peak wave number and full width at half maximum of the Si–O absorption band due to the Si–O–Si antisymmetric stretching vibration mode were changed to 1077 $cm^{-1}$ and 72 $cm^{-1}$, respectively. The density of silicon dangling bonds was reduced from $2.0 \times 10^{17}$(as deposited) to $1.4 \times 10^{15}$ $cm^{-3}$ by heat treatment. The effective surface recombination velocity of the p-type silicon wafer that was coated with $SiO_x$ films was markedly reduced from 405 cm/s (as deposited) to 13 cm/s by heat treatment with $2.1 \times 10^6$ Pa-$H_2O$ vapor at 260°C for 3 h. The interfaces retained the low recombination velocity 8000 h after keeping the sample in air. Effective field effect passivation was demonstrated using a $SiO_x$/$SiO_2$ double layered structure formed by the combination of thermal evaporation and heat treatment with high-pressure $H_2O$ vapor.

KEYWORDS: $SiO_x$, Si–O–Si bonding state, activation energy for oxidation, density of interface trap state, surface recombination velocity

## 1. Introduction

The formation of good-quality $SiO_2$ films and $SiO_2$/Si interfaces at low processing temperatures is important for device fabrication. Many fabrication processes at low temperatures have been developed. For example, plasma-enhanced chemical vapor deposition (PECVD) has been reported as one of the methods for the passivation of solar cells at low temperatures.[1,2] Defect reduction at interfaces between insulator and silicon using hydrogen plasma or hydrogen radicals has also been reported.[3,4] Plasma oxidation is also a possible technique for the formation of $SiO_2$/Si interfaces at low temperatures.[5] We have recently developed a simple heat treatment method using high-pressure $H_2O$ vapor. Heat treatment with high-pressure $H_2O$ vapor at approximately 300°C improves the properties of bulk $SiO_2$ and $SiO_2$/silicon interfaces formed by the PECVD method. The decrease in the densities of fixed positive charges for $SiO_2$ films and the interface trap states at $SiO_2$/Si is achieved by the heat treatment.[6] Strains of the Si–O–Si bonding networks near the $SiO_2$/Si interface are also relaxed.[7]

In this paper, we discuss the passivation of the silicon surface using high-pressure $H_2O$ vapor heating. We report a drastic change in bulk properties of $SiO_x$ films formed on the silicon surface by heat treatment with high-pressure $H_2O$ vapor. The reduction of the densities of defect states in bulk and $SiO_2$/Si interfaces is also shown. The simple process steps can realize a long lifetime and a low recombination velocity of carriers. We demonstrate that the present passivation with a low recombination velocity is stable. Moreover, we also discuss effective field effect passivation using double insulating layers of top $SiO_x$ overlaying $SiO_2$/Si interfaces.

## 2. Experimental

$SiO_x$ films were deposited at room temperature on silicon substrates by the thermal evaporation of powdered SiO in vacuum at a base pressure of $4 \times 10^{-4}$ Pa using a turbo molecular pump. A pressure-proof stainless-steel chamber was used for heat treatment with high-pressure $H_2O$ vapor. The samples and pure $H_2O$ were placed in the chamber and sealed with a metal seal. The chamber was put into an electric furnace. $H_2O$ was evaporated and vapor pressure increased in the chamber during heating. Si–O–Si bonding states were investigated by taking the optical absorption spectra of the films using a Fourier-transform infrared spectrometer (FT-IR). Metal-oxide-semiconductor structures were fabricated on p-type silicon with an orientation of (100) and a resistivity of 10 Ωcm. Aluminum electrodes with a thickness of 100 nm were deposited on the samples by thermal evaporation in vacuum. Capacitance response versus voltage at a frequency of 1 MHz was measured to investigate the electrical properties of the $SiO_2$/Si interfaces. In order to estimate the spin density in the films, the microwave absorption of unpaired electrons was observed using the electron spin resonance method for $SiO_x$/quartz before and after heat treatment with high-pressure $H_2O$ vapor. The effective lifetime and the effective recombination velocity of excess carriers were measured by observation of the decay in the reflectivity of a 14-GHz-microwave probe when the excess carriers were induced by 200 ns pulsed-laser irradiation with a wavelength of 904 nm.[8] The recombination velocity was estimated using the equation, $1/\tau_{\mathrm{eff}} = 1/\tau_{\mathrm{b}} + D/S_{\mathrm{f}} + D/S_{\mathrm{r}}$, where $\tau_{\mathrm{eff}}$ is the effective lifetime, $\tau_{\mathrm{b}}$ is the bulk lifetime, $D$ is the thickness of silicon wafers, and $S_{\mathrm{f}}$ and $S_{\mathrm{r}}$ are the recombination velocities at front and rear surfaces, respectively. The bulk lifetime $\tau_{\mathrm{b}}$ was estimated when the silicon surfaces were coated with ethyl alcohol solution containing 3 wt% iodine, which achieved a recombination velocity of 10 cm/s. Changes in the effective carrier lifetime and the recombination velocity were measured while the samples were kept under an illumination of 300 mW/$cm^2$ as well as in the dark at room temperature.

## 3. Results and Discussions

$SiO_x$ films formed by thermal evaporation were oxidized at low temperatures by heat treatment with high-pressure $H_2O$ vapor. Figure 1(a) shows the peak wave number and the full-width at half maximum (FWHM) of the optical absorption band due to the Si–O antisymmetric stretching vibration mode as a function of heating temperature for heat treatment with $1.0 \times 10^6$ Pa $H_2O$ for 3 h. A very broad absorption band with a low peak wave number and a large FWHM was observed for as-deposited $SiO_x$ samples. On the other hand, the shape of the spectrum was markedly changed after heat treatment. The peak wave number was increased to 1077 $cm^{-1}$

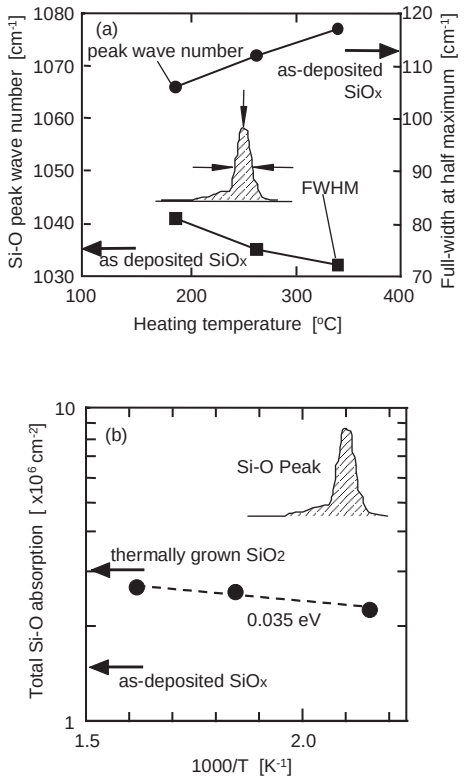


Fig. 1. (a) Peak wave number and the FWHM of the optical absorption band due to the Si–O antisymmetric stretching vibration mode as a function of heating temperature for heat treatment with $1.0 \times 10^6$ Pa $H_2O$ vapor for 3 h, and (b) the volume density of the total infrared absorption as a function of reciprocal heating temperature for heat treatment for 3 h with $1.0 \times 10^6$ Pa high-pressure $H_2O$. Volume density was obtained by the integrating the absorption coefficient between 800 $cm^{-1}$ to 1300 $cm^{-1}$.

and the FWHM was decreased to 72 $cm^{-1}$ as the heating temperature was increased to 340°C. These results show that the $SiO_x$ films was oxidized by heat treatment with high-pressure $H_2O$ vapor and the resulting films had Si–O–Si bonding states similar to those of thermally grown $SiO_2$. In order to investigate the oxidation ratio of $SiO_x$ in high-pressure $H_2O$ vapor, the change in the total infrared absorption of the Si–O antisymmetric stretching vibration mode, which was determined from the integration of the absorption coefficient between 800 $cm^{-1}$ to 1300 $cm^{-1}$, was measured. Figure 1(b) shows the volume density of the total infrared absorption as a function of reciprocal heating temperature for heat treatment for 3 h with $1.0 \times 10^6$ Pa high-pressure $H_2O$.

As-deposited $SiO_x$ films had a low total Si–O absorption of $1.39 \times 10^6$ $cm^{-2}$, which corresponded to 0.46 times that of thermally grown $SiO_2$ films. This shows that there were many oxygen vacancies in the initial $SiO_x$ films formed by thermal evaporation. The total infrared absorption increased to $2.65 \times 10^6$ $cm^{-2}$ as the heating temperature was increased to 340°C. This means that the density of Si–O bonds increased to $4.0 \times 10^{22}$ $cm^{-3}$, which was 87% of that of thermally grown $SiO_2$ through the oxidation process in $H_2O$ vapor. The thermal activation energy for the total infrared absorption was 0.035 eV. This low activation energy means that $SiO_x$ films were easily oxidized at low temperatures by heat treatment with high-pressure $H_2O$ vapor. Oxygen vacancies were effectively eliminated via Si–O bond formation. Because the absorption spectral line shape due to the Si–O–Si antisymmetric stretching vibration mode after heat treatment with high-pressure $H_2O$ vapor was almost the same as that of thermally grown $SiO_2$ films, the total infrared absorption of 87% at maximum compared to that of thermally grown $SiO_2$, probably indicates the existence of voids in the films, which reduces the average volume density of Si–O bonds. Thermal evaporation would not result in films as dense as thermally grown films.

Figure 2 shows the spin density associated with unpaired electrons as a function of heating temperature for heat treatment with a $H_2O$ vapor pressure of $1.0 \times 10^6$ Pa for 3 h. A spin density of $2.0 \times 10^{17}$ $cm^{-3}$ was observed for as-deposited $SiO_x$ films. The spin density was markedly reduced to $1.4 \times 10^{15}$ $cm^{-3}$ by $1.0 \times 10^6$ Pa $H_2O$ vapor heating at 260°C for 3 h, and was almost equal to the detection limit of our ESR measurement. Analyses of FTIR and ESR absorption spectra revealed that the defect states caused by dangling bonds of silicon in SiO films were annihilated in association with the oxidation of $SiO_x$ in high pressure $H_2O$ vapor at 260°C. The ratio of the density of defect states to that of the of SiO bonds was markedly reduced from $9.3 \times 10^{-6}$ to $3.7 \times 10^{-8}$ by $1.0 \times 10^6$ Pa $H_2O$ vapor heating at 260°C for 3 h. $H_2O$ vapor annealing resulted in the reformation of Si–O bonds with a low density of defect states.

Figure 3 shows the densities of interface trap states and fixed positive charges as functions of heating temperature, which were obtained from the data of capacitance vs volt-

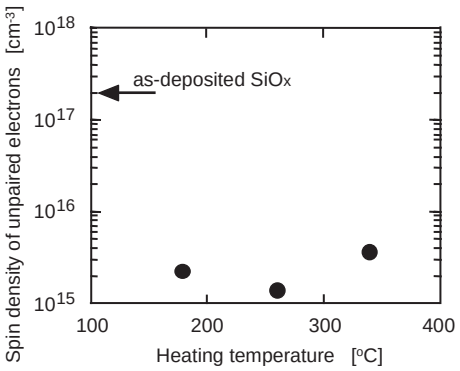


Fig. 2. Spin density associated with unpaired electrons as a function of heating temperature for heat treatment with $H_2O$ vapor pressure of $1.0 \times 10^6$ Pa for 3 h.

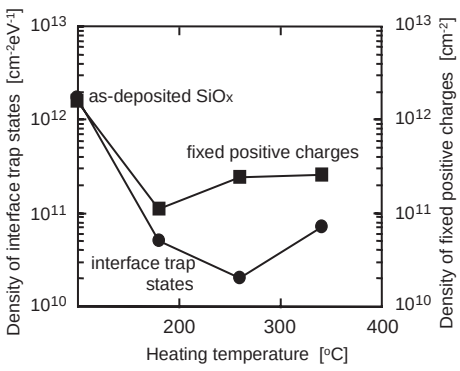


Fig. 3. Densities of interface trap states and fixed positive charges as functions of heating temperature, obtained from the data of capacitance vs voltage applied to MOS capacitors. The sample was annealed with 0.5 $cm^3$ $H_2O$ for 3 h.

age applied to MOS capacitors when the sample was annealed with 0.5 $cm^3$ $H_2O$ for 3 h. The density of fixed positive charges was markedly reduced from $2.0 \times 10^{12}$ $cm^{-2}$ to $2 \times 10^{11}$ $cm^{-2}$ by heat treatment at 260°C because the number of Si dangling bonds in $SiO_x$ films due to oxygen defects was reduced by oxidation in high-pressure $H_2O$ vapor, as shown in Fig. 2, so that the density of positive charge trap states, for example, the $E'$ center, was reduced. Although the density of interface trap states was high at $1.7 \times 10^{12}$ $cm^{-2}eV^{-1}$ for the as-deposited samples, it was reduced to $2 \times 10^{10}$ $cm^{-2}eV^{-1}$ by heat treatment at 260°C. This result means that Si dangling bonds at $SiO_2$/Si interfaces were effectively reduced by low-temperature annealing with high-pressure $H_2O$ vapor.

These investigations of the optical and electrical properties by FTIR, ESR and $C$–$V$ measurements revealed that high-pressure $H_2O$ vapor annealing oxidized SiO and changed its bonding network to that similar to thermally grown $SiO_2$, and that the densities of defect states in bulk and at interfaces were markedly reduced. In order to determine the possibility of application of the present $H_2O$ vapor annealing method to the surface passivation of photovoltaic devices, the change in the effective lifetime of excess carriers with high-pressure $H_2O$ vapor annealing was investigated because the lifetime is sensitive to the properties of the silicon surface. Figure 4 shows the effective carrier lifetime and the effective surface recombination velocity for 5000 Ωcm p-type silicon coated with $SiO_x$ films as functions of heating temperature for heat treatment with high-pressure $H_2O$ vapor. A short effective lifetime of 0.4 ms was measured for the case of as-deposited $SiO_x$ films. A marked increase in the effective carrier lifetime was obtained after heat treatment. In particular, the effective carrier lifetime increased to 1.8 ms after heat treatment with $2.1 \times 10^6$ Pa $H_2O$ vapor at 260°C for 3 h. The recombination velocity was reduced from 405 cm/s (as-deposited $SiO_x$) to 13 cm/s. These results show that high-pressure $H_2O$ vapor heating improved the properties at the $SiO_2$/Si interface. The initial $SiO_x$ films had high densities of interface trap states of $\sim 10^{12}$ $cm^{-2}eV^{-1}$ and fixed oxide charges of $\sim 10^{12}$ $cm^{-2}$, as shown in Fig. 3. According to the Shockley-Read-Hall theory,[9–11] interface trap state increases the effective surface recombination velocity. On the other hand, a high density of fixed oxide charges induces high electrical field in the oxide layer and band bending in the silicon surface region, which results in an increase in carrier density. A high carrier density at the $SiO_2$/Si interface reduces the effective surface recombination velocity because of the reduction of the capture cross section of carriers. The reduction of both the densities of the interface trap states and the fixed oxide charges by heat treatment with high-pressure $H_2O$ vapor shown in Fig. 3 means that the marked reduction of the effective surface recombination velocity after heat treatment as shown in Fig. 4 was achieved by the improvement of interface properties accompanied with the reduction of the density of interface trap states. Figure 5 shows changes in the effective carrier lifetime and the effective surface recombination velocity as a function of time when samples were kept under the illumination of a halogen lamp with in 300 mW/$cm^2$ in air at 30°C as well as in the dark after treatment at 260°C with $2.1 \times 10^6$ Pa $H_2O$ vapor for 3 h. There were no decrease in the effective carrier lifetime and no increase in the effective surface recombination velocity 8000 h after keeping the sample in the dark and 1200 h after keeping it under illumination at 300 mW/$cm^2$. These results suggest that stable $SiO_x$/Si interfaces were formed at low temperature by the simple heating method using high-pressure $H_2O$ vapor.

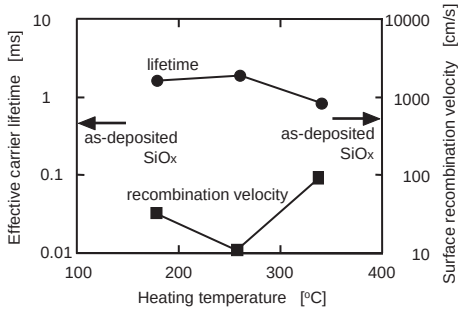


Fig. 4. Effective carrier lifetime and surface recombination velocity for 5000 Ωcm P-type silicon coated with $SiO_x$ films as functions of heating temperature for heat treatment with high-pressure $H_2O$ vapor. $H_2O$ vapor pressure was $1.0 \times 10^6$ Pa (saturation) at 180°C, $2.1 \times 10^6$ Pa at 260°C and $2.4 \times 10^6$ Pa at 340°C.

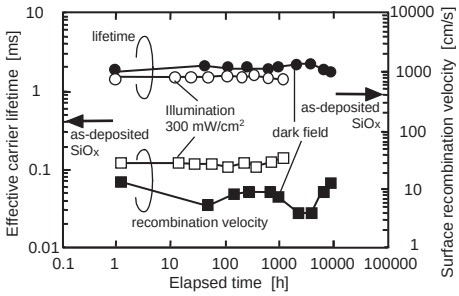


Fig. 5. Changes in the effetive carrier lifetime and the surface recombination velocity as a function of time when samples were kept under the illumination of a halogen lamp with an intensity of 300 mW/$cm^2$ in air at 30°C as well as in the dark after treatment at 260°C with $2.1 \times 10^6$ Pa $H_2O$ vapor for 3 h.

Moreover, we investigated the field effect passivation of silicon surface using present technologies. We initially used 50 Ωcm n-type silicon wafer both of surfaces of which had 90-nm-thick $SiO_2$ layers formed by the thermal oxidation method in HCl ambient. Because the initial $SiO_2$/Si interfaces had very good properties, the effective carrier lifetime was 1.4 ms, as shown in Fig. 6. $SiO_x$ films 210 nm thick were additionally deposited on both surfaces by thermal evaporation at room temperature. The carrier lifetime markedly increased from 1.4 to 4.6 ms after $SiO_x$ deposition, as shown in Fig. 6. This increase in the effective lifetime clearly shows that field effect passivation was caused by $SiO_x$ top layers. A high electrical field of ~1 MV/cm was induced in the underlying thermally grown $SiO_2$ by the high density of positive fixed charges of $\sim 2 \times 10^{12}$ $cm^{-2}$ located in the top defective $SiO_x$ films. The electrical field induced band bending and increased the density of electron carriers. The high carrier density reduced the carrier capture cross section and the effective carrier recombination velocity. If the maximum effective lifetime of 4.6 ms was assumed as the bulk lifetime of silicon, the effective carrier recombination velocity was estimated to be 12 cm/s for initial thermally grown $SiO_2$/Si interfaces. No change in the effective lifetime was observed when samples were kept for 3500 h in air at room temperature. This suggests that this field effect passivation using the

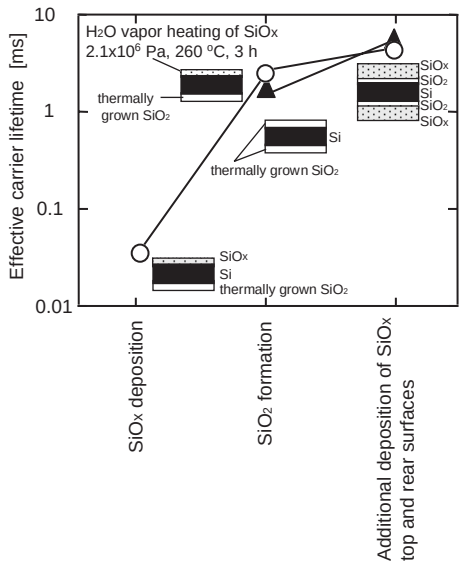


Fig. 6. Effective carrier lifetime for (1-1) the top surface coated with as-deposited $SiO_x$ films with a thickness of 160 nm and the rear surface with 90-nm-thick thermally grown $SiO_2$ films (open circle), (1-2) treated at 260°C with $2.1 \times 10^6$ Pa $H_2O$ vapor for 3 h (open circle), (1-3) additional deposition of $SiO_x$ films 210 nm thick to both surfaces (open circle), (2-1) both surfaces coated with 90-nm thick-thermally grown $SiO_2$ films (solid triangle), (2-2) additional deposition of $SiO_x$ films 210 nm thick to both surfaces (solid triangle).

$SiO_x$ top layer is stable. We also investigated the application of heat treatment with high-pressure $H_2O$ vapor to field effect passivation. The thermally grown $SiO_2$ layer at one side of initial samples was removed. $SiO_x$ film with a thickness of 160 nm was deposited on the bare silicon surface. Although the effective lifetime was as short as 0.03 ms because of the defective as-deposited $SiO_x$ layer, the heat treatment at 260°C with $2.1 \times 10^6$ Pa $H_2O$ vapor for 3 h changed $SiO_x$ to $SiO_2$ and increased the effective lifetime to 2.0 ms because the density of interface trap states was reduced to the order of $10^{10}\,cm^{-2}eV^{-1}$, as shown in Fig. 3. This resulted in a low recombination velocity of 1.7 cm/s, which was lower than that of thermally grown $SiO_2$/Si interfaces. The additional deposition of 200 nm $SiO_x$ films on the $SiO_2$ layer increased the effective lifetime to 4.3 ms, as shown in Fig. 6. Field effect passivation also occurred by the combination of good $SiO_2$/Si interfaces with remote defective $SiO_x$ layers.

The experimental results confirmed the possibility of surface passivation at low temperatures using simple heat treatment with high-pressure $H_2O$ vapor. Moreover, defective $SiO_x$ films can be used for the effective field effect passivation. The initial $SiO_x$ films that were thermally evaporated have a high density of fixed oxide charges. $SiO_x$ films also induced a high density of interface trap states at $SiO_x$/Si, which results in a high effective carrier recombination velocity and a low effective carrier lifetime, as shown in Figs. 3 and 4. Field effect passivation does not occur in the $SiO_x$/Si sample because the accumulation of free carriers at the interfaces is not achieved due to the high density of trap states. The reduction of the density of the trap states is essential for the reduction of effective carrier recombination velocity. Heat treatment with high-pressure $H_2O$ vapor leads to the reduction of effective carrier recombination velocity because it reduces the density of interface trap states to the order of $10^{10}\,cm^{-2}eV^{-1}$, as shown in Fig. 3, although it reduces the density of fixed oxide charges to $2 \times 10^{11}\,cm^{-2}$. Field effect passivation must be, therefore, much lower for $SiO_2$/Si after heat treatment with high-pressure $H_2O$ vapor. The $SiO_x$/$SiO_2$ double-layered structure formed by additional $SiO_x$ deposition after heat treatment realizes the very good $SiO_2$/Si interfaces and field effect passivation caused by fixed oxide charge apart from the interfaces. The process steps are simply conducted at low temperatures. No toxic material or plasma is necessary. These are useful information for the surface passivation of photovoltaic devices.

## 4. Summary

We applied high-pressure $H_2O$ vapor heating in order to improve the $SiO_x$ film and $SiO_x$/Si interface properties for passivation of silicon surface. $SiO_x$ films were deposited on p-type CZ silicon substrates by thermal evaporation in vacuum. Marked changes in the optical absorption band due to Si–O–Si antisymmetric stretching vibration mode for $SiO_x$ films revealed that the Si–O–Si bonding network became similar to that of the thermally oxidized $SiO_2$ through high-pressure $H_2O$ vapor heating at 260–340°C. The peak wave number increased to $1077\,cm^{-1}$ and the FWHM of the Si–O absorption band decreased to $72\,cm^{-1}$ by heat treatment. The volume density of the Si–O bonds increased with a low activation energy of 0.035 eV when heat treatment was conducted at a $H_2O$ pressure of $1.0 \times 10^6$ Pa for the heat treatment. The density of dangling bonds due to oxygen vacancies was also reduced to $\sim 10^{15}\,cm^{-3}$. The density of fixed positive charges was markedly reduced from $2.0 \times 10^{12}\,cm^{-2}$ to $2 \times 10^{11}\,cm^{-2}$ by heat treatment at 260°C at $2.1 \times 10^6$ Pa $H_2O$ vapor because the number of Si dangling bonds in $SiO_x$ film was reduced through oxidation in high-pressure $H_2O$ vapor. The density of interface trap states was also reduced from $1.7 \times 10^{12}$ to $2 \times 10^{10}\,cm^{-2}eV^{-1}$ by heat treatment at 260°C. The Si dangling bonds at $SiO_2$/Si interfaces were effectively terminated. The effective carrier recombination velocity was reduced from 405 cm/s (as-deposited $SiO_x$) to 13 cm/s by heat treatment with $2.1 \times 10^6$ Pa $H_2O$ vapor at 260°C for 3 h for the $SiO_x$ film. The effective recombination velocity was kept at a low value of ~10 cm/s, 8000 h after the samples were kept at room temperature in air. Furthermore, there is no change in the effective recombination velocity of 27 cm/s, 1200 h after keeping the samples under illumination with an intensity of $300\,mW/cm^2$ in air. Field effect passivation was demonstrated using a double-layered structure fabricated with a combination of $SiO_2$ formation by heat treatment with high-pressure $H_2O$ vapor at 260°C with the formation of a remote defective $SiO_x$ layer on $SiO_2$. Heat treatment with high-pressure $H_2O$ vapor realized $SiO_2$/Si interfaces with a long carrier lifetime of 2.0 ms, which was longer than that of thermally grown $SiO_2$/Si interfaces. Additional deposition of $SiO_x$ increased the effective carrier lifetime to 4.3 ms because a high electrical field of ~1 MV/cm was induced at the bottom $SiO_2$ layer by remote defective $SiO_x$ layers. An effective recombination velocity lower than 1.7 cm/s was estimated. No change in the effective carrier lifetime and the recombination velocity was observed for 3500 h. Heat treatment with high-pressure $H_2O$ vapor will be useful for silicon surface passivation at low temperatures.

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