Investigation of Silicon Surface Passivation by Microwave Annealing Using Multiple-Wavelength Light-Induced Carrier Lifetime Measurement

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A simple annealing method using a commercial 2.45 GHz microwave oven is reported to increase the minority carrier lifetime $\tau_{\text{eff}}$ for 4-in.-size 500-μm-thick 20 Ω·cm n-type silicon substrates coated with 100-nm-thermally grown SiO$_2$ layers. The microwave annealing was conducted with 2-mm-thick glass substrates, which sandwiched a silicon sample to maintain the thermal energy in silicon and realize gradual cooling. A 9.35 GHz microwave transmittance measurement system was used to measure $\tau_{\text{eff}}$ in the cases of continuous-wave 635 and 980 nm laser diode (LD) light illuminations. Radio-frequency Ar plasma irradiation at 50 W for 60 s to the top surface of a silicon sample markedly decreased $\tau_{\text{eff}}$ in the range from $6.0 \times 10^{-8}$ to $2.4 \times 10^{-5}$ s and from $4.2 \times 10^{-5}$ to $6.4 \times 10^{-5}$ s in the cases of 635 and 980 nm light illuminations, respectively, while $\tau_{\text{eff}}$ had the same distribution from $1.6 \times 10^{-7}$ to $3.1 \times 10^{-3}$ s for the initial samples. The finite element numerical analysis revealed that Ar plasma irradiation caused high densities of recombination defect states at the silicon top surface in the range from $1.3 \times 10^{13}$ to $5.0 \times 10^{15}$ cm$^{-2}$. Microwave annealing at 700 W for 120 s markedly increased $\tau_{\text{eff}}$ in the range from $8.0 \times 10^{-8}$ to $2.5 \times 10^{-3}$ s, which were close to those of the initial samples. The density of recombination defect states was well decreased by microwave annealing to low values in the range from $7.0 \times 10^{10}$ to $3.4 \times 10^{11}$ cm$^{-2}$. The high $\tau_{\text{eff}}$ achieved by microwave annealing was maintained for a long time above 5000 h.

1. Introduction

The long minority carrier effective lifetime $\tau_{\text{eff}}$ of semiconductors is important for solar cells and photosensors.1–11) A long $\tau_{\text{eff}}$ allows the minority carriers to well diffuse in the whole region of a semiconductor substrate with a low annihilation rate. It therefore results in a high short-circuit current and a high open circuit voltage for semiconductor solar cells. It also gives high photo-sensitivity for photosensor devices. The amount of defect states causing carrier recombination should be reduced for achieving a long $\tau_{\text{eff}}$. Surface passivation and improvement in the crystalline quality of semiconductors are therefore important. Several techniques have been developed for surface passivation, for example, hydrogenation12,13) and high pressure H$_2$O vapor heat treatments.14,15) Thermal annealing is also important to reduce the amount of defects generated during device fabrication processes. We have recently reported a marked decrease in $\tau_{\text{eff}}$ by plasma treatment, which is a very conventional method for semiconductor device fabrication processing.16) Post-annealing is necessary to increase $\tau_{\text{eff}}$ again. Moreover, a short annealing in a low-temperature atmosphere is attractive in the low thermal budget for a low fabrication cost.

In this paper, we report the precise investigation of the change in $\tau_{\text{eff}}$ for n-type silicon substrates by a simple annealing method using a commercial 2.45 GHz microwave oven with no previous substrate heating.17) We apply the present method to the curing of serious carrier recombination defects caused by Ar plasma irradiation. To investigate the change in $\tau_{\text{eff}}$, we developed a system of microwave absorption induced by light illumination at wavelengths of 635 and 980 nm.18–20) The penetration depth at 635 nm was about 3 μm, while it is very deep, 125 μm, for 980 nm light.21) Photo-induced carriers generated in the deep region of semiconductors are alive until they meet carrier recombination defect states when a high density of carrier recombination defect states are localized at the surfaces. Therefore, $\tau_{\text{eff}}$ is high when carrier generation occurs in the deep region far from the surface. On the other hand, $\tau_{\text{eff}}$ is low when carrier generation occurs close to the carrier recombination defect states. In contrast, $\tau_{\text{eff}}$ will not depend on the carrier generation position if the density of carrier recombination defect states is low because a low recombination velocity allows a long carrier diffusion length longer than the substrate thickness. We report the $\tau_{\text{eff}}$ spatial distribution measured by light illumination with the two different wavelengths in the process steps of initial, Ar plasma, and microwave annealing treatments. We discuss carrier recombination velocity and recombination defect states on the basis of numerical analysis of the experimental results of $\tau_{\text{eff}}$. We demonstrate that high $\tau_{\text{eff}}$ and low recombination defect density are achieved by microwave annealing. We also report that the high $\tau_{\text{eff}}$ is maintained for a long time.

2. Experimental Procedure

20Ω·cm n-type silicon substrates with a thickness of 500 μm and a diameter of 4 in. were prepared. The top and rear surfaces were coated with 100-nm-thick thermally grown SiO$_2$ layers. The top surfaces of the samples were irradiated by 13.56 MHz radio-frequency (RF) Ar plasma at 50 W and 1.0 Pa for 60 s, as shown by the schematic image in Fig. 1.16) A sample was placed on a metal plate electrically grounded in a chamber facing a metal electrode. Ar gas was introduced at 5 sccm under evacuation using a turbo-molecular pump. Ar plasma was generated by applying RF voltage at the electrode at room temperature. Samples were subsequently treated with microwave irradiation using a commercial 2.45 GHz microwave oven at 700 W, as shown by the schematic image in Fig. 2. A silicon sample was sandwiched in two 2-mm-thick glass substrates with the low heat conductivity to keep heated energy in the silicon sample, as shown by cross section in Fig. 2. We also heated Ar plasma irradiated-sample at 500°C using a furnace in comparison.

Figure 3 shows a schematic of the 9.35 GHz microwave transmittance measurement system with waveguide tubes, which had a narrow gap for placing a sample wafer. The X–Y moving stage moved the sample to measure the $\tau_{\text{eff}}$. 

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spatial distribution over the whole surface area. Continuous wave (CW) 635 and 980 nm laser diode (LD) lights were introduced in the waveguide tube, as shown in Fig. 3. The light intensities were set at 1.5 and 0.98 mW/cm$^2$ at the sample surface for 635 and 980 nm lights, respectively, to realize the same photon flux between the two-different wavelength lights. The microwave which transmitted samples was rectified using a high-speed diode and was integrated. The integrated voltage was detected by a digital electrometer and analyzed to obtain $\tau_{\text{eff}}$\textsuperscript{18–20}). We constructed a finite-element numerical calculation program including theories of carrier generation associated with optical absorption coefficients\textsuperscript{21)}, carrier diffusion, and annihilation \textsuperscript{18,19,22)} for estimating the surface recombination velocity at the top surface $S_{\text{top}}$ and the rear surface $S_{\text{rear}}$ and the bulk lifetime $\tau_b$. The most possible $S_{\text{top}}$ and $S_{\text{rear}}$ were determined by best coincidence between experimental and calculated $\tau_{\text{eff}}$.

Figure 4 shows demonstration of the calculation of $\tau_{\text{eff}}$ as a function of the wavelength of the light illuminated to the top surface under conditions of 20 $\Omega$ cm n-type 500-µm-thick silicon substrate with $\tau_b$ of 0.1 s, $S_{\text{rear}}$ of 10 cm/s, and different $S_{\text{top}}$ values ranging from 10 to 10000 cm/s.

3. Results and Discussion

The change in $\tau_{\text{eff}}$ with the duration of microwave irradiation was first investigated. Figure 5(a) shows $\tau_{\text{eff}}$ as a function of duration of 2.45 GHz microwave irradiation at 700 W for 120 s in the case of 635 nm light illumination for samples Ar plasma irradiated for 60 s. $\tau_{\text{eff}}$ was markedly decreased from 5.0 $\times$ 10$^{-2}$ s at 1100 nm. When $S_{\text{top}}$ was large, minority carriers generated near the top surface by short-wavelength light illumination were rapidly annihilated by recombination defect states located at the top surface. In contrast, $\tau_{\text{eff}}$ was large in the case of long-wavelength light illumination because the low optical absorption coefficient at a long wavelength allowed minority carrier generation in deep regions. This effect became much more substantial as $S_{\text{top}}$ increased. When $S_{\text{top}}$ was only 50 cm/s, $\tau_{\text{eff}}$ was high, $7.1 \times 10^{-3}$ s, at 1100 nm. $\tau_{\text{eff}}$ strongly depends on carrier generation depth in the case of a large surface recombination velocity.
1.9 × 10^{-5} \text{s} by Ar plasma irradiation. $\tau_{\text{eff}}$ markedly increased to 2.0 × 10^{-3} \text{s} as the duration of microwave irradiation at 700 W increased to 60 s. The $\tau_{\text{eff}}$ of 2.0 × 10^{-3} \text{s} was almost the same value as the initial one. $\tau_{\text{eff}}$ almost leveled off for the duration of microwave irradiation between 60 and 120 s. This result in Fig. 5(a) shows that substantial carrier recombination defect states were generated in the sample by Ar plasma irradiation for 60 s, so that $\tau_{\text{eff}}$ seriously decreased from the initial values. It also shows that the carrier recombination defect states were markedly decreased by microwave irradiation at 700 W for a short time. Figure 5(b) presents $\tau_{\text{eff}}$ as a function of duration of heating in the furnace at 500°C for an Ar plasma-irradiated sample. $\tau_{\text{eff}}$ was decreased to 2.0 × 10^{-3} \text{s} by Ar plasma irradiation for 60 s. It was increased to 1.2 × 10^{-3} \text{s} by heating in the furnace as the heating duration increased to 1 h. It was much higher than that of the as-Ar plasma treated sample, but still lower than the initial value of 2.1 × 10^{-3} \text{s}. $\tau_{\text{eff}}$ almost leveled off for heating at 500°C up to 2 h. Heat treatment at 500°C for 1 h was effective in curing carrier recombination defect states caused by Ar plasma, but it was not sufficient to make the surface state return to the initial state. The present microwave irradiation effectively cured the carrier recombination defect sites with in a short time in room-temperature atmosphere, as shown in Fig. 5(a). On the basis of the result in Fig. 5, we set the duration of microwave irradiation to 120 s for the following measurements of the $\tau_{\text{eff}}$ spatial distribution. Figure 6 shows $\tau_{\text{eff}}$ spatial distribution for the initial 4-in.-size sample in the cases of 635 nm light illumination (a) and 980 nm light illumination (b). $\tau_{\text{eff}}$ in regions 1.2 cm from the sample edges was not presented because our microwave tube had a cross section of 2.3 × 1.0 cm².

Fig. 5. $\tau_{\text{eff}}$ as a function of duration of 2.45 GHz microwave irradiation at 700 W for 120 s in the cases of 635 nm light illumination for samples Ar plasma irradiated for 60 s (a) and $\tau_{\text{eff}}$ as a function of duration of heating in the furnace at 500°C for samples Ar plasma irradiated for 60 s (b). Arrows indicate $\tau_{\text{eff}}$ for the initial samples. Ar plasma irradiation decreased $\tau_{\text{eff}}$ to 1.9 × 10^{-5} \text{s} in the case of (a) and 2.0 × 10^{-5} \text{s} in the case of (b).

Fig. 6. $\tau_{\text{eff}}$ spatial distribution for the initial sample coated with 100-nm-thick thermally grown SiO$_2$ layers in the cases of 635 nm light illumination (a) and 980 nm light illumination (b). $\tau_{\text{eff}}$ in regions 1.2 cm from edges was not presented because our microwave tube had a cross section of 2.3 × 1.0 cm². Accurate measurement was not possible in the edge regions. $\tau_{\text{eff}}$ had high values in the range from 1.6 × 10^{-3} to 3.1 × 10^{-3} \text{s} in both the light illumination cases, as shown in Fig. 6. This means that the silicon surface was well passivated by the thermally grown SiO$_2$ layers. The calculation result in Fig. 4 supports that low $S_{\text{top}}$ and $S_{\text{rear}}$ resulted in the same $\tau_{\text{eff}}$ for the cases of 635 and 980 nm light illumination. Figure 7 shows the $\tau_{\text{eff}}$ spatial distribution for the sample Ar plasma irradiated for 60 s in the cases of 635 nm light illumination (a) and 980 nm light illumination (b). $\tau_{\text{eff}}$ markedly decreased to values in the range from 6.0 × 10^{-6} to 2.4 × 10^{-5} \text{s} in the case of 635 nm light illumination. On the other hand, $\tau_{\text{eff}}$ distributed from 4.2 × 10^{-5} to 6.4 × 10^{-5} \text{s} in the case of 980 nm light illumination, as shown in Fig. 7(b). The results in Fig. 7 show that substantial recombination defect states were generated by Ar plasma irradiation in the silicon surface region. Figure 8 shows the $\tau_{\text{eff}}$ spatial distribution for the sample subsequently treated with 2.45 GHz microwave irradiation at 700 W for 120 s in the cases of 635 nm light illumination (a) and 980 nm light illumination (b).
illumination (b). \( \tau_{\text{eff}} \) markedly increased to values in the range from \( 8.0 \times 10^{-4} \) to \( 2.5 \times 10^{-3} \) s in the case of 635 nm light illumination, and \( \tau_{\text{eff}} \) had almost the same distribution in the case of 980 nm as that for 635 nm light illumination. Free majority electrons in silicon substrates absorbed the 2.45 GHz microwave and the substrates were effectively heated during operation of the microwave oven. Although the temperature increase was not precisely measured, our careful visual observation indicated that the samples were not heated higher than \( 700^\circ\text{C} \) for the 700 W microwave irradiation treatment for 120 s because the color of the samples was still very dark during microwave irradiation. The dark light emission from the sample was governed by the black body radiation rule. The substrate cooled down after termination of the microwave irradiation. The glass substrates that covered the both sides of silicon surface played the role of thermal insulators because of their low heat conductivity.\(^{23}\) We believe that gradual cooling was achieved with a low cooling rate, which was essential for realizing a low density of defect states.\(^{24}\)

Figure 9 shows the calculated relations (curves) of \( \tau_{\text{eff}} \) in the cases of 635 nm (horizontal) and 980 nm (vertical) light illumination under the conditions of \( \tau_b \) of 0.1 s, \( S_{\text{rear}} \) of 8 cm/s, and \( S_{\text{top}} \) ranging from 8 to 30000 cm/s. The calculated \( \tau_{\text{eff}} \) had the same values between 635 and 980 nm illumination cases for \( \tau_{\text{eff}} \) higher than \( 7.0 \times 10^{-4} \) s. On the other hand, \( \tau_{\text{eff}} \) for the 980 nm illumination case was larger than that for 635 nm illumination case when \( \tau_{\text{eff}} \) was lower than \( 7.0 \times 10^{-4} \) s. \( \tau_{\text{eff}} \) decreased to \( 2.9 \times 10^{-6} \) s as \( S_{\text{top}} \) increased to 30000 cm/s in the case of 635 nm light illumination, while it was still high at \( 3.9 \times 10^{-5} \) s at an \( S_{\text{top}} \) of 30000 cm/s in the case of 980 nm light illumination because a diffusion time was necessary for carriers generated in the deep region by 980 nm light illumination to reach the top surface. Figure 9 also shows the experimental relations (dots) of \( \tau_{\text{eff}} \) for the cases of 635 nm (horizontal) and 980 nm (vertical) light illumination for the initial (a), as-Ar plasma-irradiated (b), and subsequent microwave-annealed (c) samples. The experimental \( \tau_{\text{eff}} \) for the initial sample had a good agreement with the calculated curves with \( S_{\text{top}} \) ranging from 8 to 23 cm/s. From the relations between the recombination velocity and the density of surface recombination defect states, which Fitzgerald and Grove reported,\(^{25}\) the results in Fig. 9(a) show that the initial samples had a low density of surface recombination defect states in the range from \( 5 \times 10^{10} \) to \( 1.5 \times 10^{11} \) cm\(^{-2}\). The \( \tau_{\text{eff}} \) was markedly decreased by Ar plasma irradiation. The relations of \( \tau_{\text{eff}} \) between 635 and 980 nm illumination agreed well with the calculated relation, as shown in Fig. 9(b). This clearly means...
that Ar plasma irradiation caused substantial recombination defect states at the interface of SiO$_2$/Si. Deep ultra violet light generated from Ar plasma probably caused serious damage in silicon and resulted in serious recombination defect states. The result in Fig. 9(b) shows $S_{\text{top}}$ ranging from 2000 to 8000 cm/s, which gives a density of recombination defect states ranging from $1.3 \times 10^{13}$ to $5.0 \times 10^{13}$ cm$^{-2}$. The wide distribution of the density of recombination defect states probably resulted from non-uniformity of the plasma density in our equipment. High surface recombination velocity means low photo sensitivity. This is a serious problem for photosensitive devices such as solar cells and photo sensors because plasma processing is widely used in semiconductor device fabrication.

Microwave irradiation treatment markedly increased $\tau_{\text{eff}}$ to close to those of the initial samples, as shown in Figs. 9(a) and 9(c). $S_{\text{top}}$ decreased to values in the range from 12 to 54 cm/s. This indicates that the density of surface recombination defect states decreased to values in the range from $7.6 \times 10^{10}$ to $3.4 \times 10^{11}$ cm$^{-2}$. The density of recombination defect states caused by Ar plasma irradiation was effectively reduced by microwave irradiation. Similar $\tau_{\text{eff}}$ spatial distribution patterns were observed between the samples treated with Ar plasma irradiation and subsequent microwave annealing, as shown in Figs. 9(b) and 9(c). The regions in which Ar plasma irradiation decreased $\tau_{\text{eff}}$ to very low values still had a low $\tau_{\text{eff}}$ after microwave irradiation annealing. This indicates that an optimized condition to realize a high $\tau_{\text{eff}}$ everywhere has not yet been found.

Moreover, we believe that the microwave intensity is not yet uniform in our commercial equipment. Conformation of the uniformity of microwave intensity and the design of a uniform microwave irradiation system are important for practical application to device fabrication.

Figure 10 shows $\tau_{\text{eff}}$ measured in a central region of the sample as a function of elapsed time after microwave annealing at 700 W for 120 s for samples treated with Ar plasma irradiation. $\tau_{\text{eff}}$ maintained high values for a long time, above 5000 h. This means that stable reduction of recombination defect states caused by Ar plasma irradiation was successfully achieved by microwave annealing.

The experimental results of Figs. 5 to 10 demonstrated the simple-thermal passivation method using microwave irradiation. Free carriers in silicon effectively absorbed the microwave and silicon samples were heated. The two glass substrates probably played the role of maintaining heat energy. Gradual cooling with a low cooling rate was effective in reducing the density of defect states. This method will be useful for curing minority carrier annihilation defects generated in semiconductor device fabrication.

4. Conclusions

We reported a simple annealing method using a commercial 2.45 GHz microwave oven at 700 W to increase $\tau_{\text{eff}}$ for 4-in.-size 500-μm-thick 20 Ω cm n-type silicon substrates coated with 100-nm-thick thermally grown SiO$_2$ layers. The microwave annealing was conducted with 2-mm-thick glass substrates, which sandwiched the silicon samples to maintain the thermal energy and realize gradual cooling. We used a 9.35 GHz microwave transitance measurement system to precisely measure $\tau_{\text{eff}}$ in the cases of CW 635 and 980 nm LD light illumination. An X–Y moving stage allowed measurement of the $\tau_{\text{eff}}$ spatial distribution of samples. Experimental $\tau_{\text{eff}}$ values with the two-different wavelength light illuminations were analyzed by numerical calculation with a finite-element program including models of photo-induced carrier generation, and their diffusion and annihilation with $\tau_{\text{b}}$, $S_{\text{top}}$, and $S_{\text{rear}}$. High $\tau_{\text{eff}}$ values in the range from $1.6 \times 10^{-3}$ to $3.1 \times 10^{-3}$ s between 635 and 980 nm LD light illuminations were observed for the initial samples. This means that the silicon surfaces were well passivated by the thermally grown SiO$_2$ layers and the silicon sample had a high crystalline quality with a high $\tau_{\text{b}}$. Ar plasma irradiation at 50 W for 60 s markedly decreased $\tau_{\text{eff}}$ to values in the range from $6.0 \times 10^{-6}$ to $2.4 \times 10^{-5}$ s in the case of 635 nm

Figure 10. $\tau_{\text{eff}}$ as a function of elapsed time after microwave annealing at 700 W for 120 s for samples treated with Ar plasma irradiation.
light illumination and from $4.2 \times 10^{-5}$ to $6.4 \times 10^{-5}$ s in the case of 980 nm light illumination. Numerical analysis revealed that high densities of recombination defect states localized at the silicon top surface in the range from $1.3 \times 10^{13}$ to $5.0 \times 10^{13}$ cm$^{-2}$ caused far different experimental $\tau_{\text{eff}}$ values between the 635 and 980 nm CW light illuminations. Microwave annealing at 700 W for 120 s increased $\tau_{\text{eff}}$ to values in the range from $8.0 \times 10^{-4}$ to $2.5 \times 10^{-3}$ s, which are close to the values of the initial samples. The density of recombination defect states caused by Ar plasma irradiation was greatly decreased by microwave annealing to low values in the range from $7.0 \times 10^{10}$ to $3.4 \times 10^{11}$ cm$^{-2}$. The high $\tau_{\text{eff}}$ obtained by microwave annealing was maintained for a long time, above 5000 h.

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