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Characterization of SiO_x/Si Interface Properties by Photo Induced Carrier Microwave Absorption Method

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Abstract. We investigated photo induced carrier density and effective minority carrier lifetime by a 9.35 GHz microwave free carrier absorption caused by 532 nm light induced photo carriers for crystalline silicon samples coated with vacuum evaporated SiO_x layers and spin-coated polysilazane (-(SiH2NH)-) layers. In the case of 55 nm thick SiO_x film evaporated on n-type silicon substrate, the photo induced carrier density and the effective minority carrier lifetime were increased from 1.5×10^{12} to 1.6×10^{13} cm^{-2} and from 31 to 350 μs, respectively by 1.2×10^6 Pa H_2O vapor heat treatment at 260°C for 1 h under the light illumination at 20.8 mW/cm^2 because of passivation of SiO_x/Si interfaces. High pressure H_2O vapor treatment was more effective in decrease the density of carrier recombination sites for hole minority carriers. From the investigation of polysirazane coated samples, we confirmed that our microwave measurement system could detect small photo carrier density on the order of 10^{10} cm^{-2} and small effective minority carrier lifetime on the order of 10^{-6} s.

Introduction

Defect passivation has an important role for improvement in device characteristics especially for silicon solar cells and thin film transistors. Low temperature fabrication process for the passivation films is required especially for the devices on glass or plastic substrates. Therefore, non destructive and non contact measurement method of interface electrical properties is attractive as monitoring samples during the device fabrication. Analysis of photo induced carrier behavior is also important for developing photovoltaic devices. Photo induced minority carrier lifetime is one of the most important characteristics. Measurements of microwave photo conductive decay (μ-PCD) [1] and quasi steady state photoconductance [2] have been widely used for the measurement of the photo induced minority carrier lifetime. We recently have proposed that the microwave free carrier absorption effect is attractive for the investigation of photo induced minority carrier properties [3, 4].

In this paper, we report a precise investigation of photo induced carrier properties in both n-type and p-type crystalline silicon samples coated with thermally grown SiO_2 layers as well as SiO_x layers fabricated by low temperature processes. Photo induced carrier density and its spatial distribution depend on the bulk and interface properties. Defects induce carrier recombination and reduce the density of photo induced carriers. We demonstrate quantitative evaluation of carrier recombination properties using photo induced carrier microwave absorption measurement. We also discuss changes in the photo induced carrier density and the effective minority carrier lifetime induced by surface passivation by high pressure H_2O vapor heat treatment [5].

Experimental

In order to investigate SiO_x/Si interface properties on photo induced carriers, both n-type and p-type single crystalline silicon wafers were prepared. Carrier concentration of n-type silicon wafer was 2.8 x 10^{14} cm^{-3} and that of p-type wafer was 1.4 x 10^{15} cm^{-3}. The thicknesses of both types of wafers were 525 µm. The both surfaces of silicon wafer were coated with 100 nm thick thermally grown SiO_2 layers at first. The silicon wafers coated with as-thermally grown SiO_2 layers were used as reference.

SiO_x films were deposited at room temperature on the top surface of silicon wafers by the vacuum evaporation of powdered SiO after removing the thermally grown SiO_2 layer by buffered HF solution at the top surface and still keeping the thermally grown SiO_2 layer at the rear surface. Heat treatment in 1.2 x 10^6 Pa H_2O vapor at 260°C for 1h was also applied to the samples [5].

Polysilazane (-(SiH2NH)-) films were coated on the top surface of silicon wafers after removing the top surface of thermally grown SiO_2 layer. Thermally grown SiO_2 layer at the rear surface was still keeping. Heat treatments in 1.2 x 10^6 Pa H_2O vapor at 260°C for 1h and 6h were also applied to the samples.

Optical reflectivity spectra in ultraviolet and visible range were measured and analyzed for investigating film thickness and optical properties of films. Thickness of SiO_x and polysilazane films were evaluated 55 nm and 180 nm, respectively by the spectral fitting of optical reflectivity.

Figure 1 shows a schematic of photo induced carrier microwave absorption measurement system. The 9.35 GHz microwave was emitted by a field effect transistor type oscillator and that was introduced using a waveguide tube. There was a 1 mm gap for measurement of sample wafers. A thin light scattering plate was inserted into the gap facing to the top surface of samples as shown in Fig. 1. A laser light at 532 nm was introduced using optical fibers to the light scattering plate, which gave uniform illumination of the green light to the samples. The intensity of the laser light was modulated at a frequency of 1 Hz (sufficiently slower than the photo carrier generation and recombination) and controlled from 0 to 20.8 mW/cm^2 at the surface. The intensity of microwave transmitted through the sample was measured by Agilent U2000 power sensor. The transmissivity of sample T was obtained by the ratio of intensities of microwave with the sample I_s to without sample I_{air}, as $T = I_s / I_{air}$. A finite element numerical calculation including Fresnel optical interference effect induced by in-depth change in

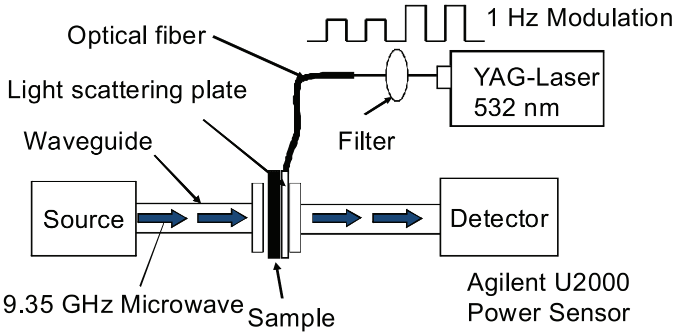


Fig. 1 Schematic diagram of photo induced carrier microwave absorption measurement system.

refractive index owing to photo induced free carrier diffusion was constructed to estimate the density of free carriers from the experimental transmissivity [6, 7].

Results and Discussion

Figure 2 shows the microwave transmissivity as a function of the intensity of 532 nm light illumination for n-type samples (a) and p-type samples (b). Solid circles and squares show the transmissivity for the samples with the top surface coated with as-deposited SiO_x layers, and samples subsequently treated with treated with 1.2 x 10^6 Pa H_2O vapor at 260°C for 1h, respectively. Open circles show the transmissivity for the sample with both surfaces coated with thermally grown SiO_2 layers as reference. Transmissivity without light illumination were ranging from 24.0 to 24.5 % for the n-type samples and from 13.8 to 15.2 % for the p-type samples, respectively. The difference of transmissivity resulted in the carrier concentration ranging from 2.8 x 10^{14} to 2.9 x 10^{14} cm^{-3} for the n-type samples and from 1.4 x 10^{15} to 1.5 x 10^{15} cm^{-3} for the p-type samples, respectively.

The transmissivity monotonously decreased as the light intensity increased from 0 to 20.8 mW/cm^2 for every sample, because of free carrier absorption by photo induced carriers. The n-type silicon sample with SiO_x layer on the top surface annealed with high pressure H_2O vapor for 1h showed the highest decrease in transmissivity from 24.5 to 9.6 % as the light intensity increased from 0 to 20.8 mW/cm^2, while the n-type silicon sample with as-deposited SiO_x layer on the top surface showed the decrease in transmissivity from 24.2 to 21.9 %, as shown in Fig. 2(a). On the other hand, the p-type silicon sample with SiO_x layer on the top surface annealed with high pressure H_2O vapor for 1h showed decrease in transmissivity from 15.2 to 12.8 % as the light intensity increased from 0 to 20.8 mW/cm^2, while the p-type silicon sample with as-deposited SiO_x layer on the top surface showed the lowest decrease in transmissivity from 14.7 to 14.4 %, as shown in Fig. 2(b).

The density of photo induced minority carriers per unit area was obtained by analysis of the experimental transmissivity using the free carrier absorption theory. Figure 3 shows the densities of photo induced minority carriers per unit area as a function of the intensity of 532 nm light illumination for n-type samples (a) and p-type samples (b). Photo induced minority

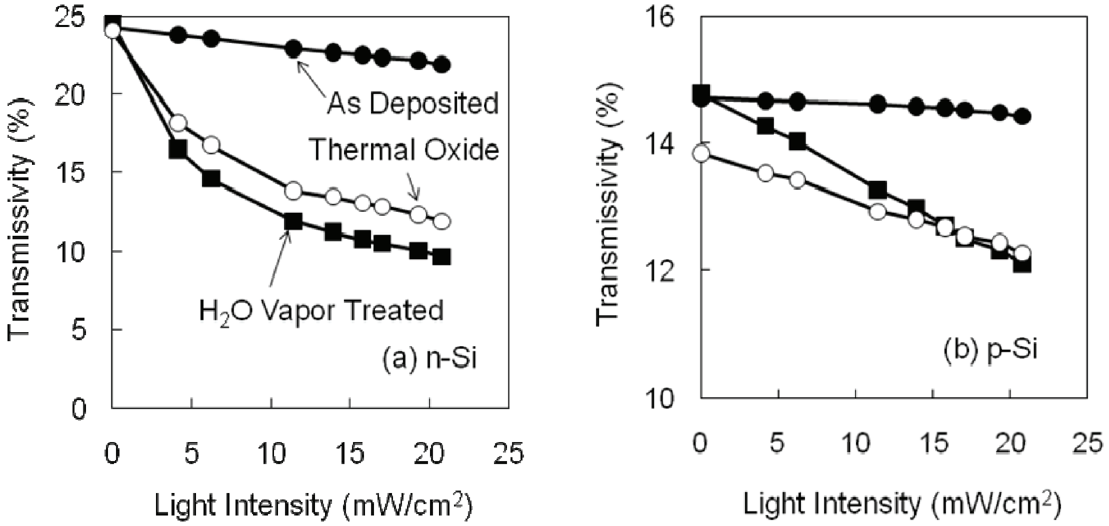


Fig. 2 Transmissivity as a function of the intensity of 532 nm light illumination for n-type (a) and p-type (b) crystalline silicon samples coated with thermally grown SiO_2 (open circles) and as-deposited SiO_x layers on the top surface (solid circles) and annealed with high-pressure H_2O vapor for 1h (solid squares).

carriers increased as the intensity of light illumination increased for every sample. Both n-type and p-type samples with as-deposited SiO_x layer on the top surface show the low photo induced carrier density. The n-type silicon sample with SiO_x layer on the top surface annealed with high pressure H_2O vapor for 1h had the highest density of photo induced carriers of 1.6×10^{13} cm^{-2} at 20.8 mW/cm^2. It was larger than the density of photo induced carriers for the sample with both surfaces coated with thermally grown SiO_2 (1.2×10^{13} cm^{-2} at 20.8 mW/cm^2). This result indicates that the extensive defect passivation was achieved for the SiO_x deposited sample by the high pressure H_2O vapor heat treatment. The p-type silicon samples with as-deposited SiO_x layer on the top surface also shows increase in photo induced carrier density by the high pressure H_2O vapor annealing for 1h. It was also higher that for sample coated with thermally grown SiO_2 layers. However the photo induced carrier density increased to 3.7×10^{12} cm^{-2} at most at 20.8 mW/cm^2, which was lower than that for n-type samples. The origin of the difference of photo induced carrier density between n-type samples and p-type samples is supposed to be the difference of effective minority carrier lifetime.

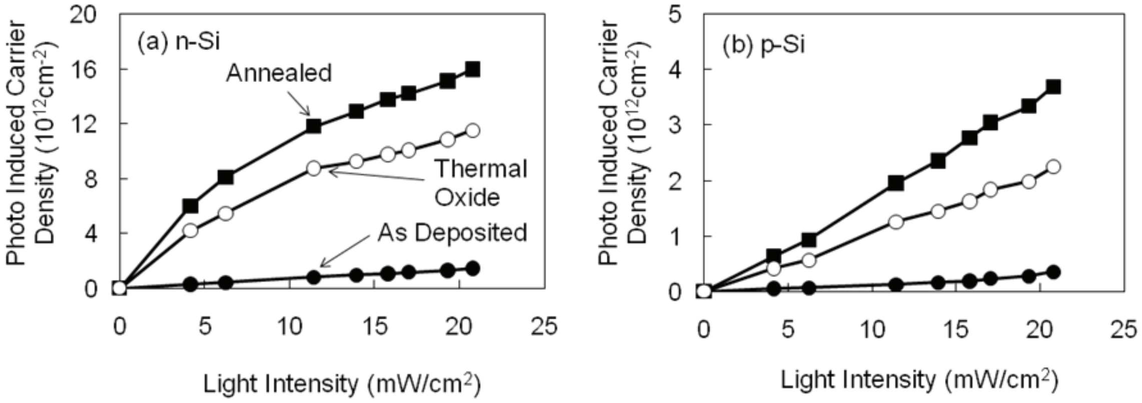


Fig. 3 Density of photo induced minority carriers per unit area as a function of the intensity of 532 nm light illumination for n-type samples (a) and p-type samples (b).

Figure 4 shows the effective minority carrier lifetime τ_{eff} as a function of the intensity of 532 nm light illumination for n-type samples (a) and p-type samples (b). The lowest τ_{eff} at around 6.0 μs was obtained for the p-type silicon with as-deposited SiO_x layer on the top surface. It indicated the as-deposited SiO_x/Si interface had substantial defect states that reduced τ_{eff}. τ_{eff} was increased by high pressure H_2O vapor heat treatment because of the passivation of SiO_x/Si interfaces. The samples H_2O vapor heat treated had the highest τ_{eff} ranging from 350 to 660 μs for the n-type silicon and ranging from 73 to 87 μs for the p-type silicon under the light intensity ranging from 4.1 to 20.8 mW/cm^2. These τ_{eff} were higher than that of samples both side coated with thermally grown SiO_2 and showed the profitability of high pressure H_2O vapor heat treatment.

In the case of as-deposited SiO_x samples, τ_{eff} was small because of high surface recombination velocity S due to high density of defects states at the top surface. In the case of very long minority bulk carrier lifetime and very small recombination velocity at the rear surface, τ_{eff} is approximately given as $\tau_{eff} = d / S$, where d is the substrate thickness and S is the surface recombination velocity at the front surface [8]. The ratio of τ_{eff} on p-type and n-type samples directly gives the ratio of S, as $\tau_{eff\text{-}e}/\tau_{eff\text{-}h} = S_h / S_e$, where h and e of subscript expressed hole and electron (minority carrier), respectively. Experimental S_h / S_e ranged from 0.17 to 0.27, which depended on the light intensity for as-deposited SiO_x samples. This means that recombination of electron minority carriers seriously occurred. On the other hand, it ranged from 0.11 to 0.24 after the high pressure H_2O vapor heat treatment. The results of Fig. 4 clearly show that high pressure H_2O vapor heat treatment effectively decreased the density of carrier recombination sites and increased the effective minority carrier lifetime for both n-type and p-type samples. Moreover, slight decrease in the ratio of the minority carrier surface recombination velocity given above indicate that high pressure H_2O vapor heat treatment is more effective in decrease the density of carrier recombination sites for hole minority carriers.

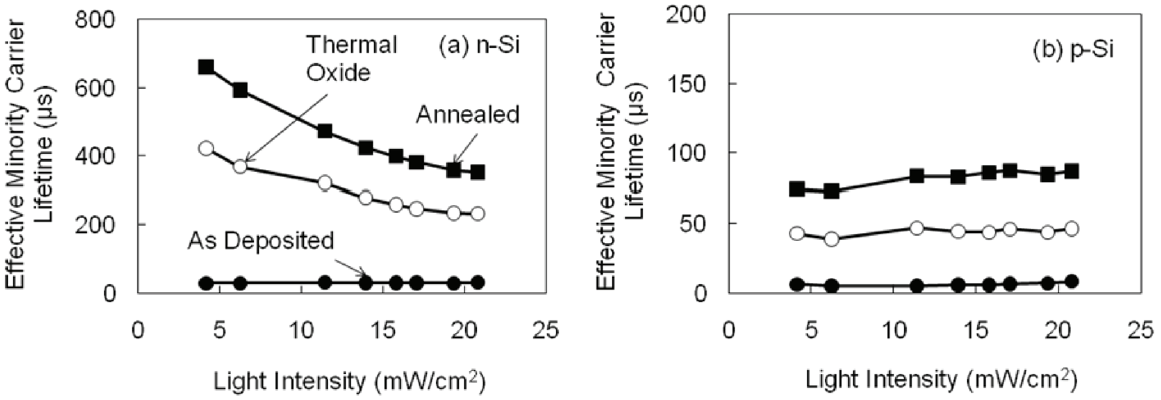
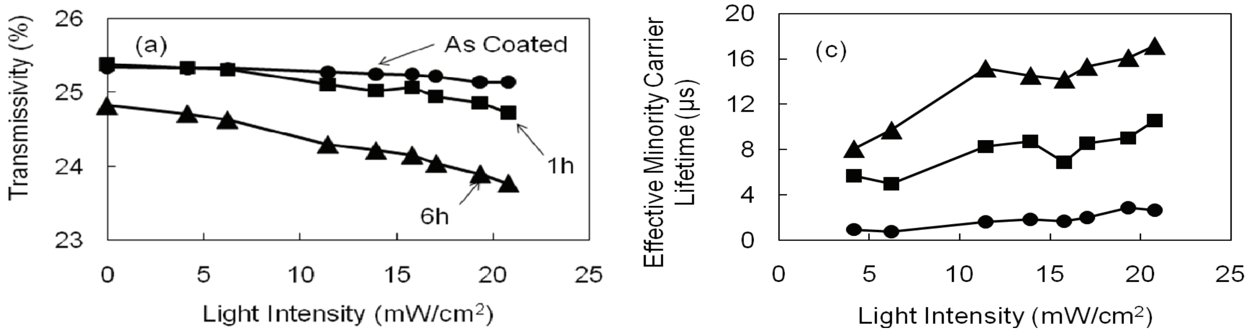


Fig. 4 Effective minority carrier lifetime analyzed from the results of Fig. 2 as a function of the intensity of 532 nm light illumination for n-type samples (a) and p-type samples (b).

Figure 5 shows (a) transmissivity, (b) density of photo induced minority carriers per unit area and (c) effective minority carrier lifetime as a function of the intensity of 532 nm light illumination for n-type silicon samples coated with polysilazane (-(SiH2NH)-) on the top surface after removing the thermally grown SiO_2 layer. Decreases in transmissivity as the light intensity increased from 0 to 20.8 mW/cm^2 for the samples of as-coated and H_2O vapor heat treated for 1 and 6 h were 0.2, 0.6 and 1.0%, respectively. The density of photo induced minority carriers per unit area obtained by analysis of fig. 5(a) increased as the intensity of light illumination increased for every sample, as shown in fig. 5(b). The highest density of photo induced carriers of 6.0 x 10^{11} cm^{-2} and effective minority carrier lifetime of 17 μs at 20.8 mW/cm^2 was obtained for the sample H_2O vapor heat treated for 6 h. These results indicated



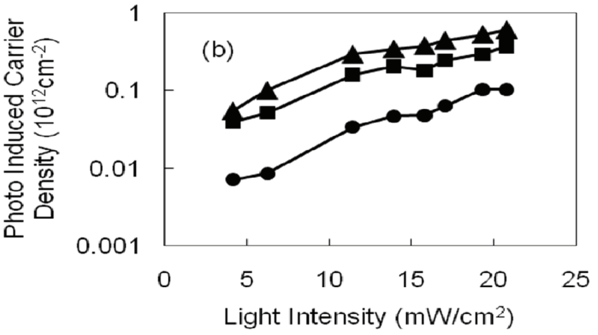


Fig.5 Transmissivity (a), density of photo induced minority carriers per unit area (b) and effective minority carrier lifetime (c) as a function of the intensity of 532 nm light illumination for the n-type silicon samples coated with polysilazane and heat treated with high-pressure H_2O vapor for 1 and 6 h.

that the interface between polysilazane and silicon was passivated by high pressure H_2O vapor heat treatment, though the improvement was smaller than the SiO_x coated samples. We confirmed that our microwave measurement system could detect small photo carrier density on the order of 10^{10} cm^{-2} and small effective minority carrier lifetime on the order of 10^{-6} s from the analysis of polysilazane coated samples. This method has high sensitivity compared with the conventional μ-PCD. It is because our method measures the quasi static density of photo induced carrier not the decay of carrier density.

Summary

We investigated photo induced carrier recombination properties for crystalline silicon coated thermally grown SiO_2 layers, vacuum evaporated SiO_x layers and spin-coated polysilazane layers by the transmissivity measurements of 9.35 GHz microwave under illumination of 532 nm green light to the top surface. Photo induced carrier density and effective minority carrier lifetime were analyzed by free carrier photo absorption and carrier diffusion theories.

In the case of 55 nm thick SiO_x film evaporated on n-type silicon substrate, the photo induced carrier density and the effective minority carrier lifetime under the light illumination at 20.8 mW/cm^2 were increased from 1.5×10^{12} cm^{-2} to 1.6×10^{13} cm^{-2} and from 31 μs to 350 μs, respectively by 1.2×10^6 Pa H_2O vapor heat treatment at 260°C for 1h. The minority carrier lifetime after the H_2O vapor heat treatment exceeded that of sample both side coated with thermally grown SiO_2. This result showed the profitability of high pressure H_2O vapor heat treatment to reduce the carrier recombination defects.

From the result of polysirazane film coated on silicon substrate, we confirmed that our microwave measurement system could detect small photo carrier density on the order of 10^{10} cm^{-2} and small effective minority carrier lifetime on the order of 10^{-6} s.

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References

[1] J. M. Borrego, R. J. Gutmann, N. Jensen and O. Paz: Solid State Electronics **30** (1987) 195.

[2] G. S. Kousik, Z. G. Ling and P. K. Ajmera: J. Appl. Phys. 72 (1992) 141.

[3] T. Sameshima, H. Hayasaka and T. Haba: Jpn. J. Appl. Phys. **48** (2009) 021204.

[4] T. Sameshima, H. Hayasaka and T. Haba: Proc. in Workshop on Active Matrix Flat Panel Displays (Tokyo, 2008) p205-208.

[5] T. Sameshima and M. Satoh: Jpn. J. Appl. Phys. **36** (1997) L687.

[6] M. Born and E. Wolf: *Principles of Optics* (Pergamon, New York, 1974) Chaps. 1 and 13.

[7] Andrew S. Grove: *Physics and Technology of Semiconductor Devices* (Wiley, New York, 1967) Chap. 5.

[8] T. Sameshima, M. Shimokawa, J. Takenezawa, T. Nagao, M. Hasumi, S. Yoshidomi, N. Sano and T. Mizuno: to be published in Proc. in 6th Thin Film Materials and Device Meeting (Kyoto, 2009).