ELSEVIER

Solar Energy Materials & Solar Cells 65 (2001) 565–570

Solar Energy Materials & Solar Cells

www.elsevier.com/locate/solmat

Field effect surface passivation of SiO_2/Si interfaces by heat treatment with high-pressure H_2O vapor

K. Sakamoto, K. Asada, T. Sameshima*

Tokyo University of Agriculture & Technology, 2-24-16 Nakamachi, Koganei, Tokyo 184-8588, Japan

Abstract

We investigated a simple field effect passivation of the silicon surfaces using the high-pressure H_2O vapor heating. Heat treatment with 2.1×10^6 Pa H_2O 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_2O 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_2O vapor at approximately 300°C for reduction of the bonding strain at thermally

* Corresponding author. Tel.: + 81-42-388-7436; fax: + 81-42-388-7436.

E-mail address: tsamesim@cc.tuat.ac.jp (T. Sameshima).

PII: S0927-0248(00)00142-2

grown SiO_2/Si interfaces. High-pressure H_2O 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_2O 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_2O vapor at 260°C.

2. Experimental

The SiO_x films (30–220 nm) were deposited on p-type silicon substrates with a resistivity of 5000 Ω cm by thermal evaporation of powdered SiO with a purity of 99.99% in vacuum at a room temperature. The samples and pure H_2O 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 2.1×10^6 Pa H_2O 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 2.1×10^6 Pa H_2O 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 2.1×10^6 Pa H_2O 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_2O vapor heating at 260°C. The

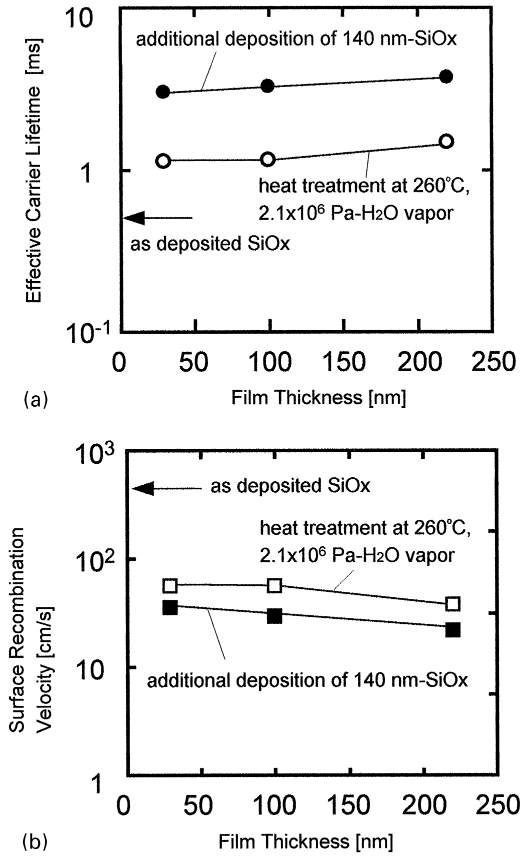

Fig. 1. The effective carrier lifetime (a), and the surface recombination velocity estimated from the effective lifetime (b), as functions of SiO_2 film thickness for p-type silicon coated with the SiO_2 films formed by 2.1×10^6 Pa H_2O vapor heating of SiO_x films at 260°C for 3 h.

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 ($\sim 10^{12}\,\mathrm{cm}^{-2}$) 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_2O vapor. The surface recombination velocity was estimated using the equation

$$\frac{1}{\tau_{\mathrm{eff}}} = \frac{1}{\tau_{\mathrm{b}}} + \frac{s_{\mathrm{f}}}{D} + \frac{s_{\mathrm{r}}}{D},$$

where τ_{eff} is the effective lifetime, τ_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 τ_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 2.1×10^6 Pa H_2O 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 2.1×10^6 Pa H_2O 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 2.5×10^{11} to $1.5 \times 10^{11}\,cm^{-2}\,eV^{-1}$ 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 1.1×10^{11} to $1.4 \times 10^{12}\,cm^{-2}$ after the 140 nm SiO_x deposition. These characteristics suggest that improvements of effective carrier lifetime and recombination velocity for p-type silicon wafer 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

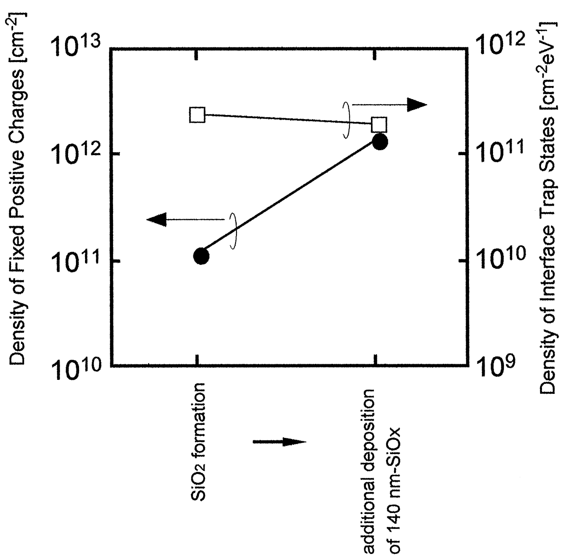

Fig. 2. The density of fixed positive charges and the density of interface trap states with conditions of the sample after SiO_2 formation by the heat treatment of SiO_x film deposited on p-type silicon with 2.1×10^6 Pa H_2O vapor at 260°C for 3 h and after additional deposition of 140 nm SiO_x films.

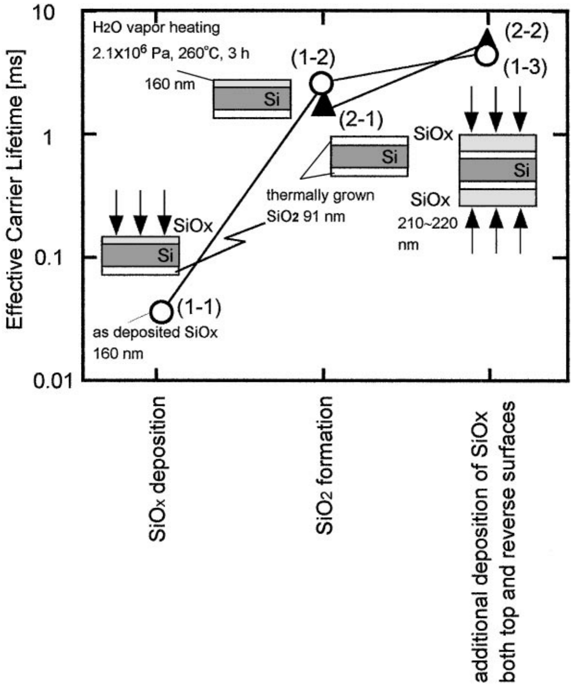

Fig. 3. The effective carrier lifetime for (1–1) the top surface coated with as-deposited SiO_x films with a thickness of 160 nm and the rear surface with 90 nm thick thermally grown SiO_2 films (open circle), (1–2) treated at 260°C with 2.1×10^6 Pa H_2O vapor for 3 h (open circle), (1–3) additional 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).

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 2.1×10^6 Pa H_2O 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_2O 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_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_x films with high-pressure H_2O vapor heating at low temperatures would be useful for surface passivation for photovoltaic devices.

4. Summary

SiO_x film formation and high-pressure H_2O vapor heating were applied to field effect passivation of silicon surfaces. The surface recombination velocity was 1150 cm/s when 220 nm SiO_x film was deposited on p-type silicon substrate at room temperature. It was reduced to 38 cm/s after the 2.1×10^6 Pa H_2O vapor heating at 260°C for 3 h. Additional deposition of SiO_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_x films from 1.1×10^{11} to 1.4×10^{12} cm^{-2}. We also demonstrated field effect passivation at good SiO_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_x deposition with a thickness of 210 nm on the thermally grown SiO_2 layers. On the same n-type silicon surfaces, field effect passivation was achieved by combination of heat treatment of initial SiO_x film in 2.1×10^6 Pa H_2O vapor for 3 h at 260°C with additional 200-nm-thick SiO_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

[1] S.J. Pertron, J.W. Corbett, T.S. Shi, Appl. Phys. A 43 (1987) 153.
[2] H. Nagayoshi, Y. Onozawa, M. Ikeda, M. Yamaguchi, Y. Yamamoto, T. Uematsu, T. Saitoh, K. Kamisako, J. Appl. Phys. 35 (1996) L1047.
[3] T. Sameshima, M. Satoh, Jpn. J. Appl. Phys. 36 (1997) L687.
[4] T. Sameshima, K. Sakamoto, M. Satoh, Thin Solid Films 335 (1998) 138.
[5] T. Sameshima, K. Sakamoto, Y. Tsunoda, T. Saitoh, Jpn. J. Appl. Phys. 37 (1998) L1452.