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Minority Carrier Lifetime Measurement by Photo-Induced Carrier Microwave Absorption Method

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Abstract. We propose a measurement system of photo-induced minority carrier absorption of 9.35 GHz-microwave using periodically pulsed light illumination at 620 nm. The ratio of average carrier density during light illumination ON to light illumination OFF, *P*, was theoretically analyzed for different light pulse widths. Analysis of *P* resulted in a formula giving minority carrier lifetime, τ_{eff}, of silicon under continuous light illumination. τ_{eff} for hole was experimentally determined by the formula and its recombination sites were obtained for n-type silicon substrates coated with thermally grown SiO_2 layers. We also demonstrated increase in τ_{eff} with high pressure H_2O vapor heat treatment.

Introduction

Semiconductor solar cells have been attractive as a device producing electrical power from sun light [1]. High quality of semiconductor and its surfaces are demanded for achieving high conversion efficiency. Analysis of photo induced carrier properties of semiconductor is therefore important. Nondestructive and noncontact measurement system is attractive. Measurements of microwave photo-conductive decay and quasi-steady-state photo conductance have been widely used for the measurement of the photo induced minority carrier lifetime. We have developed a microwave free carrier absorption measurement system with continuous wave (CW) light illumination [2]. Free carriers in semiconductors respond to the incident electrical field of microwave on the order of GHz and complex refractive indexes can be changed so that the transmissivity changes with the density of free carriers. When CW light is illuminated to a semiconductor sample, the density of minority carrier per unit area *N* is effectively given by the carrier generation rate *G* per unit area, and the effective minority carrier lifetime τ_{eff}^{cw} as,

$$N = \tau_{eff}^{cw} G \quad . \tag{1}$$

N was precisely measured by change in microwave intensity under illumination of CW light. However, it is not easy to experimentally determine τ_{eff}^{cw} because *G* strongly depends on light reflection loss, which is sometimes unknown. Transient measurement system is therefore important to obtain the minority carrier lifetime.

In this paper, we propose a free carrier microwave absorption measurement system with periodically pulsed light illumination which precisely gives the effective minority carrier lifetime τ_{eff} under a low light intensity. A ratio of the average carrier density during dark and light illumination *P* is measured by time integration during illumination with many light pulses. Analysis of *P* gives a formula determining τ_{eff} which is close to τ_{eff}^{cw}. We discuss carrier annihilation properties using *P* and τ_{eff}. We demonstrate measurement of τ_{eff} using the present method without information of *G* for n-type crystalline silicon. We also demonstrate increase in τ_{eff} with high pressure H_2O vapor heat treatment.

Theory

We supposed that photo-induced carriers were annihilated at recombination sites which concentrated at the surfaces and uniformly distributed in the bulk substrate. The recombination sites at the surfaces gave the surface recombination velocities, S_{top} and S_{rear}. S_{top} was defined as the surface recombination velocity at the top surface illuminated with light. S_{rear} was one at the other surface. The recombination sites uniformly distributed in the bulk substrate gave the bulk lifetime τ_b. When light was absorbed at the top surface region of semiconductor with a sufficiently high absorption coefficient, generation of photo-induced carriers was limited just at the top surface region. The photo induced carriers diffused with time. The carrier volume density $n(x,t)$ at a depth of x and at the time of t was calculated using a time-evolution type finite element differentially diffusion model when light was periodically illuminated for duration of T, and light was subsequently off for T. The minority carrier density per unit area $N(t)$ was also calculated by integration of $n(x,t)$ with x from 0 to the thickness of substrate. $N(t)$ increases during light illumination and decreases in dark. It is essential that $N(t)$ must periodically changes according to periodic light illumination after sufficient times from initiation of illumination. $N(t)$ consists of the zero frequency (CW) component, which includes information of τ_{eff}^{cw}, as well as components of integral multiples of the fundamental frequency of $0.5T^{-1}$. After sufficient time passed, time zero (t = 0) was defined in order to calculate periodic $N(t)$ during light ON and OFF. The average carrier density during light illumination, N_{on}, was calculated by time integration from 0 to T. The average density of residual carriers in dark (light OFF), N_{off}, was also obtained by time integration from T to $2T$. We defined $P(T)$ as the ratio of N_{off}/N_{on} as,

$$P(T) = \frac{N_{off}}{N_{on}} = \frac{\frac{1}{T}\int_T^{2T} N(t)dt}{\frac{1}{T}\int_0^T N(t)dt} \quad . \tag{2}$$

We calculated $P(T)$ as a function of T with different τ_b, S_{top}, and S_{rear} in cases of minority carriers of hole. When $S_{top} = S_{rear} = 0$, $N(t)$ was simply expressed by a model with a single time constant τ_b. Therefore, $P(T)$ was given as,

$$P(T) = \frac{N_{off}}{N_{on}} = \frac{\frac{\tau_b}{T}\left(1-e^{-\frac{T}{\tau_b}}\right)}{1+e^{-\frac{T}{\tau_b}} - \frac{\tau_b}{T}\left(1-e^{-\frac{T}{\tau_b}}\right)} \quad . \tag{3}$$

$P(T)$ monotonously decreased from 1 to 0 as T increased. When $T = \tau_b$, $P(T)$ was as,

$$P(\tau_b) = \frac{e-1}{2} \sim 0.859 \quad . \tag{4}$$

When light pulses with a width as τ_b was periodically illuminated, the most of minority carriers remained in semiconductor in dark duration in the case of $S_{top} = S_{rear} = 0$. When $T = 2\tau_b$, $P(T)$ was as,

$$P(2\tau_b) = \frac{1-e^{-2}}{1+3e^{-2}} \sim 0.615 \quad . \tag{5}$$

$P(T)$ decreased from 0.859 to 0.615 as T increased from τ_b to $2\tau_b$. We named the pulse width for $P(T)$ at 0.859 as τ_{pulse} in general cases, as,

$$\tau_{pulse} = T\left(P = 0.859\right) \quad . \tag{6}$$

Moreover, we defined R as,

$$R = \frac{T\left(P = 0.615\right) - T\left(P = 0.859\right)}{T\left(P = 0.859\right)} \quad . \tag{7}$$

τ_{pulse} and R were τ_b and 1 in the limited case of $S_{top} = S_{rear} = 0$. τ_{pulse} and R were used to characterize minority carrier annihilation properties and to obtain the effective minority carrier lifetime for the present method.

According to the free carrier absorption model in semiconductors, the absorption coefficient α was approximately proportional to $n(x,t)$ and the carrier mobility μ. Integration of $n(x,t)$ with depth gave a relation between microwave transmittance T_r and $N(t)$ as,

$$\ln T_r - \ln T_{ro} \sim -CN(t) \tag{8}$$

where T_{r0} was the microwave transmittance in the dark field and C was a constant including μ. $P(T)$ defined by eq. (2) is therefore experimentally obtained by logarithm of the microwave transmittance as,

$$P(T) = \frac{\int_T^{2T} \left(\ln T_{ro} - \ln T_r\right) dt}{\int_0^T \left(\ln T_{ro} - \ln T_r\right) dt} \quad . \tag{9}$$

Experimental Procedure

N-type silicon substrates with a resistivity of 15 Ωcm and a thickness of 520 μm were prepared. The both surfaces were coated with 100 nm thick thermally grown SiO_2 layers (sample I). The SiO_2 layer at the top surface was thinned to about 2 nm by 5% diluted hydro florid acid to make a defective surface with a high surface recombination velocity at the top surface (sample II). We also prepared n-type silicon substrates with a 4-inch diameter and a 150-μm thickness coated with 10-nm thick thermally grown SiO_2 layers (sample III). We then annealed them with $1x10^6$ Pa H_2O vapor at 300^oC in for 30min (sample IV). Moreover we prepared silicon substrates coated with 100 nm thermally grown SiO_2 layers and different minority carrier lifetimes to evaluate the theory described above.

The 9.35 GHz microwave transmittance measurement system was constructed by waveguide tubes, as shown in Fig. 1. It had a narrow gap for placing a sample wafer. A small hole was opened at a wall of the waveguide tube to place an optical fiber for introducing light of 620 nm light emitting diode (LED). The light was switched with pulse widths ranging from $5x10^{-5}$ to $1x10^{-2}$ s. A Teflon plate was aslant placed in the waveguide tube to reflect and diffuse LED light. Consequently, the sample was uniformly illuminated at 0.8 mW/cm^2 with periodic light pulses. Microwave was coincidentally switched with light pulse ON or OFF, respectively, using a coincident switching circuit to obtain changes in microwave transmittance during light ON or OFF. The microwave, which transmitted the sample, was rectified by a high speed diode and integrated with time with a time constant of 5 s. Change in transmittance of microwave was also measured in the case of CW light illumination for comparison.

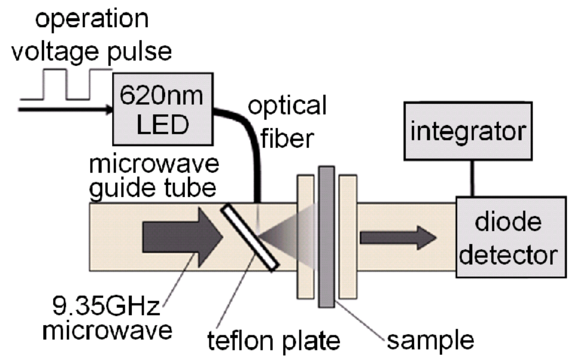

Fig. 1 Schematic experimental apparatus

Results and discussion

Figure 2 shows calculated $P(T)$ as a function of T for the hole minority carrier for 520 μm- thick silicon substrate in cases of τ_b [s], S_{top} [cm/s], S_{rear} [cm/s] as; A: $1\text{x}10^{-5}$, 0, 0, B:1, 0, 5200, C: 1, 5200, 0, D: 1, 2600, 2600 (a) and as, E: $4\text{x}10^{-4}$, 0, 0, F: 1, 0, 130, G: 1, 130, 0, and H: 1, 65, 65 (b), respectively. In order to discuss minority carrier annihilation properties, an effective lifetime $\tau_{classical}$, which has been widely used [3], is also introduced as,

$$\frac{1}{\tau_{classical}} = \frac{1}{\tau_b} + \frac{S_{top}}{d} + \frac{S_{rear}}{d} \quad . \tag{10}$$

$\tau_{classical}$ was $1\text{x}10^{-5}$ s for the four cases shown in Fig. 2(a), and $4\text{x}10^{-4}$ s for the four cases shown in Fig. 2(b). $P(T)$ was high almost 1 when T was shorter than $1\text{x}10^{-5}$ s for the every case, as shown in Fig. 2(a). This means that the average carrier density was almost same between light ON and OFF states because light switching was sufficiently rapid compared with carrier annihilation rate. $P(T)$ monotonously decreased as T increased. The average carrier density during light OFF was lower than that during light ON when T was long because minority carriers annihilated during a long dark duration. Change in $P(T)$ with T was simply described by a single time constant of $1\text{x}10^{-5}$ s in the case A, as given in eq. (3). On the other hand, $P(T)$ kept 1 until T of $7\text{x}10^{-5}$ s in the case B because minority carriers were alive until time of diffusion from the top surface to the rear surface. $P(T)$ then rapidly decreased as T increased from $7\text{x}10^{-5}$ s. On the other hand, $P(T)$ gradually decreased as T increased in the case of defective top surface C. Photo-induced carriers effectively annihilated at the surface for any pulse widths. But some carriers diffused into the substrate and were alive for a long time until back to the top surface because there was almost no defect in bulk and at the rear surface. $P(T)$ value was therefore rather high for a long pulse width case. Photo-induced carriers annihilate at the top surface as well as the rear surface in the case D. It was similar to case C for a half of the substrate thickness. $P(T)$ was therefore lower than that in the case C. Those results of the cases from A to D shown in Fig. 2(a) indicate that the present method can characterize the defect localization. On the other hand, $P(T)$ characteristics were similar among cases from E to H, as shown in Fig. 2(b). Those results come from that low carrier annihilation rate gave similar density of photo-induced carriers and its in-depth distribution for any defect localization types. In low carrier annihilation cases, $\tau_{classical}$ goes effect and defect localization cannot be distinguished.

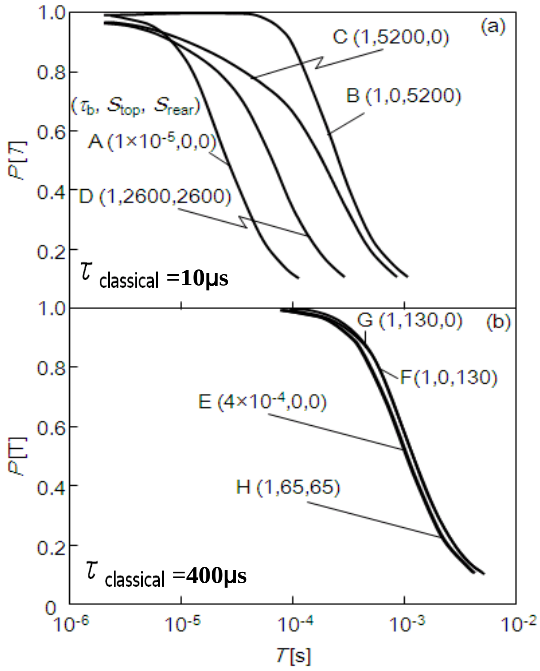

Fig. 2 Calculated $P(T)$ for the hole minority carrier for 520μm-thick. $\tau_{classical}$ was $1\text{x}10^{-5}$ s (a), and it was $4\text{x}10^{-4}$ s (b).

The effective carrier lifetime were obtained by analysis of $P(T)$ values. Through many numerical investigations, we propose the effective carrier lifetime τ_{eff} as,

$$\tau_{eff} = \frac{\tau_{pulse}}{1+\log(R)} \quad . \tag{11}$$

τ_{eff} was equivalent to $\tau_{classical}$ in a limited condition of $S_{top} = S_{rear} = 0$. In this case, $P(T)$ was governed by τ_b as given by eq. (3). τ_{pulse} was τ_b equivalent to $\tau_{classical}$ as given by eqs. (3) and (10). R was 1 in this condition as given by eq. (7). In other cases, especially highly defective surfaces, τ_{eff} was not equivalent to $\tau_{classical}$, as discuss above. The advantage of the present method of microwave transmission measurement under periodically pulsed light illumination is that no information of the carrier generation rate G is necessary. Therefore, the present method can be applied to measurement of the minority carrier lifetime for sample with complicated surface structure with no information of surface reflectivity.

Figure 3 shows experimental $P(T)$ as a function of T for sample I and II in the cases of pulsed light illumination to the top and rear surfaces. The R of sample I was almost 1 and τ_{eff} obtained by eq. (11) was 1.05×10^{-3} s. $P(T)$ were shifted to short pulse width regions for sample II. In the case of illumination to the top surface, $P(T)$ gradually decreased as T increased. R was 1.5 and τ_{eff} was 7.0×10^{-5} s. On the other hand, $P(T)$ was almost 1 until 8×10^{-5} s in the case of illumination to the rear surface. R was 0.8 and τ_{eff} was 1.7×10^{-4} s. Two different τ_{eff} clearly indicate that carrier annihilation property depends on light illumination way for a defective sample. Analysis of $P(T)$ curves resulted in most possible τ_b, S_{top}, and S_{rear} to be 5.2×10^{-3} s, 680 cm/s, and 20 cm/s, respectively, for sample II. Etching of SiO_2 layer increased the recombination velocity at the top surface.

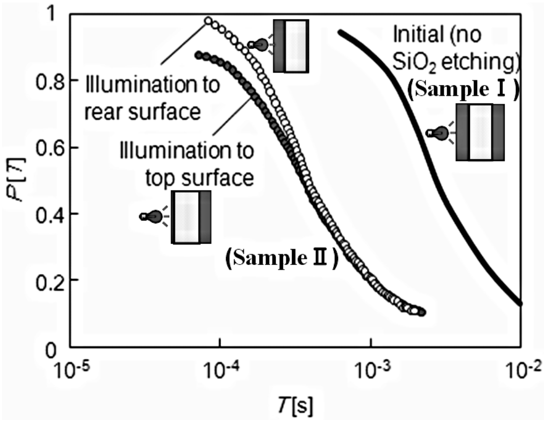

Fig.3 $P(T)$ for sample I and sample II in the cases of pulsed light illumination to the top surface with a 2 nm thick SiO_2 layer and to the rear surface with a 100 nm thick SiO_2 layer.

Figure 4 shows logarithmic change in experimental transmissivity caused by CW light illumination, $\ln T_{r0}$ - $\ln T_r$, as a function of τ_{eff} obtained by periodical pulsed light illumination for the different silicon samples coated with 100 nm thick thermally grown SiO_2. $\ln T_{r0}$ - $\ln T_r$ was clearly proportional to τ_{eff}. From the present theory and experimental demonstration of Figs. 2 and 3, we believe τ_{eff} was equivalent to τ_{eff}^{cw} and $\tau_{classical}$ when τ_{eff} was high enough. This results in a carrier generation rate of 1.5×10^{15} $s^{-1}cm^{-2}$ in the present condition from Fig. 4 and by eqs. (1) and (8). The carrier generation rate allows accurate measurement of τ_{eff}^{cw} even if τ_{eff}^{cw} was very low. Moreover, we measured a transient decay signal of microwave transmittance when light turned off after light ON for 1×10^{-2} s for a silicon sample, which had a long τ_{eff} of 1.03×10^{-3} s, using digital oscilloscope [4]. This is a sort of photoconductive decay method. A time constant, which was defined as a time at which $\ln T_r$ decreased to $\ln T_r/e$ since light pulse off, was 1.06×10^{-3} s, which was almost equivalent to τ_{eff} obtained by the present method.

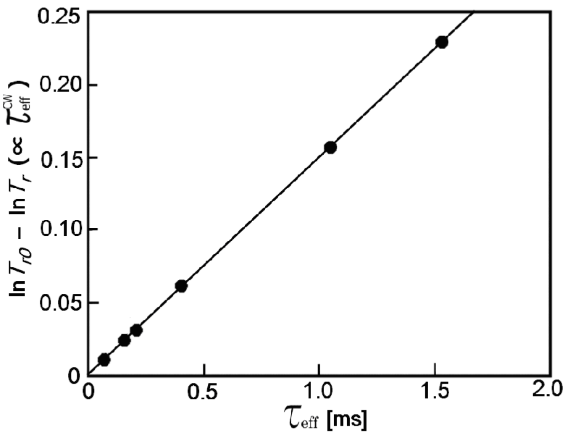

Fig.4 Logarithmic change in transmissivity caused by CW light illumination as a function of τ_{eff}

Figure 5 shows the spatial distribution of τ_{eff} for sample III analyzed from $P(T)$ curves. R was 1.0 in every measurement point and τ_{eff} ranged from 4.6×10^{-4} to 5.9×10^{-4} s. τ_{eff} was increased by 1×10^6 Pa H_2O vapor heat treatment at 300°C for 30 min (sample IV). It ranged from 7.8×10^{-4} to 1.06×10^{-3} s. Figure 6 shows surface recombination velocity S for different measurement points of samples III and IV. S was obtained by eq. (10) for $S_{top} = S_{rear}$ and long τ_b. The recombination velocity in every measurement point was markedly decreased by 1×10^6 Pa H_2O vapor heat treatment. Moreover, the recombination velocity had a lower limit of 7.1 cm/s at the present condition, as shown by the dashed line in Fig.6. This may suggest a possibility of uniform and long τ_{eff} over the silicon wafer by an optimized condition of high pressure H_2O vapor heat treatment.

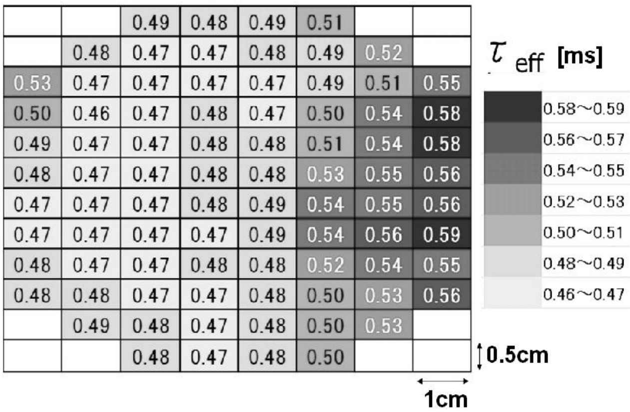

Fig. 5 Spatial distribution of τ_{eff} for Sample III

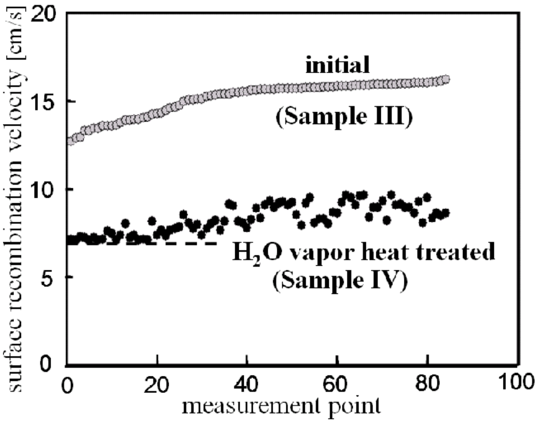

Fig. 6 Surface recombination velocity for different measurement point for Samples III and IV

Summary

We reported the measurement system of photo-induced minority carrier absorption of 9.35 GHz microwave using periodically pulsed light illumination at 620 nm at 0.8 mW/cm^2. We also developed numerical analysis of photo-induced carrier generation, diffusion, and annihilation at surfaces with S_{top}, S_{rear} and in bulk substrate with τ_b. The ratio of average carrier density during light illumination ON to light illumination OFF, $P(T)$, was introduced to investigate carrier annihilation properties. We defined the effective minority carrier lifetime τ_{eff} using $P(T)$ curves. We demonstrated that τ_{eff} well agreed with the minority carrier lifetime for CW light illumination. It is possible to determine the minority carrier lifetime without information of carrier generation rate including surface reflection loss using our method. τ_{eff} for hole minority carrier was experimentally demonstrated for n-type silicon samples coated with 100 nm thick SiO_2 layers. When the SiO_2 layer at the top surface was etched to 2 nm, we measured two different τ_{eff} of 7x10^{-5} and 1.7x10^{-4} s in the cases of light illumination to the top and rear surface, respectively. This indicated that carrier annihilation property depended on light illumination way for defective samples. We also demonstrated spatial distribution of τ_{eff} in 4 inch n-type silicon samples. τ_{eff} ranged from 4.6x10^{-4} to 5.9x10^{-4} s for initial sample. it was increased from 7.8x10^{-4} to 1.06x10^{-3} s by 1x10^6 Pa H_2O vapor heat treatment at 300^{o}C for 30 min.

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