Field effect surface passivation of SiO$_2$/Si interfaces by heat treatment with high-pressure H$_2$O vapor

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Abstract

We investigated a simple field effect passivation of the silicon surfaces using the high-pressure H$_2$O vapor heating. Heat treatment with $2.1 \times 10^6$ Pa H$_2$O vapor at 260°C for 3 h reduced the surface recombination velocity from 405 cm/s (before the heat treatment) to 38 cm/s for the thermally evaporated SiO$_x$ film/Si. Additional deposition of 140 nm-SiO$_x$ films ($x < 2$) with a high density of fixed positive charges on the SiO$_2$/Si samples further decreased the surface recombination velocity to 22 cm/s. We also demonstrated the field effect passivation for n-type silicon wafer coated with thermally grown SiO$_2$. Additional deposition of 210 nm SiO$_x$ films on both the front and rear surfaces increased the effective lifetime from 1.4 to 4.6 ms. Combination of thermal evaporation of SiO$_x$ film and the heat treatment with high-pressure H$_2$O vapor is effective for low-temperature passivation of the silicon surface. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Additional deposition of SiO$_x$; Density of fixed positive charges; Effective carrier lifetime

1. Introduction

Defects reduction and surface passivation are very important for technology of device fabrications. Low cost and simple technologies have been investigated. For example, hydrogenation using hydrogen plasma or hydrogen radical has been studied widely [1,2]. We had previously reported a simple heat method with high-pressure H$_2$O vapor at approximately 300°C for reduction of the bonding strain at thermally...
grown SiO$_2$/Si interfaces. High-pressure H$_2$O vapor heating also realizes reduction in the density of the interface trap states and the fixed positive charges for the SiO$_2$/Si surfaces [3–5]. In this paper, we report field effect passivation of the silicon surfaces using the formation of defective SiO$_x$ films and high-pressure H$_2$O vapor heating. We report an increase in the effective lifetime of excess carriers and a decrease in the surface recombination velocity by combination of simple technologies, the thermal evaporation of SiO$_x$ at room temperature (RT) and heat treatment with high-pressure H$_2$O vapor at 260°C.

2. Experimental

The SiO$_x$ films (30–220 nm) were deposited on p-type silicon substrates with a resistivity of 5000Ω·cm by thermal evaporation of powdered SiO with a purity of 99.99% in vacuum at a room temperature. The samples and pure H$_2$O were then placed into a pressure-proof stainless-steel chamber using a metal seal. The chamber was put on a heater plate. The samples were heated with $2.1 \times 10^6$ Pa H$_2$O vapor at 260°C for 3 h. This heating condition was determined by increase of the effective surface passivation reported before [5]. The effective lifetimes of excess carriers for p-type silicon were measured by observation 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, for estimation of the recombination velocity at the silicon surfaces. After the measurement, the SiO$_x$ films with a thickness of 140 nm were deposited again on the samples by the thermal evaporation. The effective lifetime was also measured for the samples with the SiO$_x$/SiO$_2$/Si substrate structure. Metal-oxide-semiconductor (MOS) structure was fabricated and its capacitance response to the voltage at 1 MHz was observed to investigate the density of the interface trap states and the fixed positive charges for SiO$_2$/Si samples. Moreover, we also used a good SiO$_2$/Si interface formed on n-type silicon wafer by the thermal oxidation method in HCl ambient. 210 nm SiO$_x$ films were additionally deposited on front and rear surfaces in order to cause field effect passivation. SiO$_2$/Si interfaces were formed on the n-type silicon by $2.1 \times 10^6$ Pa H$_2$O vapor annealing of 160-nm-thick SiO$_x$/Si at 260°C for 3 h after removing oxide layers at the top surface. SiO$_x$. Additional deposition of 200-nm-thick SiO$_x$ films was conducted in order to investigate field effect passivation.

3. Results and discussions

Fig. 1(a) shows the effective lifetime of excess carriers as a function of thickness of the SiO$_2$ layer formed by heat treatment at 260°C with $2.1 \times 10^6$ Pa H$_2$O vapor for 3 h. Low effective lifetimes of about 0.1 ms were measured for sample with as-deposited SiO$_x$ films. After the heat treatment, the effective lifetime markedly increased to about 1 ms. The SiO$_x$ films were oxidized and changed into SiO$_2$ films with low interface trap states by high-pressure H$_2$O vapor heating at 260°C. The
Fig. 1. The effective carrier lifetime (a), and the surface recombination velocity estimated from the effective lifetime (b), as functions of SiO$_2$ film thickness for p-type silicon coated with the SiO$_2$ films formed by 2.1 × 10$^6$ Pa H$_2$O vapor heating of SiO$_x$ films at 260°C for 3h.

Improvement of SiO$_2$/Si interface properties resulted in an increase in the minority carrier lifetime. The lifetime gradually increased as the SiO$_x$ film thickness increased. Further increase in the effective lifetime of about 2 ms was achieved by additional deposition of the SiO$_x$ films with a thickness of 140 nm after the heat treatment. These results suggested that the increase in the effective lifetime was caused by field effect by high density of fixed positive charges (≈ 10$^{12}$ cm$^{-2}$) located in additionally deposited top SiO$_x$ films. Fig. 1(b) demonstrates the surface recombination velocity as a function of thickness of the initial SiO$_2$ layer treated with heating in high-pressure H$_2$O vapor. The surface recombination velocity was estimated using the equation

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \frac{s_r}{D} + \frac{s_r}{D},$$

where $\tau_{\text{eff}}$ is the effective carrier lifetime, $\tau_b$ is the bulk lifetime, $s_r$ is the surface recombination velocity, and $D$ is the diffusion constant.
where \( \tau_{\text{eff}} \) is the effective lifetime, \( \tau_b \) is the bulk lifetime, \( D \) is the thickness of the silicon wafers, \( S_f \) and \( S_r \) are the surface recombination velocity on the front and rear surfaces, respectively. The bulk lifetime \( \tau_b \) was estimated when the silicon surfaces were coated with ethyl-alcohol liquid containing 3 wt% iodine, whose passivation achieves a surface recombination velocity of 10 cm/s. The surface recombination velocity was reduced from 405 to 38 cm/s after heat treatment with \( 2.1 \times 10^6 \) Pa H\(_2\)O vapor at 260°C because of improvement of initial SiO\(_2\) films and SiO\(_2\)/Si interface properties. A further decrease in the recombination velocity to 22 cm/s was obtained after an additional deposition of 140 nm SiO\(_x\) film on the SiO\(_2\) film because of increase of the minority carrier density due to the positive electrical field caused by defective SiO\(_x\) formation via the good SiO\(_2\) intermediate layer. Fig. 3 shows the density of interface trap states and the fixed positive charges given from capacitance responses to 1 MHz voltage for Al gate MOS capacitors for the samples after the SiO\(_2\) formation by \( 2.1 \times 10^6 \) Pa H\(_2\)O vapor heating at 260°C and after additional SiO\(_x\) deposition with a thickness of 140 nm, respectively. A slight decrease in the density of the interface trap states was observed from \( 2.5 \times 10^{11} \) to \( 1.5 \times 10^{11} \text{cm}^{-2}\text{eV}^{-1} \) through additional deposition of SiO\(_x\) films as shown in Fig. 2. On the other hand, a marked increase in the density of fixed positive charges was observed from \( 1.1 \times 10^{11} \) to \( 1.4 \times 10^{12} \text{cm}^{-2} \) after the 140 nm SiO\(_x\) deposition. These characteristics suggest that improvements of effective carrier lifetime and recombination velocity for p-type silicon wafers were achieved by the field effect passivation. We also performed the field effect passivation using the thermally evaporated SiO\(_x\) on thermally grown SiO\(_2\) layers as shown in Fig. 3. An effective carrier lifetime of 1.4 ms was observed for the silicon coated with

Fig. 2. The density of fixed positive charges and the density of interface trap states with conditions of the sample after SiO\(_2\) formation by the heat treatment of SiO\(_x\) film deposited on p-type silicon with \( 2.1 \times 10^6 \) Pa H\(_2\)O vapor at 260°C for 3 h and after additional deposition of 140 nm SiO\(_x\) films.
Fig. 3. The 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$_2$O 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).

thermally oxidized SiO$_2$ films with a thickness of 91 nm for both surfaces. The effective lifetime markedly increased to 4.6 ms by additional deposition of 210 nm SiO$_x$ films on the front and back surfaces of the silicon. This result shows that the recombination velocity at silicon surface was reduced by electrical field effect of thermal evaporation of defective SiO$_x$ with high density of the fixed positive charges. An effective lifetime of 4.3 ms has been observed when keeping samples for 3500 h in air at room temperature after the top SiO$_x$ deposition. This suggests that the present field effect passivation using the SiO$_x$ is stable. After the experiment, the SiO$_2$ layers were removed at the top surface. The SiO$_x$ film with a thickness of 160 nm was then deposited on the surface. A heat treatment at 260 °C with $2.1 \times 10^6$ Pa H$_2$O vapor for 3 h was conducted. As a result of the treatment, the effective lifetime increased from 0.03 ms (as deposited SiO$_x$) to 2.0 ms. This means that high-pressure H$_2$O vapor heating realized SiO$_2$/Si interfaces as good as thermally grown SiO$_2$/Si interfaces. 200 nm SiO$_x$ films were additionally deposited on both front and rear surfaces again. The effective lifetime was further increased to 4.3 ms as shown in Fig. 3. The electrical field passivation also occurred at the SiO$_2$/Si interfaces. Band bending at silicon
surfaces was caused by the electrical field induced by additional deposition of defective SiO\textsubscript{x} films; A high density of electrons was caused at the surface and the surface recombination velocity of silicon was reduced because of reduction of the capture cross section of carriers. The present simple field effect passivation using combination of formation of SiO\textsubscript{x} films with high-pressure H\textsubscript{2}O vapor heating at low temperatures would be useful for surface passivation for photovoltaic devices.

4. Summary

SiO\textsubscript{x} film formation and high-pressure H\textsubscript{2}O vapor heating were applied to field effect passivation of silicon surfaces. The surface recombination velocity was 1150 cm/s when 220 nm SiO\textsubscript{x} film was deposited on p-type silicon substrate at room temperature. It was reduced to 38 cm/s after the 2.1 × 10\textsuperscript{6} Pa H\textsubscript{2}O vapor heating at 260°C for 3 h. Additional deposition of SiO\textsubscript{x} film with a thickness of 140 nm reduced the surface recombination velocity to 22 cm/s because field effect passivation occurred with increase of the fixed positive charges of SiO\textsubscript{x} films from 1.1 × 10\textsuperscript{11} to 1.4 × 10\textsuperscript{12} cm\textsuperscript{-2}. We also demonstrated field effect passivation at good SiO\textsubscript{2}/n-type Si interface formed by thermal oxidation. The effective carrier lifetime increased from 1.4 to 4.6 ms as a result of the additional SiO\textsubscript{x} deposition with a thickness of 210 nm on the thermally grown SiO\textsubscript{2} layers. On the same n-type silicon surfaces, field effect passivation was achieved by combination of heat treatment of initial SiO\textsubscript{x} film in 2.1 × 10\textsuperscript{6} Pa H\textsubscript{2}O vapor for 3 h at 260°C with additional 200-nm-thick SiO\textsubscript{x} films deposition. The effective carrier lifetime increased to 4.3 ms. No change in the effective carrier lifetime 3500 h after keeping samples in air at room temperature means that the present field effect passivation is stable. The present simple method will be effective for surface passivation of silicon surface.

References