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# High-pressure $H_2O$ vapor heating used for passivation of $SiO_2$/Si interfaces

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**Abstract**

High-pressure $H_2O$ vapor heating was applied to oxidation of $SiO_x$ ($x < 2$) films formed on silicon substrates at room temperature by thermal evaporation in vacuum, in order to improve properties of $SiO_x$/Si interfaces for passivation of silicon surfaces. The $SiO_x$ films were oxidized with an activation energy of 0.035 eV. The spin density of unpaired electron decreased from $2.3 \times 10^{17}$ to $1.4 \times 10^{15}\,cm^{-3}$ by the heat treatment at 260°C with $2.1 \times 106$ Pa $H_2O$ vapor for 3 h. The surface recombination velocity for excess carriers decreased from 405 (as deposited $SiO_x$ film) to 13 cm/s. There was no change in the surface recombination velocity after keeping the samples at an atmospheric pressure and at room temperature for 8000 h. Suitable passivation of silicon surface was achieved by simple heating with high-pressure $H_2O$ vapor at low temperature. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* $SiO_x$; Total Si-O absorption; Activation energy of oxidation; Surface recombination velocity

## 1. Introduction

Surface passivation technologies at low temperatures have been widely studied to achieve simple and low-cost process for the solar cells. Plasma-enhanced chemical vapor deposition (PECVD) has become the conventional method, which realized low surface recombination velocity of silicon smaller than 100 cm/s with low processing temperatures between 250°C and 350°C [1,2]. On the other hand, we have reported a simple heating method using high-pressure $H_2O$ vapor at approximately 300°C for the improvement of the bulk properties of $SiO_2$ films and $SiO_2$/Si properties. The high-pressure $H_2O$ vapor heating reduces the density of fixed oxide charges in films

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and the density of the interface trap states for $SiO_2$/Si formed by PECVD [3]. This heating method also decreases the bonding strain at the $SiO_2$/Si interfaces [4]. In this paper, we present the surface passivation on silicon using high-pressure $H_2O$ vapor heating at 180–340°C. The Si–O–Si bonding networks of the $SiO_x$ films deposited by thermal evaporation in vacuum are changed similar to that of thermally oxidized $SiO_2$ films by the heating method. Activation energy of oxidation reaction and change in the density of dangling bonds by the heat treatment are discussed. We report reduction in the surface recombination velocity of excess minority carriers at the $SiO_x$/Si interfaces by the heat treatment with high-pressure $H_2O$ vapor and its stability under keeping samples in air.

## 2. Experimental

$SiO_x$ films were formed on the silicon surface at room temperature by thermal evaporation of powdered SiO with a purity of 99.99% in vacuum [5]. The samples and pure $H_2O$ were placed in a pressure-proof stainless-steel chamber using a metal seal. The chamber was put in an electric furnace. The $H_2O$ evaporated during heating and the pressure in the chamber increased. The samples were heated with $1.0 \times 10^6$–$2.4 \times 10^6$ Pa $H_2O$ vapor at 180–340°C for 3 h. In order to investigate changes in Si–O bonding states for the samples heated with $1.0 \times 10^6$ Pa $H_2O$ vapor, the optical absorption spectra caused by the Si–O antisymmetric stretching vibration mode was observed by Fourier transform spectrometer (FTIR) for the samples as $SiO_x$ deposition and after the heat treatment. The density of the dangling bond was estimated by electron spin resonance (ESR) method that observed the microwave absorption associated with the unpaired electrons. We also investigated properties of $SiO_2$/Si interfaces. The effective excess carrier lifetime for p-type silicon with an orientation of (1 0 0) and resistivity of 5000 Ω cm was investigated by observation decay in the reflectivity of 14 GHz-microwave probe when the excess minority carriers were induced by 200 ns-pulsed laser irradiation with a wavelength of 904 nm, for the estimation of the recombination velocity at the Si surfaces. Changes in the carrier lifetime and the surface recombination velocity with time were investigated when the samples were kept under dark field and light illumination with an intensity of 300 $mW/cm^2$ in air at room temperature.

## 3. Results and discussions

The total infrared absorption caused by the Si–O–Si antisymmetric stretching vibration mode was delivered from integration of the absorption coefficient between 800 and 1300 $cm^{-1}$. Fig. 1 indicates the total infrared absorption as a reciprocal function of heating temperature for the $SiO_x$ films, which is heated with $1.0 \times 10^6$ Pa $H_2O$ vapor at 180–340°C for 3 h. A low total Si–O absorption of $1.39 \times 10^6$ $cm^{-2}$, corresponding to 0.46 times that of thermally grown $SiO_2$ films was obtained for $SiO_x$ films immediately after deposition. This shows that there are many oxygen vacancies

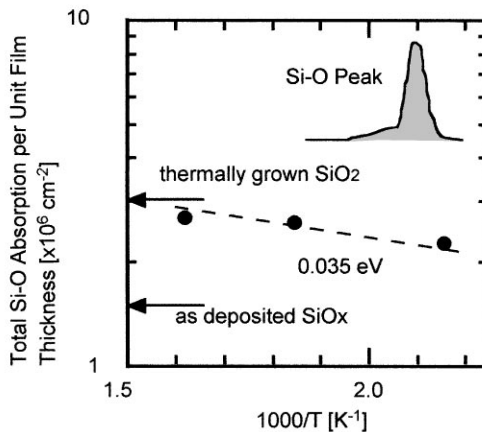


Fig. 1. The total infrared absorption caused by the Si–O–Si antisymmetric stretching vibration mode delivered from integration of the absorption coefficient between 800 and 1300 $cm^{-1}$ as a function of reciprocal heating temperature for treatment with $1.0 \times 10^6$ Pa $H_2O$ vapor for 3 h.

in the initial $SiO_x$ films. The total Si–O absorption was increased as the heating temperature increased for treatment with $1.0 \times 10^6$ Pa $H_2O$ vapor. It reached to $2.65 \times 10^6$ $cm^{-2}$, corresponding to 0.87 times that of thermally oxidized $SiO_2$, for the heat treatment at 340°C. This shows that the $SiO_x$ films were changed to $SiO_2$ via oxidation of $SiO_x$ and increase of number of SiO bonding during the present treatment at low temperatures. As thermally grown $SiO_2$ films has $4.6 \times 10^{22}$ $cm^{-3}$ of Si–O bonding number, number of the Si–O bonding was increased from $2.1 \times 10^{22}$ $cm^{-3}$ (initial) to $4 \times 10^{22}$ $cm^{-3}$ for the heat treatment of $SiO_x$ films at 340°C with $1.0 \times 10^6$ Pa $H_2O$–vapor. The activation energy of increase in the total Si–O absorption with per film thickness was obtained as 0.035 eV. This low activation energy reveals that the high-pressure $H_2O$ vapor heating could oxidize the $SiO_x$ films and change them to $SiO_2$ films at a low temperature. Fig. 2 shows the spin density associated with the unpaired electrons caused by silicon dangling bonds (*E*'center) as a reciprocal function of heating temperature for the treatment for 3 h at $1.0 \times 10^6$ Pa $H_2O$ vapor. High spin density of $2.3 \times 10^{17}$ $cm^{-3}$ was observed for initial $SiO_x$ films. This value is close to the density of fixed oxide charges that is given from measurements of capacitance–voltage characteristic of metal-oxide-semiconductor capacitor reported previously [6]. This is very low compared with the low density of Si–O bonds, $2.1 \times 10^{22}$ $cm^{-3}$, estimated from the measurement of total Si–O absorption. We consider that the small defects would have resulted from intrinsic structure as Si–Si and Si–O bonds in the $SiO_x$ films. The spin density of defects was widely reduced after the heat treatment with high-pressure $H_2O$ vapor. The defect density decreased with increase of treatment temperature. The defect density was reduced to $1.4 \times 10^{15}$ $cm^{-3}$ by the $1.0 \times 10^6$–Pa $H_2O$ vapor heating at 260°C for 3 h. However, the defect density slightly increased to $3.7 \times 10^{15}$ $cm^{-3}$ with increase of heating temperature to 340°C. Fig. 3 shows the effective excess carrier lifetime and the surface

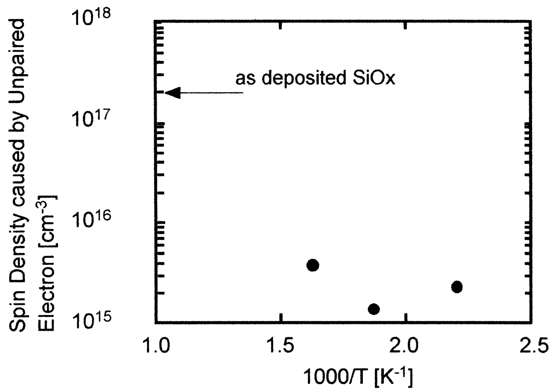


Fig. 2. The spin density associated with the unpaired electrons caused by dangling bonds as a function of reciprocal heating temperature for treatment with $1.0 \times 10^6$ Pa $H_2O$ vapor for 3 h.

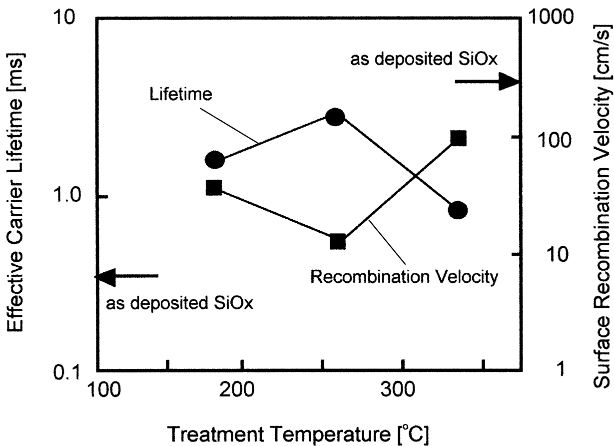


Fig. 3. The effective excess carrier lifetime for p-type silicon and the surface recombination velocity estimated from the effective lifetime as functions of heating temperature. The pressure of $H_2O$ vapor were $1.0 \times 10^6$ Pa at 180°C, $2.1 \times 10^6$ Pa at 260°C and $2.4 \times 10^6$ Pa at 340°C, respectively.

recombination velocity for p-type silicon coated with the $SiO_x$ films as functions of heating temperature for treatment with high-pressure $H_2O$ vapor. The recombination velocity was estimated by the equation

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

where $\tau_{\text{eff}}$ is the effective lifetime, $\tau_{\text{b}}$ is the bulk lifetime, $D$ is the thickness of the silicon wafers, $S_{\text{f}}$ and $S_{\text{r}}$ are the recombination velocity at the front and rear surfaces,

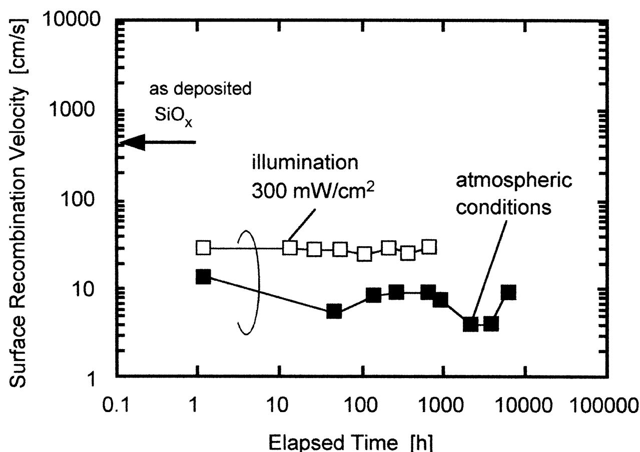


Fig. 4. The surface recombination velocity estimated from the effective carrier lifetime as a function of elapsed time of keeping samples in air at room temperature in dark field and under illumination with intensity of 300 mW/cm$^2$ after the $2.1 \times 10^6$ Pa $H_2O$ vapor heating at 260°C for 3 h.

respectively. The bulk lifetime $\tau_b$ was estimated when the silicon surfaces were coated with ethyl alcohol liquid containing 3 wt% iodine, which realized a surface recombination velocity of 10 cm/s. Low effective lifetime of 0.4 ms was observed for the initial sample with a surface coated with the as-deposited $SiO_x$ films. Marked increase of the effective lifetime was obtained after the heat treatment. Especially, the effective lifetime increased to 1.8 ms by the 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 (as-deposited $SiO_x$) to 13 cm/s by heating at 260°C. These results show that the high-pressure $H_2O$ vapor heating vastly improved the properties of the $SiO_x$/Si interfaces. Fig. 4 shows change in the surface recombination with time after the high-pressure $H_2O$ vapor treatment at 260°C with $2.1 \times 10^6$ Pa $H_2O$ vapor for 3 h. Samples were kept in air at room temperature in dark field and illumination with an intensity of 300 mW/cm$^2$. There was no increase in the surface recombination velocity after keeping the samples in the dark field in air for 8000 h. No increase in the surface recombination velocity was observed after keeping the samples under illumination with an intensity of 300 mW/cm$^2$ for 720 h. These results suggest that suitable $SiO_x$/Si interface is formed at low temperature by the simple heating method using high-pressure $H_2O$ vapor.

## 4. Summary

We investigated improvement of $SiO_2$/Si interface properties using the heat treatment with high-pressure $H_2O$ vapor for passivation of silicon surfaces. The activation energy of the oxidization reaction for the $SiO_x$ films deposited by thermal evaporation was estimated as 0.035 eV from changes in the total Si–O infrared absorption. The

spin density of the unpaired electron for the $SiO_x$ film decreased from $2.3\times10^{17}$ to $1.4\times10^{15}\,cm^{-3}$ by the heat treatment at 260°C with $2.1\times10^{6}$ Pa $H_2O$ vapor for 3 h. The surface recombination velocity of the electron minority carriers was reduced from 405 (as deposition) to 13 cm/s by the heat treatment at 260°C with $2.1\times10^{6}$ Pa $H_2O$ vapor for 3 h. The recombination velocity was about 10 cm/s keeping the samples in the dark field in air for 8000 h. It was 27 cm/s during when the samples were kept under illumination with an intensity of 300 mW/cm$^2$ in air for 720 h. Suitable surface passivation was achieved by a simple heating method using high-pressure $H_2O$ vapor at a lower temperature than 300°C.

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