

# Temperature Dependence of Carrier Recombination Lifetime in Si Wafers

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## ABSTRACT

The temperature dependence of carrier recombination lifetime for n- and p-type Si wafers is measured by the photoconductivity decay method in a temperature range between room temperature and about 90 K. The carrier lifetime of as-polished wafers has very weak temperature dependence, while the carrier lifetime decreases steeply with decreasing temperature for oxidized wafers. For all samples, a slow component appears in the photoconductivity decay curves after an initial fast decay at temperatures below 150 K. From a numerical simulation, we conclude that the decrease in the carrier lifetime with decreasing temperature is due to recombination through shallow recombination centers with an energy level within 0.15 eV from the bandedge, and that the slow component is due to minority carrier traps with a small majority carrier capture cross section.

## Introduction

Carrier recombination lifetime is definitely the most influential parameter for devices such as bipolar transistors and solar cells, where minority carriers play the dominant role. In addition, the carrier lifetime is extremely sensitive to defect and impurity concentration and thus can be used as a good measure of perfectness of semiconductor crystals. So far, several kinds of lifetime measurement techniques have been developed, and many reports have been published especially for lifetime in silicon.<sup>1</sup> However, there are only a limited number of reports on temperature dependence of the lifetime,<sup>2-15</sup> and almost half of them are for Si wafers doped with some metal impurities, such as Au and Fe.<sup>10-15</sup> Thus data are scarce for ordinary Si wafers, which do not contain intentionally introduced recombination centers. Moreover, the temperature dependence has been studied in a temperature range above room temperature in most of the previous studies, and there are only a limited data on the recombination lifetime at cryogenic temperatures. Lack of data on the temperature dependence of the carrier lifetime is a serious problem in device modeling calculation. Although Klaassen tried to express the temperature dependence by an empirical equation,<sup>16</sup> its physical basis is not clear.

In this study, we investigate the temperature dependence of the carrier lifetime in Si wafers by the photoconductivity decay method. The sample temperature is varied between room temperature and about 90 K. To our knowledge, this paper is the first comprehensive report on the temperature dependence of carrier lifetime in ordinary Si wafers in a cryogenic temperature range. Comparing the experimental results with those of a theoretical calculation, we discuss the properties of dominant recombination centers. Properties of defect levels in various semiconductors have been investigated by the deep-level-transient spectroscopy (DLTS), but the detection limit of a usual DLTS system is about 1/1000 of the dopant concentration. For high-quality Si wafers, the defect concentrations are sometimes smaller than this detection limit. Compared with the DLTS signal, the carrier lifetime is often influenced significantly by a smaller number of recombination centers, of the order of  $10^{10} \text{ cm}^{-3}$ . Thus, the carrier lifetime measurement can in principle be utilized as a highly sensitive defect characterization technique. In this study, we demonstrate that some defect properties can be deduced from the temperature dependence of the carrier lifetime.

## Experimental

Si wafers characterized in this study are as follows

A: as-polished p-type (B-doped) wafers of about 10  $\Omega$  cm resistivity.

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B: p-type wafers cut from the same ingot as sample A but with thermal oxide layers on both the surfaces.

C: as-polished n-type (P-doped) wafers of about 4  $\Omega$  cm resistivity.

D: n-type wafers cut from the same ingot as sample C but with thermal oxide layers.

E: oxidized n-type wafers of about 20  $\Omega$  cm resistivity, cut from a different ingot and having significantly shorter lifetime at room temperature than sample D.

All wafers are CZ-grown and about 600  $\mu\text{m}$  thick. The oxide layers were formed in dry oxygen at 1000°C and are about 0.1  $\mu\text{m}$  thick. The carrier concentrations of samples A and B and samples C and D are both expected to be about  $1 \times 10^{15} \text{ cm}^{-3}$  from their resistivity. Each wafer was cut to rectangles, about  $1.5 \times 1.5 \text{ cm}$ , and two ohmic contacts were made on them using In-Ga paste. For oxidized wafers, windows for the contact were opened using dilute HF. The distance between the two ohmic contacts is about 1 cm.

Photoconductivity decay was measured using a 904 nm laser diode as the excitation source. The pulse width is 100 ns, much shorter than the lifetime. The diameter of the illuminated region is about 1 cm on the sample surface, and the photon density is about  $5 \times 10^{12} \text{ cm}^{-2}$ . The penetration depth of the light is about 20  $\mu\text{m}$  at room temperature and about 40  $\mu\text{m}$  at 77 K, and thus the initial excess carrier concentration, which is approximately given by the areal photon density divided by the penetration depth, is of the order of  $10^{15} \text{ cm}^{-3}$ . Considering the fact that excited carriers are expected to be spread over a  $>100 \mu\text{m}$  thick region within several microseconds, effects of high-level injection will be negligible at least for samples A-D. The change in the voltage drop across the sample after the laser pulse injection was measured under constant current condition. A voltage supply and a series resistance at least 20 times larger than the sample resistance were connected to the sample. The resistance of the sample was constantly monitored to confirm that rapid increase in the resistance due to freeze-out of carriers did not occur. The voltage drop across the sample was set at about 0.5 V in the dark at any temperature. The electric field in the sample is so weak that the generated excess carriers are expected to recombine before being separated by the electric field. Thus, the measured photoconductivity decay is thought to represent the recombination process in the sample. The samples were cooled in a liquid-nitrogen cryostat with an optical window.

## Results

Figure 1 shows the decay curves of photoconductivity for sample A (as-polished p-type wafer) at three different temperatures. The time constant of the initial part of the decay is weakly dependent on temperature, slightly smaller at 210 and 110 K than at 290 K. At 110 K, a slow decay component was observed after the initial fast decay. The decay curves for sample B, the oxidized p-type wafer, are

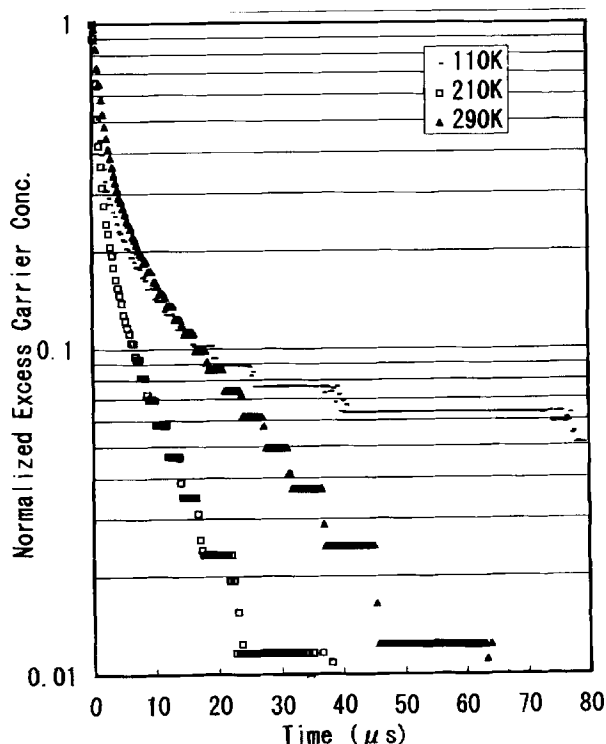


Fig. 1. Decay curves of photoconductivity (excess carriers) for the p-type, as-polished wafer at three different temperatures.

shown in Fig. 2. In contrast to sample A, clear temperature dependence of the carrier lifetime was observed for sample B. The time constant decreases considerably with decreasing temperature. The slow component was observed at 110 K, as for sample A.

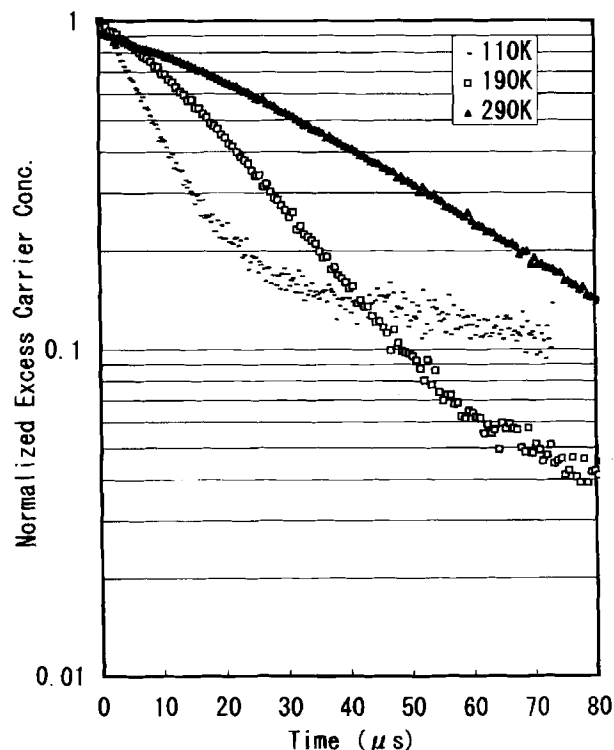


Fig. 2. Decay curves of photoconductivity for the p-type, oxidized wafer at three different temperatures.

The relation between the temperature and the carrier lifetime of the initial part of the decay is plotted in Fig. 3. The lifetime of the initial part here is defined as a time interval of decay from  $1/e$  to  $1/e^2$  of the peak. We confirmed the decay to be almost exponential within this part of the curve. The upper part of the decay curve (from the peak to  $1/e$ ) is not used in the analysis because it is sometimes affected by noise from the laser driver. As shown in Fig. 3, the carrier lifetime for sample B decreases from 45  $\mu$ s to about 10  $\mu$ s as the temperature decreases from room temperature to 100 K. On the other hand, the temperature dependence is weak for the as-polished wafer, sample A. The lifetime seems to increase slightly below 100 K for both the samples, but this seems to be because the slow component overlaps the initial fast decay and increases the apparent time constant.

Similar results were obtained for n-type wafer, samples C and D. Figures 4 and 5 show the decay curves for samples C and D, respectively. For the as-polished wafer, the time constant of the initial decay at 90 K is almost the same as at 290 K, but a slow component appears in the later part of the decay at 90 K. For sample D, the decay at room temperature is slow, with time constant larger than 100  $\mu$ s, as shown in Fig. 5. The decay at 90 K has a fast initial component in a time range of <50  $\mu$ s and a slow component in a range of >50  $\mu$ s. The temperature dependence of the carrier lifetime is shown in Fig. 6. The lifetime is obtained from the decay from  $1/e$  to  $1/e^2$ , and data points are excluded from the figure when the decay curve is strongly nonexponential in that range because of overlap of the slow component. The tendency is similar to Fig. 3, i.e., the lifetime decreases steeply with decreasing temperature for the oxidized wafers, while the temperature dependence is weak for the as-polished wafer.

Figure 7 shows the decay curves for sample E. Although sample E was oxidized, the lifetime at room temperature obtained from  $1/e$ - $1/e^2$  decay is about 25  $\mu$ s, much shorter than for sample D. This indicates that the bulk crystal of sample E is more defective than that of sample D. A slow decay component is clearly observed at temperatures below 200 K, and it becomes relatively large as the temperature is reduced. The lifetime of the initial part of the

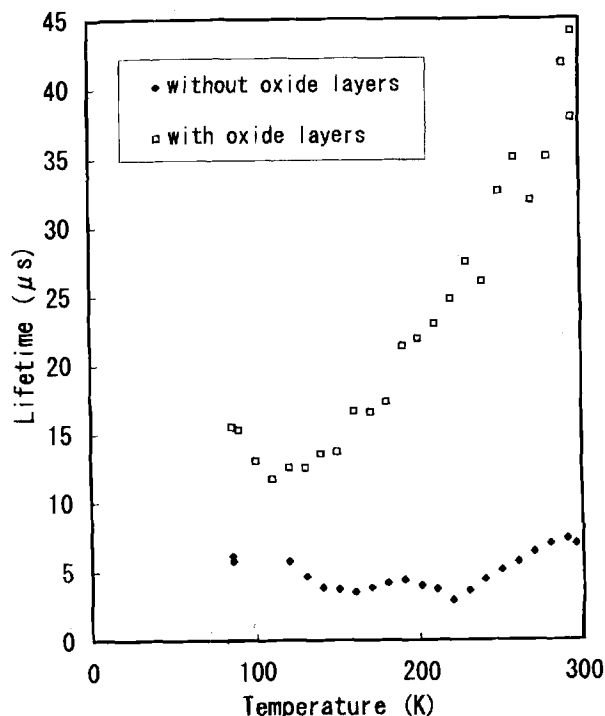


Fig. 3. Dependence of the carrier lifetime on temperature for the p-type wafer.

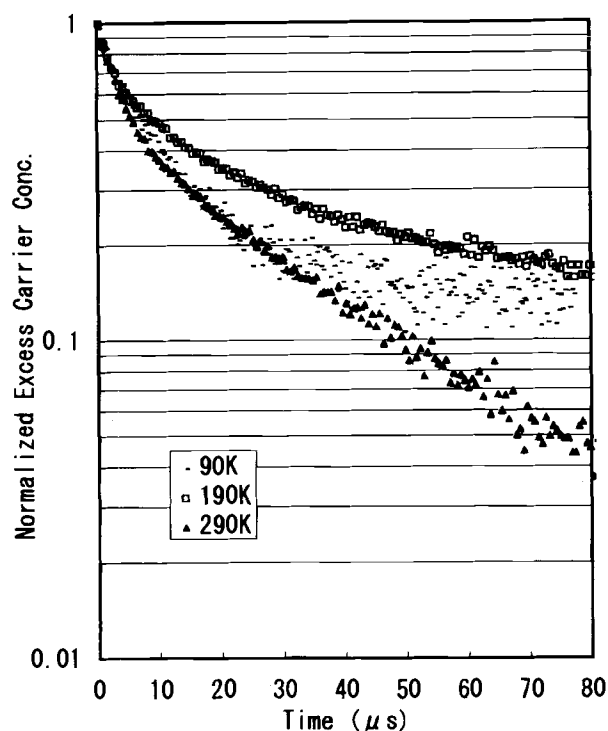


Fig. 4. Decay curves of photoconductivity for the n-type, as-polished wafer at three different temperatures.

decay is nearly constant (about 25  $\mu\text{s}$ ), independent of temperature, until the slow component begins to overlap the initial fast decay at temperatures below 120 K.

### Discussion

*Initial decay.*—As shown in the previous section, the carrier lifetime of the initial part of the decay decreases

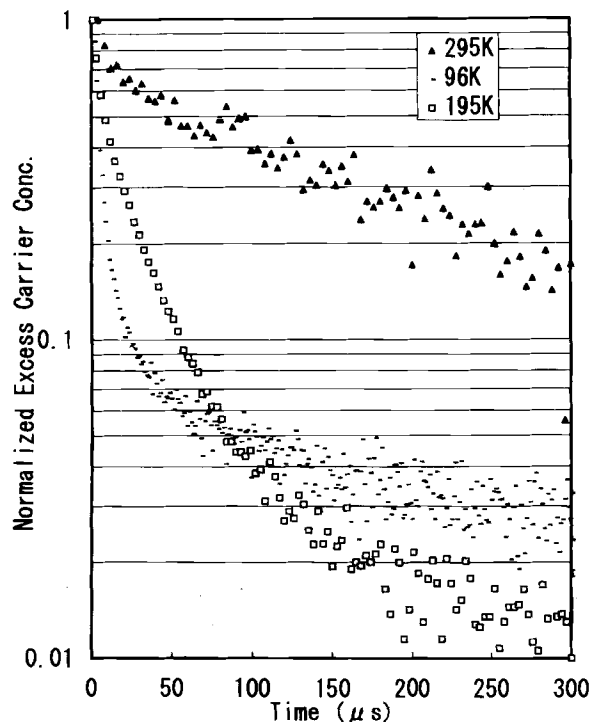


Fig. 5. Decay curves of photoconductivity for the n-type, oxidized wafer at three different temperatures.

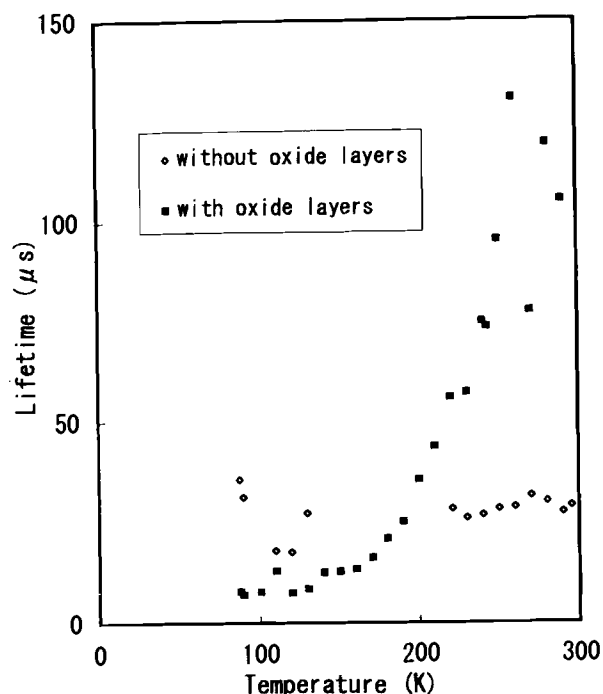


Fig. 6. Dependence of the carrier lifetime on temperature for the n-type wafer.

steeply with decreasing temperature for the oxidized wafers (samples B and D), while its temperature dependence is weak for the as-polished wafers (samples A and C) and for the defective wafer (sample E). In this subsection, we discuss factors which influence the temperature dependence of the lifetime.

*Shockley-Read theory.*—According to the Shockley-Read (SR) recombination theory, the rate of recombination

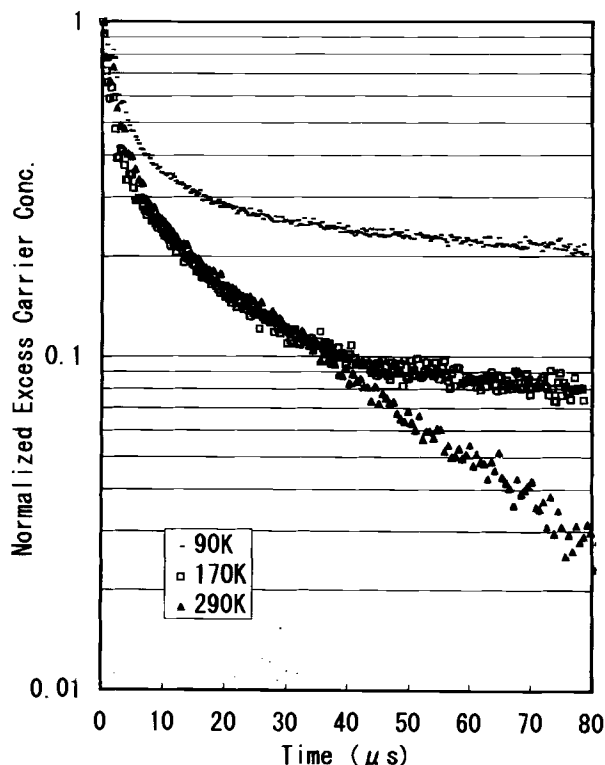


Fig. 7. Decay curves of photoconductivity for the n-type, oxidized wafer with inferior quality.

$\Delta p/\tau$  through a single kind of recombination center is given by<sup>17</sup>

$$\frac{\Delta p}{\tau} = \frac{v_{thn} v_{thp} \sigma_n \sigma_p (np - n_i^2)}{v_{thp} \sigma_p (p + N_v \exp\{-(E_c - E_v)/kT\}) + v_{thn} \sigma_n (n + N_c \exp\{-(E_c - E_t)/kT\})} \quad [1]$$

where  $E_t$  is the energy level of the center,  $N_t$  the concentration of the center,  $\Delta p$  the excess carrier concentration, the  $E_c$  ( $E_v$ ) the conduction (valence) bandedge,  $v_{thn}$  ( $v_{thp}$ ) the thermal velocity of an electron (a hole),  $\sigma_n$  ( $\sigma_p$ ) the capture cross section for electrons (holes),  $N_c$  ( $N_v$ ) the effective density of states of the conduction (valence) band,  $k$  the Boltzmann constant,  $T$  temperature, and  $n$  and  $p$  the carrier concentrations. Temperature influences the recombination carrier lifetime  $\tau$  through  $v_{th}$ , the capture cross sections, and the exponential terms in the denominator.  $v_{th}$  varies as  $T^{1/2}$ , which leads to  $T^{-1/2}$  dependence of  $\tau$ . The relationship between  $T$  and the capture cross section  $\sigma$  depends on type of potential of the center.  $\sigma$  of a coulombic center increases with decreasing temperature. On the other hand, if the center has an energy barrier against the carrier capture because of electron-lattice coupling,  $\sigma$  will decrease exponentially with decreasing temperature in a certain temperature range. The exponential terms in the denominator represent rates of re-emission of carriers from the center, and they decrease with decreasing temperature. When the re-emission rate is large, the center cannot be an efficient recombination center. The re-emission rate is large for defects with an energy level close to the bandedge, and thus it is usually thought that the energy level of the dominant recombination center is deep. If the energy level is near the middle of the bandgap, the exponential terms are much smaller than the sum of the other two terms in the denominator in the temperature range below room temperature. Then, the re-emission rate is negligible and does not influence  $\tau$  significantly.

**Oxidized wafers (samples B and D).**—First, we discuss the temperature dependence of the carrier lifetime for the oxidized wafers (sample B and D). It is known that the surface recombination of Si wafers is suppressed by oxidation. In fact, the lifetime at room temperature is much higher for the oxidized wafers than for the as-polished wafers. Thus, we may consider that the bulk recombination rather than surface recombination is dominant for the oxidized wafers. As shown in Fig. 3 and 6, the carrier lifetime decreases with decreasing temperature. As noted above, if the dominant recombination center has a deep energy level, the re-emission rate is negligible at any temperature below room temperature. However, if a shallow center is the dominant recombination center, the lifetime can decrease with decreasing temperature because the re-emission is suppressed at low temperatures.

For quantitative discussion, we carry out a numerical calculation considering two species of recombination centers. One of them has a deep energy level, just at the midgap, and the level of the other is located near the bandedge. The rate of the recombination through each recombination center is given by Eq. 1 with parameters of the respective center substituted, and the total recombination rate  $\Delta p/\tau$  is given by the sum of these two rates. The majority carrier concentration is set  $1 \times 10^{15} \text{ cm}^{-3}$ , as expected from the resistivity of the samples characterized here.  $\sigma_n$  and  $\sigma_p$  of the deep recombination center are assumed to be  $1 \times 10^{-15} \text{ cm}^2$ , a typical value for a deep level without a capture barrier (about the size of an atom).

Figure 8 shows the calculated temperature dependence of the carrier lifetime  $\tau$  for the n-type sample with energy level of the shallow center  $\Delta E = E_c - E_t$  as a parameter. Although we assume the shallow level to be in the upper half of the bandgap, the calculated results do not significantly depend on whether the level is closer to  $E_v$  or  $E_c$ , and are dominantly determined by the energy difference from the nearer bandedge. The concentration of the deep center  $N_{rd}$  is assumed to be  $3 \times 10^{11} \text{ cm}^{-3}$ , and that of the shallow one  $N_{rs} 1 \times 10^{13} \text{ cm}^{-3}$ .  $\tau$  at low temperatures ( $\sim 100 \text{ K}$ ) is

mainly determined by the concentration of the shallow center, and thus its value was chosen so that the calculated

lifetimes at low temperatures agree with the corresponding experimental values ( $\approx 10 \mu\text{s}$ ). As shown in the figure, the lifetime decreases with decreasing temperature. A reasonably good fit is obtained when  $\Delta E = 0.12 \text{ eV}$ .

In Fig. 9, the energy level of the shallow center is fixed at  $0.12 \text{ eV}$ , and the carrier lifetime  $\tau$  is given for various concentrations of the deep center,  $N_{rd}$ . While  $\tau$  at low temperatures is not significantly influenced by  $N_{rd}$ ,  $\tau$  near and above room temperature is mainly determined by  $N_{rd}$ . If  $N_{rd}$  is larger than  $3 \times 10^{12} \text{ cm}^{-3}$ ,  $\tau$  is almost independent of temperature. It should be noted that we are not able to deduce the concentrations of the deep and shallow centers from a fitting with the experimental data, because  $\sigma_p$  of the centers, which was only tentatively assumed to be  $1 \times 10^{-15} \text{ cm}^2$ , is, in fact, unknown.

Similar calculation results were obtained for the p-type wafer as shown in Fig. 10. The theoretical curve in the figure was obtained under the condition  $N_{rd} = 1.2 \times 10^{12} \text{ cm}^{-3}$ ,  $N_{rs} = 7 \times 10^{12} \text{ cm}^{-3}$ , and  $\Delta E = 0.14 \text{ eV}$ .

Although we have so far tried to interpret our experimental results considering the re-emission/recombination probability at the recombination centers, the temperature dependence of the lifetime might be related to temperature dependence of the capture cross section of the deep recombination center. If the capture cross section increases with decreasing temperature, the lifetime will decrease with sample cooling, as observed in our experiment. It is well known that the capture cross section of a coulombic center varies as  $T^{-n}$  ( $n = 2 \sim 4$ ).<sup>18</sup> We calculated the relation between  $\tau$  and  $T$  considering two deep recombination centers, one of which has  $\sigma$  varying as  $T^{-n}$  ( $n = 2 \sim 4$ ), and tried to fit it to the experimental data. However, the fitting is less successful than in Fig. 8 and 10. Although the temperature dependence is weak in a range  $T = 100 \sim 170 \text{ K}$  in the experimental data, such tendency was not reproduced by the calculation. Thus, change in  $\sigma$  is not thought to be the primary cause of the temperature dependence.

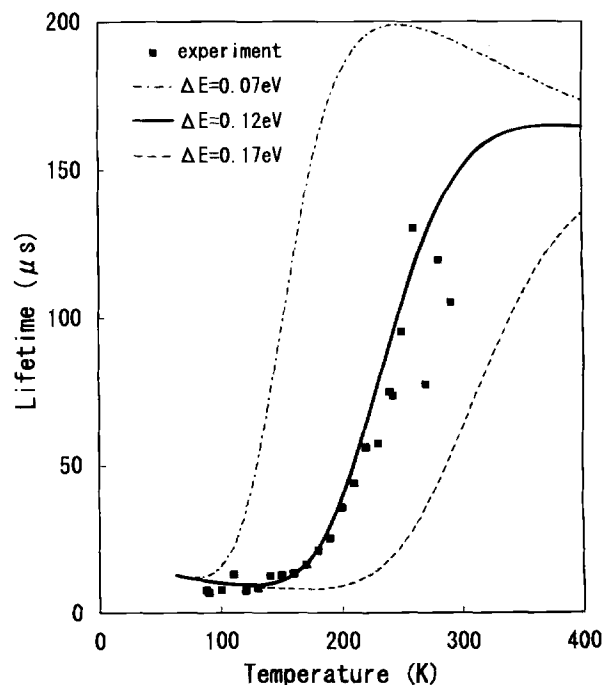


Fig. 8 Calculated temperature dependence of the carrier lifetime for n-type Si with the level of the shallow recombination center,  $\Delta E$ , as a parameter. A good fit with the experimental results is obtained when  $\Delta E = 0.12 \text{ eV}$ .



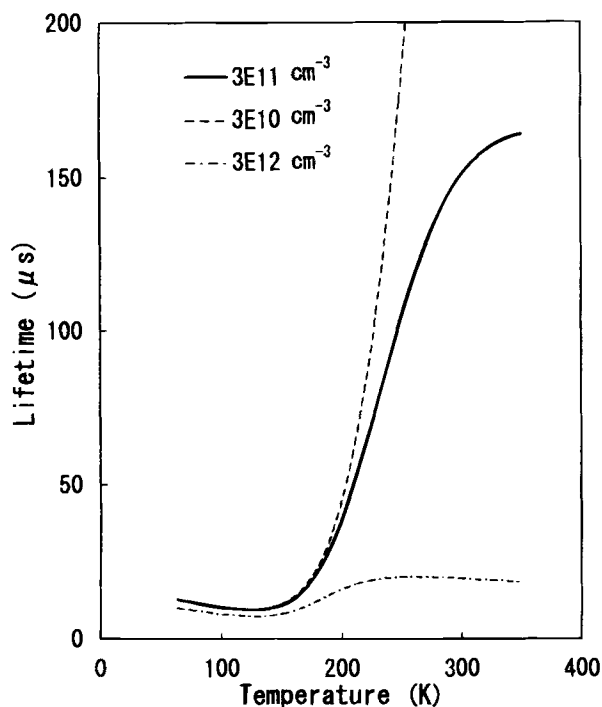


Fig. 9. Calculated temperature dependence of the carrier lifetime for n-type Si with the concentration of the deep recombination center as a parameter.

The dopant atoms might also be considered as a recombination center. The energy levels of both P and B are shallow, about 0.045 eV, and if they can effectively capture the minority carriers, the lifetime will decrease with decreasing temperature. However, the capture process will be a radiative process and thus its probability will be negligibly small. The wave function of a carrier bound to a shallow center is almost that of the band, only modified by an enve-

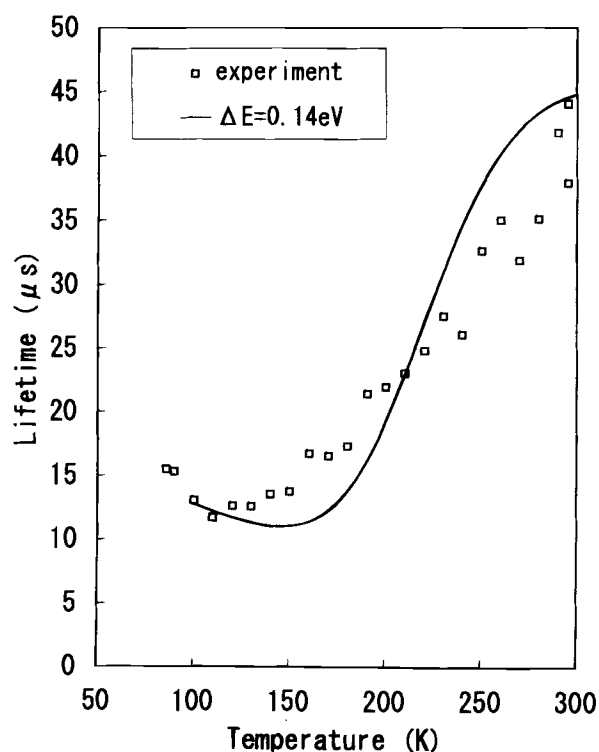


Fig. 10. Calculated temperature dependence of the carrier lifetime for p-type Si. A good fit with the experimental results is obtained when  $\Delta E = 0.14$  eV.

lope function weakly localized around the center. Thus, the recombination probability at the shallow centers should be small because of the indirect band structure of Si.

**As-polished and the defective oxidized wafers.**—The as-polished wafers have a much shorter carrier lifetime than the oxidized wafers at room temperature. Therefore, at least near room temperature, the surface recombination is dominant for the as-polished wafers. The temperature dependence of the lifetime is very weak as shown in Fig. 1 and 3. This indicates that the surface defects responsible for the surface recombination have a deep energy level and capture cross sections which do not strongly depend on temperature. According to the calculation based on Eq. 1, the center should have a level more than 0.22 eV apart from the bandedge to have weak temperature dependence of the recombination rate below room temperature.

The carrier lifetime of sample E is also only weakly dependent on temperature. Sample E has oxidized surfaces, but its lifetime at room temperature is considerably shorter than that of the other n-type, oxidized sample, i.e., sample D. This difference can be attributed to a larger density of deep recombination centers in sample E. As shown in Fig. 9,  $\tau$  near room temperature is short and its temperature dependence is weak when  $N_{\text{rd}}$  is large.

**Slow component.**—For all the samples, a slow component appeared after the initial fast decay at low temperatures. It is known that minority carrier traps can cause such a slow decay.<sup>1</sup> If a defect immediately captures a minority carrier but not a majority carrier, then an excess majority carrier survives long because the captured minority carrier cannot recombine with a majority carrier. Since the majority carrier concentration is much larger than the minority carrier concentration, the majority carrier capture is much faster than the minority carrier capture if the capture cross section is the same for both the carriers. Therefore, to cause a slow decay, the trap should have a majority-carrier capture cross section much smaller (by several orders of magnitude) than that for minority carriers.

For more quantitative discussion, we perform a numerical simulation taking into account the carrier capture and emission at (i) deep recombination centers, (ii) shallow recombination centers, and (iii) traps. The electron population in the trap level  $n_t$ , for example, is calculated by

$$dn_t/dt = \sigma_n v_{\text{th}} n (N_t - n_t) - e_n n_t - \sigma_p v_{\text{th}} p n_t - e_p (N_t - n_t) \quad [2]$$

where  $e$  is the emission coefficient,  $N_t$  the trap concentration, and  $n$  and  $p$  are the carrier concentrations.  $e_n$  is related to  $\sigma_n$  and the energy level  $E_c - E_t$  by the equation  $e_n = \sigma_n v_{\text{th}} N_c \exp[-(E_c - E_t)/kT]$ . Similar equations were written for the recombination centers, the conduction and valence bands, and these differential equations were solved simultaneously by numerical integration. From the simulation results, it was found that the majority carrier capture cross section of the trap needs to be less than  $10^{-17} \text{ cm}^2$  to cause a slow decay ( $\tau > 200 \text{ } \mu\text{s}$ ).

In the experimental results, the slow component disappears at temperatures above  $\approx 150 \text{ K}$ . We can consider three possible reasons for its disappearance. (n-Type wafers are taken as the example.)

1. The trap level is so close to the valence bandedge that in the high temperature range ( $> 150 \text{ K}$ ), the captured holes are re-emitted to the band and recombine through the recombination centers.

2. The trap level is so close to the conduction bandedge that in the high temperature range, the traps are positively ionized (if they are donor-like) and thus not able to capture excess holes.

3. The electron capture cross section of the trap has a temperature dependence. At low temperatures, the electron capture cross section of the trap is small because of the capture energy barrier. At high temperatures, the energy barrier against electron capture is not large enough to prevent the traps from capturing electrons, and thus they act as a recombination center.

At present, it is difficult to unambiguously determine which is the dominant reason. However, we think that the second one is most probable because of the following reasons.

First, if the slow decay process is limited by the re-emission process, the time constant of the slow decay will increase exponentially with decreasing temperature. However, the time constant did not change appreciably with temperature once the slow component appeared, as shown in Fig. 7. Thus case 1 above is not probable.

Second, if the traps have a majority carrier capture cross section much larger than  $1 \times 10^{-17} \text{ cm}^2$  near room temperature it should act as an efficient recombination center and considerably shorten the carrier lifetime. However, the lifetime is longer at a higher temperature. Thus case 3 is not probable.

Figure 11 shows examples of the simulated decay curves for the n-type wafer. Values of the parameters are as follows. Electron concentration  $1 \times 10^{15} \text{ cm}^{-3}$ , deep recombination center concentration;  $3 \times 10^{11} \text{ cm}^{-3}$ ; shallow recombination center concentration;  $1 \times 10^{13} \text{ cm}^{-3}$ ; its energy level; 0.12 eV;  $\sigma_p$  and  $\sigma_n$  of both the recombination center;  $1 \times 10^{-15} \text{ cm}^2$ ; trap concentration;  $1 \times 10^{13} \text{ cm}^{-3}$ ; trap energy level; 0.15 eV from the conduction band;  $\sigma_p$  of the trap;  $1 \times 10^{-15} \text{ cm}^2$ ;  $\sigma_n$  of the trap;  $2 \times 10^{-19} \text{ cm}^2$ . As can be seen from the figure, the main features of the experimental results are reproduced by the simulation (i.e., decrease in the initial decay lifetime with decreasing temperature, and appearance of the slow decay component in the low temperature range). The slow component disappears at 300 K because the traps capture holes (emit electrons) at equilibrium (case 2 above). The set of the parameters used here is not the unique one which generates results consistent with experimental data. Therefore, we are not able to obtain quantitative information about, for example, concentration and energy level of the traps. However, we may conclude that the trap level is within 0.2 eV from the bandedge. Otherwise, the slow component appears even near room temperature.

**Comparison with other research results.**—The previous studies on the temperature dependence of the carrier lifetime are either for Si doped with metallic impurities or for

Si without intentional introduction of recombination centers. For the metal doped Si, the observed temperature dependence was interpreted considering change in both the emission probability and the capture cross section of the metal impurity with temperature.<sup>10-15</sup> For Si without intentional contamination, the lifetime was found to decrease with decreasing temperature, as in this study, but the interpretation is different among them. Sandiford estimated the lifetime from current-voltage characteristics of p-n junctions in temperature range above room temperature and attributed the observed temperature dependence to change in the capture cross sections with temperature.<sup>3</sup> Jacobs et al. measured the lifetime in high-resistivity Si by the microwave photoconductivity decay ( $\mu$ -PCD) method.<sup>4</sup> They interpreted the results on the basis of the SR theory, and the energy levels were estimated to be 0.065 eV for the bulk recombination center and 0.14 eV for the surface recombination center. These values are considerably smaller than our values, i.e., 0.12–0.14 eV for the bulk and >0.22 eV for the surface. Ohsawa et al. also used the  $\mu$ -PCD technique in a temperature range 190–400 K and concluded that the energy level of the recombination center is 0.18 eV from the valence bandedge for CZ, p-type Si.<sup>7</sup> Similar conclusions were obtained by Bemski for p-type Si from the  $\tau$  measurement in a temperature range 275–400 K.<sup>2</sup> Those results seem consistent with ours, although the level is slightly shallower in our results. In the analyses in those previous studies, it was assumed that the level is in the lower half of the bandgap for p-type Si, but this assumption has no basis. We cannot determine whether the level is in the lower half or the upper half from the carrier lifetime measurement only.

Katayama and Shimura measured the temperature dependence of the lifetime in a temperature range from room temperature to 250°C for n-type wafers both before and after oxidation.<sup>8</sup> According to their results, the temperature dependence is weak for the oxidized sample. On the other hand, strong temperature dependence was observed for the as-polished samples and was interpreted considering a level at about 0.2 eV from the bandedge. We did not measure  $\tau$  in the temperature range above room temperature. As shown in Fig. 8, we predicted that the temperature dependence is weak for the oxidized wafers in the temperature range above room temperature, as in their results. For the as-polished wafer, we estimated that the level of the dominant recombination center is deeper than 0.22 eV, which is slightly larger than their estimated value, 0.2 eV.

The occupation probability of the recombination center can be changed either by changing temperature or by changing carrier concentration. Kitagawara et al. measured carrier-concentration dependence of the carrier lifetime for p-type Si, and concluded that the dominant recombination center has a level at  $E_v + 0.16 \text{ eV}$ ,<sup>19</sup> which is very close to our results ( $\Delta E = 0.14 \text{ eV}$ ).

It should be noted that data on the carrier lifetime below 200 K is very scarce. Watanabe and Munakata measured the lifetime in Au-doped Si at temperatures down to 100 K.<sup>14</sup> Dziewior and Schmid measured the lifetime at 77, 300, and 400 K.<sup>6</sup> The samples of Dziewior and Schmid were not metal-doped but were heavily doped with donors or acceptors to study the Auger lifetime. For relatively lightly doped samples, the lifetime measured by them at 77 K is about one order of magnitude smaller than that at 300 K. This result is similar to our results for the oxidized wafers. We have not found any other reports of measurement and interpretation of temperature dependence of the carrier lifetime in the cryogenic temperature range.

At present, we are not able to identify the atomic structure of the recombination center and the trap. Kitagawara et al. found a clear positive correlation between the oxygen concentration and the recombination center concentration.<sup>19</sup> Since our wafers are CZ grown, oxygen-related defects are supposed to be the dominant recombination center, as suggested by them.

The temperature dependence of the carrier lifetime is an important part of the data necessary for device modeling. In

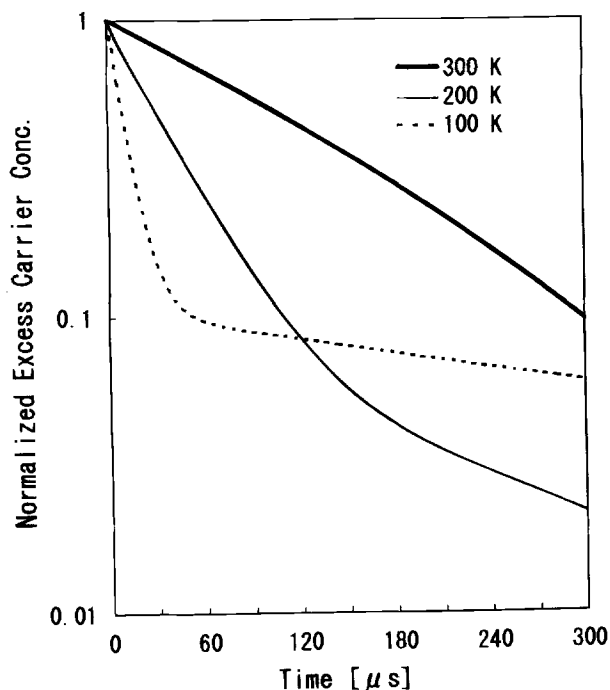


Fig. 11. Decay curves of excess carrier concentration in n-type Si calculated considering two kinds of recombination centers and a trap.

addition, as shown in the above analysis, some of the defect properties can be deduced from the dependence. Thus, the temperature dependence of the carrier lifetime should be measured for various samples, including poly-crystalline Si wafers and silicon-on-insulator (SOI) wafers.

### Conclusion

We have measured the temperature dependence of the carrier recombination lifetime for n- and p-type Si wafers by the photoconductivity decay method in a temperature range between room temperature and about 90 K. The carrier lifetime of as-polished wafers has a very weak temperature dependence, while the lifetime of the oxidized wafer decreases steeply with decreasing temperature. From the comparison with calculation results, we have concluded that the level of the dominant recombination center is shallow (<0.15 eV) in the bulk and deep (>0.22 eV) at the surface, for both n- and p-type wafers. At low temperatures, a slow component with time constant >100  $\mu$ s has been observed in the decay curve and attributed to minority carrier traps with a small capture cross section for majority carriers.

Manuscript submitted January 15, 1998; revised manuscript received April 20, 1998.

Nagoya Institute of Technology assisted in meeting the publication costs of this article.

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## Comparison of Oxidation Rates for a-Si<sub>1-x</sub>C<sub>x</sub>:H Films Deposited from Pulsed and Continuous Wave RF Plasmas

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### ABSTRACT

Oxidation rates for hydrogenated amorphous silicon carbide (a-Si<sub>1-x</sub>C<sub>x</sub>:H) films deposited from both pulsed and continuous wave (CW) SiH<sub>4</sub>/CH<sub>4</sub> rf (13.56 MHz) plasmas have been measured using Fourier transform infrared spectroscopy. Films deposited from CW plasmas oxidize much more rapidly than those deposited from equivalently powered pulsed plasmas. The effect of a diluent gas in the feed (He, Ar, or H<sub>2</sub>) on film oxidation rates has also been investigated. With He and Ar, the CW films oxidize faster than the pulsed films. With H<sub>2</sub> as the diluent, however, the CW films do not oxidize as rapidly as other CW films, even after long periods of time. This is most likely the result of hydrogen radicals annealing the films through reactions with active sites on the CW films. Addition of H<sub>2</sub> also decreases the deposition rates in both pulsed and CW systems, suggesting H<sub>2</sub> contributes to the deposition reaction scheme. Additional compositional changes in the a-Si<sub>1-x</sub>C<sub>x</sub>:H materials with addition of H<sub>2</sub> to the plasma feed gas are also discussed.

### Introduction

Hydrogenated amorphous silicon carbide (a-Si<sub>1-x</sub>C<sub>x</sub>:H) has been studied extensively for the past several years due to its unique properties.<sup>1-3</sup> This interesting material has found applications in solar cells,<sup>4,5</sup> flat panel displays, photoreceptors,<sup>6</sup> and more recently as a photoresist material.<sup>7</sup> The ratio of Si to C (as well as the amount of H) in a-Si<sub>1-x</sub>C<sub>x</sub>:H films can vary over a wide range, as can the mechanical and optical properties.<sup>8</sup> For example, the optical bandgap of a-Si<sub>1-x</sub>C<sub>x</sub>:H can vary from that of a-Si:H, ~1.75 eV, to that of a-C:H which has a bandgap as large as 4.0 eV.<sup>9</sup> The electrical properties of these films, however, tend to rapidly deteriorate as the C content increases.<sup>10,11</sup> It has also been shown that the amount of H and its bonding environment in these films are extremely important to film quality.<sup>12</sup> Because of preferential bonding of hydrogen to carbon over silicon,<sup>13</sup> CH<sub>3</sub> groups are introduced into the a-Si<sub>1-x</sub>C<sub>x</sub>:H film structure. These methyl groups are

believed responsible for microvoids and electrical instability in a-Si<sub>1-x</sub>C<sub>x</sub>:H films.<sup>14,15</sup> If this microstructure is eliminated from a-Si<sub>1-x</sub>C<sub>x</sub>:H films, better photoconductivity and higher bandgap materials would be possible.<sup>4</sup> There is, however, a lack of understanding of both the chemical structure of these films and how the structure affects their physical and electrical properties.

Another serious issue affecting the mechanical and electrical properties of plasma deposited a-Si<sub>1-x</sub>C<sub>x</sub>:H films is their tendency to oxidize rapidly upon exposure to atmosphere. Eldridge and coworkers have characterized the oxidation of a-Si<sub>1-x</sub>C<sub>x</sub>:H by X-ray photoelectron spectroscopy (XPS), Rutherford backscattering (RBS), and profilometry.<sup>16</sup> Their work demonstrated that the kinetics of oxidation are sensitive to film composition and that the oxidation rate increased with increasing amounts of both carbon and hydrogen in the films. John et al. demonstrated that normally stable a-Si<sub>1-x</sub>C<sub>x</sub>:H films can be photo-oxidized at room temperature in air using UV/visible light from a Xe arc lamp or an Ar ion laser.<sup>17,18</sup> They also noted that the rate of this process increased with increasing carbon content of

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