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Analysis of Microwave Absorption by Photo-Induced Carriers at PN Junction Formed by Ion Implantation

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Abstract.

We report photo-induced carrier recombination properties for crystalline silicon in steps of N^+P junction formation. Transmissivity of 9.35GHz microwave was measured and analyzed under illumination of 532 nm green light at 4~20 mW/cm^2 to the top or rear surface. Phosphorus ions with 2×10^{14} cm^{-2} were implanted to 525 μm thick p-type silicon coated with 100 nm thick thermally grown SiO_2 layers. The implantation markedly increased the surface recombination velocity *S* much higher than 2.6×10^4 cm/s, while *S* was 501 cm/s for initial sample. The implanted surface regions were activated by 940 nm infrared semiconductor laser irradiation at 100 kW/cm^2 for 2.5 ms. 1.3×10^6 Pa H_2O vapor heat treatment at 260°C for 3 h was also conducted for defect reduction. These processes markedly decreased *S* to 307 cm/s. When the SiO_2 layer at the top surface was removed, *S* increased to 1500 cm/s, which indicated an ability of photo-induced carrier separation by N^+P junction.

Introduction

Analysis of photo-induced carrier behavior is important for developing photovoltaic devices such as solar cells. Measurements of microwave photoconductive decay [1] and quasi-steady-state-photo-conductance [2] have been widely used for measurement of the photo induced minority carrier lifetime. We recently have developed a microwave free carrier absorption measurement system for precisely non-destructive and non-contact investigation of photo-induced carrier properties [3]. Photo induced carriers are much sensitive to properties of the surface and bulk semiconductor. Defects induce carrier recombination and reduce the density of photo induced carriers.

In this paper, we report a precise analysis of photo-induced carrier properties in processes of PN junction formation followed by infrared semiconductor laser annealing at the silicon surface using the free carrier microwave absorption method. We discuss changes in the effective minority carrier lifetime at steps of ion implantation, laser annealing [4] and high pressure H_2O vapor heat treatment [5]. The surface recombination velocity is also analyzed. We also report a role of reduction of carrier recombination velocity of PN junction.

Experimental

P type silicon substrates with resistivity of 8-9 Ωcm and a thickness of 525 μm were prepared. The both surfaces were coated with 100 nm thick thermally grown SiO_2 layers. Phosphorus atoms with a concentration of 2×10^{14} cm^{-2} were implanted to the top surface at 73 keV. They had a peak concentration of 2.0×10^{19} cm^{-3} at SiO_2/Si interfaces. Phosphorus atoms with 1×10^{14} cm^{-2} were effectively incorporated into silicon with Gaussian distribution from the surface to 140 nm deep. Samples were annealed by 940 nm contineous wave infrared semiconductor laser irradiation [6]. Laser beam at a power of 25 W was introduced to samples using an optical fiber and lens mounted on the X-Y mobile stage. The laser beam was moved at 6~10 cm/s in the X-direction. It was also moved in the Y-direction with a 25 μm step. Laser beam was focused to a spot with a Gaussian-like intensity distribution with a diameter of 150 μm at the sample surface. The laser light intensity was about 100 kW/cm^2 at the sample surface. The laser dwell time was estimated as laser beam size devided by laser moving velocity. It ranged from 1.5 to 2.5 ms. The optical reflectivity of the sample surface was 15.8 % at a wavelength of 940 nm. The optical absorption coefficient of silicon was about 3×10^{3} cm^{-1} at 940 nm. Laser light was incorporated and absorbed in silicon substrate. Optical reflectivity spectra in ultraviolet and visible ranges were also measured and analyzed for investigating recrystallization properties by laser annealing [7].

Photo induced free carrier absorption was measured using 9.35 GHz microwave circuit [3]. The microwave interferometer was constructed by waveguide tubes. It had narrow gaps for measurement of transmissivity for sample wafers. A thin light illumination plate was also inserted facing the samples. A laser light at 532 nm was introduced using optical fibers to the light illumination plate. The light intensity was controlled from 4 to 20 mW/cm^2 at the surface. Transmissivity at 9.35 GHz during light illumination to the top or rear surface was measured for samples initial, as-ion-implanted, laser annealed and heat treatment at 260°C with 1.3×10^{6} Pa H_2O vapor for 3 h [5]. A finite element numerical calculation program including Fresnel optical interference effect induced by in-depth change in refractive index owing to photo-induced free carrier diffusion was constructed to estimate the density of fee carriers from the experimental transmissivity.

Results and discussion

Figure 1 shows in-depth profiles of crystalline volume ratio analyzed from the optical reflectivity spectra for the top surface of samples. The crystalline volume ratio in top 140 nm region was decreased by phosphorus ion implantation. It was 0.27 just at the silicon surface, as shown in Fig. 1. It means that phosphorus ion implantation caused serious crystalline damage. The crystalline volume ratio in the most of implanted region was increased to 1.0 by laser irradiation for 1.5 ms. But it was 0.7 only 2 nm deep surface region. Moreover, it was completely 1.0 for sample laser annealed for 2.5 ms. The recrystallization was achieved by semiconductor laser irradiation. There was no roughness and the surface was kept flat.

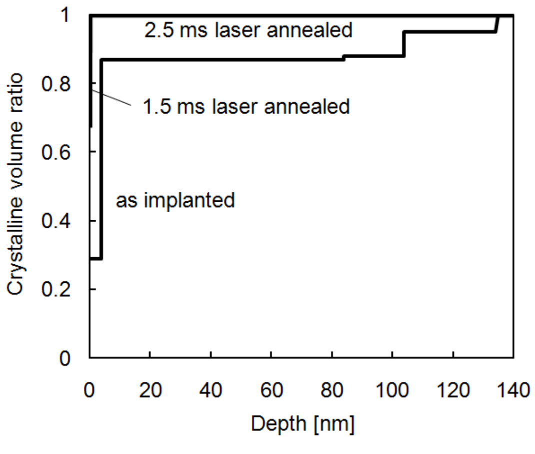

Fig. 1 In-depth profiles of crystalline volume ratio analyzed from the optical reflectivity spectra.

Figure 2 shows changes in normalized transimissivity as a function of light intensity illuminated to the top surface (ion-implanted surface) and rear surface for samples initial and as-implanted (a), laser annealed for 1.5 and 2.5 ms (b), and heated with 1.3×10^{6} Pa H_2O vapor for 3 h (c). Transmissivity was normalized by that measured in the dark field. Initial sample showed marked decreases in normalized transimissivity to 0.87 for light illumination at 20 mW/cm^2 to the top and rear surfaces. This means that the silicon surfaces were well passivaed by thermally grown SiO_2 and a high density of photo-induced carriers was existed under illumination. On the other hand, no decrease in transmissivity was observed in the case of light illumination to the top surface for as-implanted sample. Normalized transmittance slightly decreased to 0.98 in the case of light illumination at 18 mW/cm^2 to the rear surface, as shown in Fig. 2(a). This shows that phosphorus ion implantation caused substantial defects associated with serious carrier recombination in silicon.

Laser annealing for 2.5 ms caused decreases in normalized transmissivity to 0.97 and 0.95 in the case of light illumination at 20 mW/cm^2 to the top surface and 18 mW/cm^2 to the rear surface, respectively. Laser annealing reduced photo-induced carrier recombination probability compared with as-implanted states. However, decrease in normalized transmissivity was smaller than that for initial samples, although analysis of optical reflectivity spectra resulted in complete recrystallization by laser annealing for 2.5 ms, as shown in Fig. 1. The results of Fig. 2 (b) indicate that there were still defect states inducing carrier recombination after laser annealing for 2.5 ms. Normalized transmissivity slightly decreased to 0.99 and 0.96 in the case of light illumination at 20 mW/cm^2 to the top surface and 18 mW/cm^2 to the rear surface, respectively, for samples laser annealed for 1.5 ms. Small decrease in normalized transmissivity by light illumination to the top surface compared with laser annealing for 2.5 ms indicates that there was a high density of residual defect states remained.

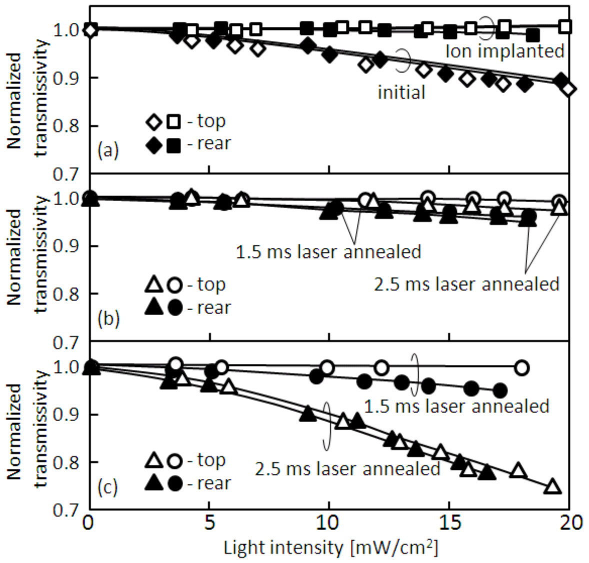

Fig.2 Changes in normalized transimissivity as a function of light intensity illuminated to the top and rear surfaces for samples initial and as-implanted (a), laser annealed for 1.5 and 2.5 ms (b), and heated with 1.3x10^6 Pa H_2O vapor for 3 h (c).

1.3x10^6 Pa H_2O vapor heat treatment at 260°C for 3 h resulted in marked decrease in normalized transmissivity to 0.77 in light illumination at 17 mW/cm^2 to the top and rear surfaces for sample laser annealed for 2.5 ms, as shown in Fig. 2(c). This degree of normalized transmissivity decrease was higher than that for initial sample, as shown in Fig. 2(a). It indicates that H_2O vapor heat treatment decreased the density of defect states inducing carrier recombination velocity. On the other hand, H_2O vapor heat treatment at 260°C for 3 h decreased the normalized transmissivity only to 0.98 and 0.95 for light illumination at 17 mW/cm^2 to the top and rear surfaces, respectively, for samples laser annealed for 1.5 ms. This indicates that there were residually serious defect states causing carrier recombination at the surface region for samples laser annealed for 1.5 ms.

The photo induced carrier density was analyzed from change in transmissivity shown in Fig. 2 by our numerical program with the effective carrier lifetime τ_{eff} and surface recombination velocities. Light illumination induces the photo carriers in silicon substrate. The carrier diffusion model gives minority carrier in-depth distribution $N_{\mathrm{photo}}(x)$ as [3,8],

$$N_{photo}(x) = N_0\left(\left(\sqrt{\frac{D}{\tau_b}}+S_2\right)\exp\left(-\frac{x}{\sqrt{D\tau_b}}\right)+\left(\sqrt{\frac{D}{\tau_b}}-S_2\right)\exp\left(-\frac{2d-x}{\sqrt{D\tau_b}}\right)\right)$$

$$N_0 = \frac{\eta(1-r)G}{\left(\sqrt{\frac{D}{\tau_b}}+S_2\right)\left(\sqrt{\frac{D}{\tau_b}}+S_1\right)-\left(\sqrt{\frac{D}{\tau_b}}-S_1\right)\left(\sqrt{\frac{D}{\tau_b}}-S_2\right)\exp\left(-\frac{2d}{\sqrt{D\tau_b}}\right)} \qquad (1),$$

where G is the photon flux per unit area with light intensity of W per unit area given by $G=W/hv$, where h is the plank constant and v is the light frequency, η is the quantum efficiency for photo induced carrier generation, which was assumed as 1 in this investigation, r is the optical reflectivity of the green laser light, D is the electron carrier diffusion coefficient of 36 cm^2/s and τ_b is the minority bulk carrier lifetime, S_1 is the surface recombination velocity at a light illumination side. S_2 is the recombination velocity at the other dark side, d is the substrate thickness. The total photo induced minority carrier density per unit area n is obtained by the integration of $N_\mathrm{photo}(x)$ from 0 to d as,

$$n = N_0\sqrt{D\tau_b}\left(1-\exp\left(-\frac{d}{\sqrt{D\tau_b}}\right)\right)\left(\sqrt{\frac{D}{\tau_b}}+S_2+\left(\sqrt{\frac{D}{\tau_b}}-S_2\right)\exp\left(-\frac{d}{\sqrt{D\tau_b}}\right)\right) \quad . \qquad (2),$$

The carrier effective lifetime is also defined from eqs. (1) and (2) as,

$$\tau_{eff} = \tau_b \frac{\sqrt{\frac{D}{\tau_b}}\left(1-\exp\left(-\frac{d}{\sqrt{D\tau_b}}\right)\right)\left(\sqrt{\frac{D}{\tau_b}}+S_2+\left(\sqrt{\frac{D}{\tau_b}}-S_2\right)\exp\left(-\frac{d}{\sqrt{D\tau_b}}\right)\right)}{\left(\sqrt{\frac{D}{\tau_b}}+S_2\right)\left(\sqrt{\frac{D}{\tau_b}}+S_1\right)-\left(\sqrt{\frac{D}{\tau_b}}-S_1\right)\left(\sqrt{\frac{D}{\tau_b}}-S_2\right)\exp\left(-\frac{2d}{\sqrt{D\tau_b}}\right)} \qquad (3),$$

τ_eff is equivalent to τ_b when S_1 and S_2 are zero.

τ_eff becomes low in the case of light illumination to the top surface if S_1 is very large. Especially in the case of very long τ_b, τ_eff is approximately given as,

$$\tau_{eff} \sim \frac{d}{S_1} \qquad (4).$$

Our experimental accuracy gave a lower limit of τ_eff as 2 μs. The maximum S_1 was therefore estimated to be 2.6×10^4 cm/s for a substrate thickness of 525 μm.

On the other hand, a substantial carrier density can remain even if there is a surface with a very high carrier recombination velocity when light is illuminated to the other surface with a low carrier recombination velocity because photo induced carriers alive during travel across the silicon substrate until reaching the other surface. The lower limit of τ_eff with a very large S_2 (dark side) and very long minority carrier bulk lifetime is given as,

$$\tau_{eff} \sim \tau_b \frac{\sqrt{\frac{D}{\tau_b}}\left(1-\exp\left(-\frac{d}{\sqrt{D\tau_b}}\right)\right)^2}{\left(\left(\sqrt{\frac{D}{\tau_b}}+S_1\right)+\left(\sqrt{\frac{D}{\tau_b}}-S_1\right)\exp\left(-\frac{2d}{\sqrt{D\tau_b}}\right)\right)} \sim \frac{d^2}{2\left(D+S_1 d\right)} \qquad (5).$$

When S_1 was 501 cm/s, τ_eff has a lower limit of 23 μ s for a substrate thickness of 525 μm.

Figure 3 shows average values of the effective carrier lifetime τ_eff (a) and surface recombination velocity when τ_b was assumed to be large enough of 0.01 s (b). τ_eff for initial samples was 50 μs in the cases of light illumination to the both surfaces. τ_eff gave a surface recombination velocity of 501 cm/s for the both surfaces under the assumption of a very long bulk lifetime of 0.01 s. Ion implantation caused no change in transmissivity for light illumination to the top surface (ion implantation side). Therefore τ_eff was less than the measurement limit of 2 μs. On the other hand, τ_eff was 8 μs in the case of at light illumination to the rear surface, which was lower than the lower limit of 23 μ s for a substrate thickness of 525 μm, as discussed above. τ_{eff} of 8 μs suggests that τ_b was decreased to very low in the top surface region, and the effective thickness with initial τ_b decreased to 245 μm according to eq. (4), although phosphorus atoms were implanted only 100 nm deep. Laser irradiation for 1.5 and 2.5 ms increased τ_{eff} to 20 and 24 μs, respectively, in the case of light illumination to the rear surface. This result indicates laser irradiation for 2.5 ms restored τ_b because τ_{eff} became larger than the lower limit τ_{eff} of 23 μs for a thickness of 525 mm. But 1.5 ms laser irradiation was not enough to restore τ_b. τ_{eff} in the case of light illumination to the top surface was still low of 4 and 13 μs for laser irradiation for 1.5 and 2.5 ms, respectively. The recombination velocity at the top surface was estimated to be 9.3×10^3 and 2.5×10^3 cm/s, respectively. Laser irradiation did not complete defect annihilation and the surface recombination velocity was still high. Especially sample had residual amorphous region at the top surface region for sample laser annealed for 1.5 ms as shown in Fig. 1. Amorphous states probably play a role of carrier recombination.

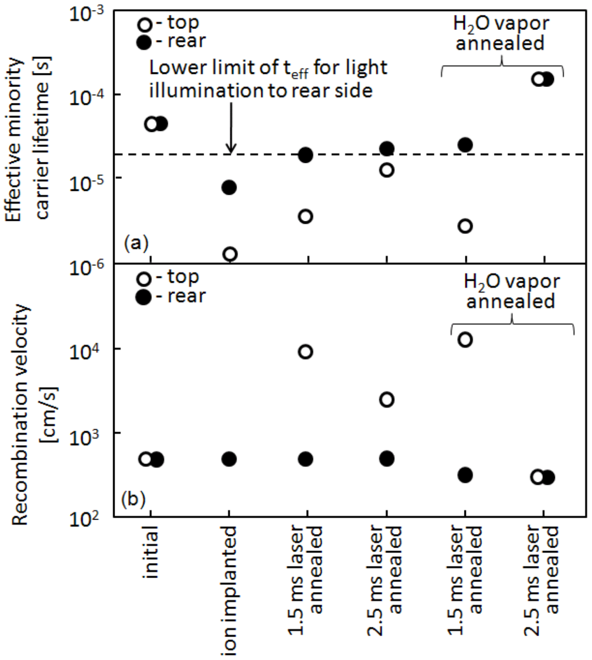

Fig.3 Average values of the effective carrier lifetime τ_{eff} for different processes (a) and surface recombination velocity when τ_b was assumed to be large enough of 0.01 s (b).

1.3×10^6 Pa H_2O vapor heat treatment at 270°C for 3 h increased τ_{eff} to150 μs in the cases of light illumination to the both surfaces for sample laser annealed for 2.5 ms as shown in Fig. 3(a). That value of τ_{eff} was higher than the initial value of 50 μs. H_2O vapor heat treatment markedly decreased the density of defect state. The surface recombination velocity was estimated 307 cm/s if τ_b was very large of 0.01 s, as shown in Fig. 3(b). On the other hand, H_2O vapor heat treatment did not increase τ_{eff} for sample laser annealed for 1.5 ms as shown in Fig. 3(a). It probably results from that recrystallization did not complete, and that amorphous structure remained.

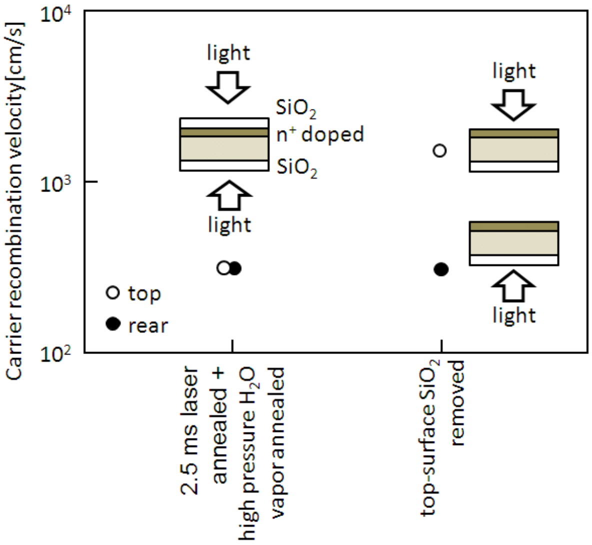

Fig. 4 Changes in surface recombination velocity by removing top SiO_2 layer when τ_b was assumed to be large enough of 0.01 s.

In order to investigate carrier recombination properties of N^+P junction formed at the top surface, the SiO_2 layer at the top surface was removed for sample laser annealed for 2.5 ms. τ_{eff} changed to 21 and 48 μs, respectively, in the cases of light illumination to the top and rear surfaces. The recombination velocity at the top N^+P junction surface was estimated to be 1500 cm/s using those τ_{eff} results and a recombination velocity of 307 cm/s at the rear surface, as shown in Fig. 4. N^+P junction separated hole and electron until compensating the internal voltage formed in the depletion region. The carrier recombination velocity of PN junction is important value for estimate solar cell characteristics. The charge separation determines the open circuit voltage. The present results means that passivation of the top surface of the N^+P junction is still important to keep photo induced carrier in silicon substrate.

Summary

We investigated photo-induced carrier recombination properties for crystalline silicon in steps of N^+P junction formation. Phosphorus ions with a concentration of 2×10^{14} cm^{-2} were implanted to 8-9 Ωcm 525 μm thick p-type silicon coated with 100 nm thick thermally grown SiO_2 layers. Phosphorus atoms were incorporated into silicon substrates. The surface region was partially amorphized from to surface to 140 nm deep region. The implanted surface regions were annealed by 940 nm infrared semiconductor laser irradiation at 100 kW/cm^2 for 1.5 and 2.5 ms. Analysis of optical reflectivity spectra at the surface revealed that the surface region was completely recrystallized by laser annealing for 2.5 ms, while there was slightly residual amorphous region just at the surface 2 nm deep for laser irradiation for 1.5 ms. 1.3×10^6 Pa H_2O vapor heat treatment at 260°C for 3 h was also conducted for defect reduction. Transmissivity of 9.35GHz microwave was measured under illumination of 532 nm green light 4~20 mW/cm^2 to the top or rear surfaces. Transmissivity was analyzed by free carrier photo absorption and carrier diffusion theories. The implantation markedly increased the surface recombination velocity higher than 2.6×10^4 cm/s, while initial samples had a surface recombination velocity of 501 cm/s. Moreover, ion implantation decreased the carrier bulk lifetime from to surface to 245 μm deep region. Laser irradiation for 2.5 ms returned the carrier bulk lifetime to the initial value. However the carrier recombination velocity at the top surface was still high of 2.5×10^3 S/cm. 1.3×10^6 Pa H_2O vapor heat treatment at 260°C for 3 h markedly increased the minority carrier lifetime to 150 μs and decreased the carrier recombination velocity to 307 cm/s for the both surfaces. When the SiO_2 layer at the top surface was removed, the carrier recombination velocity increased to 1500 cm/s, which indicated an ability of photo-induced carrier separation by N^+P junction.

Acknowledgments

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