

# Bulk carrier lifetime measurement by the microwave reflectance photoconductivity decay method with external surface electric field

Masaya Ichimura,<sup>a)</sup> Atsushi Tada, and Eisuke Arai

*Department of Electrical and Computer Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan*

Hiroyuki Takamatsu

*Process Technology Research Laboratory, Kobe Steel, Ltd., Takatsukadai, Nishi-ku, Kobe 651-2271, Japan*

Shingo Sumie

*LEO Division, Kobelco Research Institute, Inc., Takatsukadai, Nishi-ku, Kobe, 651-2271, Japan*

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We attempted to measure the bulk carrier recombination lifetime of Si wafers by the microwave reflectance photoconductivity decay (PCD) method. Voltage was applied between an external electrode and a Si wafer to suppress surface recombination. Before the measurement, the surface state density was reduced by a chemical treatment using  $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$  and diluted HF solutions. Carrier lifetime as long as 1 ms was measured by the present method for a wafer with a bare surface. Comparison with results for oxidized wafers show that the present method can suppress surface recombination more effectively than thermal oxidation, which has been often used for surface passivation in PCD measurements. © 2002 American Institute of Physics.

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The photoconductivity decay method is commonly used to measure the carrier recombination lifetime in Si wafers. The apparent lifetime is in general affected by both bulk and surface properties, and only when the surface recombination is suppressed significantly, the measured lifetime is regarded to approximate the bulk lifetime, which is a good measure of crystalline quality. To suppress the surface recombination, various methods have been proposed, such as thermal oxidation, chemical passivation by dilute HF or an iodine-ethanol solution,<sup>1,2</sup> and corona discharge.<sup>3</sup> However, each of those methods has drawbacks. Thermal oxidation is time consuming, and the bulk properties may be changed in the high-temperature process. For the chemical treatment, wafers need to be immersed in the solution during measurement. For corona discharge, stable passivation effects are obtained only when there is oxide on the surface.

In a previous paper, we proposed another method to suppress surface recombination.<sup>4</sup> The basic principle is schematically illustrated in Fig. 1. A transparent electrode is placed adjacent to the wafer surface, and dc voltage is applied between the electrode and the wafer. The laser pulse is incident on the wafer through the transparent electrode, and the decay of excess carrier concentration is monitored by the microwave reflectance photoconductivity decay method ( $\mu$ -PCD). Since the structure is basically a metal-oxide-semiconductor structure, bandbending at the wafer surface can be controlled by the applied voltage. It is known that the surface recombination velocity is maximum under the depletion condition and can be minimized under the accumulation or strong-inversion condition.<sup>5</sup> Therefore, if the applied voltage (or the surface electric field) is large enough to make the wafer surface accumulated or strongly inverted, the surface

recombination is suppressed. We have demonstrated that by applying voltage up to 2 kV to the electrode, the apparent lifetime is increased by a factor of 3 for a bare wafer. However, the voltage dependence of the lifetime does not show clear saturation, and the lifetime value is still considerably smaller than the bulk lifetime expected for commercial high-quality wafers. This indicates that the surface state density is so large that the voltage of 2 kV is not enough to bend the energy band sufficiently.

In this work, instead of increasing the voltage further, we try to reduce the surface state density by proper chemical treatments. We have already found that bandbending and effective surface recombination velocity are greatly influenced by the chemical treatment.<sup>6</sup> However, we did not find any single chemical treatment that can reduce the surface state density sufficiently. As the next step, we examine the combination of two or more treatments in this work. As shown below, several treatments can sufficiently reduce the surface state density, and we can measure the carrier lifetime as long as 1 ms by the  $\mu$ -PCD with external electric field.

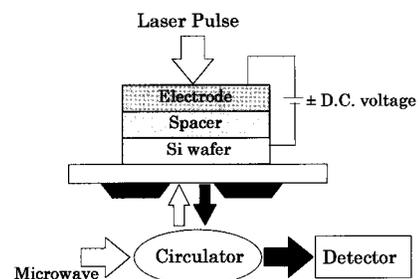


FIG. 1. Schematic illustration of the  $\mu$ -PCD with external electric field applied to the wafer surface.

<sup>a)</sup>Electronic mail: ichimura@elcom.nitech.ac.jp

TABLE I. List of the chemical treatments applied to the samples.

Treatment	Treatment process
DHF	HF-H <sub>2</sub> O(0.5% HF)→H <sub>2</sub> O rinse
SPM	H <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O <sub>2</sub> (4:1, 120 °C)→H <sub>2</sub> O rinse
HPM	HCl-H <sub>2</sub> O <sub>2</sub> -H <sub>2</sub> O(1:1:5, 70 °C)→H <sub>2</sub> O rinse
APM	NH <sub>4</sub> OH-H <sub>2</sub> O <sub>2</sub> -H <sub>2</sub> O(1:2:10, 70 °C)→H <sub>2</sub> O rinse
HNO <sub>3</sub>	HNO <sub>3</sub> (61% HNO <sub>3</sub> , 70 °C)→H <sub>2</sub> O rinse

The setup of our  $\mu$ -PCD experiment is schematically shown in Fig. 1. The sample wafer is irradiated with a pulsed laser (wavelength=904 nm) on one side. The number of photons per pulse is about  $1 \times 10^{13} \text{ cm}^{-2}$ . The opposite side of the wafer is irradiated with 10 GHz microwave, and change in its reflectance is monitored. A 25- $\mu\text{m}$ -thick plastic sheet is inserted between the electrode and the wafer as a spacer. The electrode is an indium-tin-oxide (ITO)-coated glass sheet. The measurement was done in an uncontrolled atmosphere.

The effects of the chemical treatments listed in Table I were investigated. The effects of the individual treatment have been reported in Ref. 6, and are summarized in Table II. Table II shows the dependence of the measured lifetime on voltage applied to the electrode for  $n$ -type wafers. The voltage dependence, and thus the expected position of the surface Fermi level within the gap for  $p$ -type wafers, are qualitatively the same as for  $n$ -type wafers. Properties of the SPM- and HPM-treated surface are similar to those for the initial surface, which is covered with stable native oxide. After the DHF treatment, some positive charge is induced on the surface and the surface Fermi level shifts upward within the band gap. After the APM and HNO<sub>3</sub> treatments, the voltage dependence is very weak, which indicates that the surface state density is increased by these treatments. The absolute value of the carrier lifetime is smaller after those two treatments than for the other treatments. This is also due to the enhanced surface state density.

Next, we briefly summarize results for two-step chemical treatments. Various combinations were examined, and they are classified into two groups.

(1) DHF-(APM, HPM, SPM, or HNO<sub>3</sub>): In these two-step treatments, the native oxide is first removed by DHF and then chemical oxide is formed by the second treatment (either of APM, HPM, SPM, or HNO<sub>3</sub>). The treated wafers exhibit properties similar to the APM- or HNO<sub>3</sub>-treated wafer; the measured carrier lifetime is shorter than in the initial state, and the voltage dependence is weak. This indicates that the surface state density is increased by these combined treatments. The reason for this may be as follows. By the DHF treatment, the wafer surface is deprived of oxygen and becomes chemically active. Then, metallic or organic contamination is chemically bonded to the surface and cannot be removed by the subsequent treatment.

(2) (APM, HPM, SPM, or HNO<sub>3</sub>)-DHF: When the sequence is reversed, i.e., the wafer is cleaned by one of these four treatments and then treated with DHF, the wafer surface shows quite different behavior. The measured lifetime is significantly larger than for the initial wafer, and it increases

TABLE II. Voltage dependence of the lifetime and the expected surface condition after each chemical treatment for  $n$ -type Si wafers. "Two-step (1)" is a treatment first by DHF and then by either of APM, HPM, SPM, or HNO<sub>3</sub>. "Two-step (2)" is a treatment first by either of APM, HPM, SPM, or HNO<sub>3</sub> and then by DHF.

Treatment	Applied voltage		
	$V < 0$	$V = 0$	$V > 0$
Initial surface	Increase (Strong inversion)	...	Decrease (Depletion)
DHF	Decrease (Depletion)	...	Increase (Accumulation)
SPM	Increase (Strong inversion)	...	Decrease (Depletion)
HPM	Increase (Strong inversion)	...	Decrease (Depletion)
APM	Small increase (Depletion)	...	Small decrease (Depletion)
HNO <sub>3</sub>	Small increase (Depletion)	...	Small decrease (Depletion)
Two-step (1)	Minimal change (Depletion)	...	Minimal change (Depletion)
Two-step (2)	Increase (Strong inversion)	...	Increase (Accumulation)

further with voltage application of both the polarity. This indicates that the surface state density is reduced by these two-step treatments. Among the four treatments (APM, HPM, SPM, and HNO<sub>3</sub>), we did not find a very clear difference in the resultant surface properties.

The results for the two-step treatments are also included in Table II. We also examined the complete RCA cleaning process plus subsequent DHF treatment. The resultant surface seems almost the same as for the simple (APM, HPM, SPM, or HNO<sub>3</sub>)-DHF treatment, as concerns the carrier lifetime value and its voltage dependence. Thus, we may conclude that the complete RCA process is not necessary.

To see to what extent we can suppress the surface recombination, we carried out the following experiment:

- (1) The carrier lifetime was measured for a thermally oxidized wafer.
- (2) The oxide of one side of the wafer was removed by buffered-HF (BHF) dipping. (Then the lifetime was measured, for comparison.)
- (3) The wafer was treated by the APM solution and then dipped in DHF. Here, we used APM for the cleaning process before the DHF treatment. As noted above, the other treatments (HPM, SPM, or HNO<sub>3</sub>) may be equally used for this step.
- (4) The lifetime was measured with voltage applied to the electrode, which was placed on the oxide-stripped side.

If the lifetime measured in step (4) is comparable to or larger than that measured in step (1), we can conclude that the surface recombination velocity is suppressed to the same degree as the thermal oxidation, which is commonly used for the surface passivation in the bulk lifetime measurement.

For this experiment, we used the following two  $n$ -type

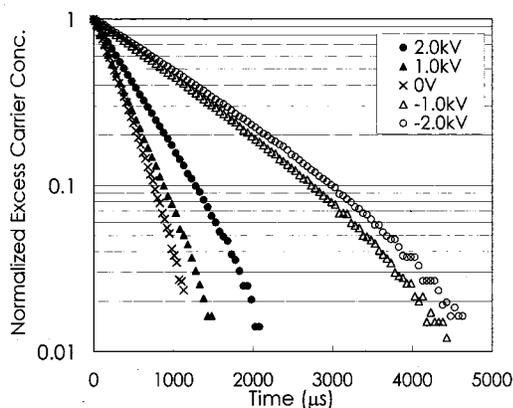


FIG. 2. Normalized decay curves of the excess carrier concentration at various voltages applied to the electrode for sample B after the oxide removal and the APM–DHF treatment.

(001) wafers: Sample A, resistivity: 3–6  $\Omega$  cm, primary mode lifetime  $\tau_1$  in step (1): 375  $\mu$ s. Sample B, resistivity: 5–8  $\Omega$  cm,  $\tau_1$  in step (1): 824  $\mu$ s. Here, we define the primary mode lifetime  $\tau_1$  as a time interval of the excess carrier concentration decay from  $1/e$  to  $1/e^2$  of the peak.

Figure 2 shows normalized decay curves of excess carrier concentration for sample B in step (4). The values of the primary-mode lifetime are plotted for both samples in Fig. 3. For comparison, the lifetime values measured in steps (1) (“oxide”) and (2) (“BHF”) are also plotted. For sample A, the lifetime was decreased from the initial value (375  $\mu$ s) to 71  $\mu$ s by the oxide removal. By the APM–DHF treatment [step (3)], the lifetime was increased to 164  $\mu$ s. It increased further by the voltage application and reaches 411  $\mu$ s at a voltage of  $-2$  kV. After the APM–DHF treatment, the lifetime increases with voltage of both the polarity. This indicates that the surface state density is so small that the surface band condition changes from the inversion to accumulation within the voltage range of  $-2$  to  $+2$  kV. The increase in the lifetime is more significant for the negative voltage. This will be because the surface Fermi level at  $V=0$  is close to the valence band rather than to the conduction band. Similar results were obtained for sample B, as shown in Fig. 3(b). At a voltage of  $-2$  kV, the lifetime of the APM–DHF-treated wafer is 1220  $\mu$ s, considerably larger than the initial value (824  $\mu$ s). Moreover, for voltages  $< -1.5$  kV, the tendency of saturation is clearly observed in the voltage dependence of the lifetime. This indicates that the surface recombination is suppressed almost completely.

As can be seen from the above results, if the wafer is properly treated, the measured carrier lifetime under the voltage application surpasses that measured before the oxide removal. Thus, the surface recombination is suppressed more effectively by the external surface electric field than by the oxide. Moreover, from the saturation tendency in the voltage dependence, we can judge that the suppression is complete. When clear saturation is observed in the dependence, we may expect that the surface recombination velocity is reduced to null in effect. This is an advantage of the present passivation method, because for the other passivation methods, we cannot know whether the passivation is complete or not. However, one possible drawback of the present method is that it is not certain to be able to suppress the surface

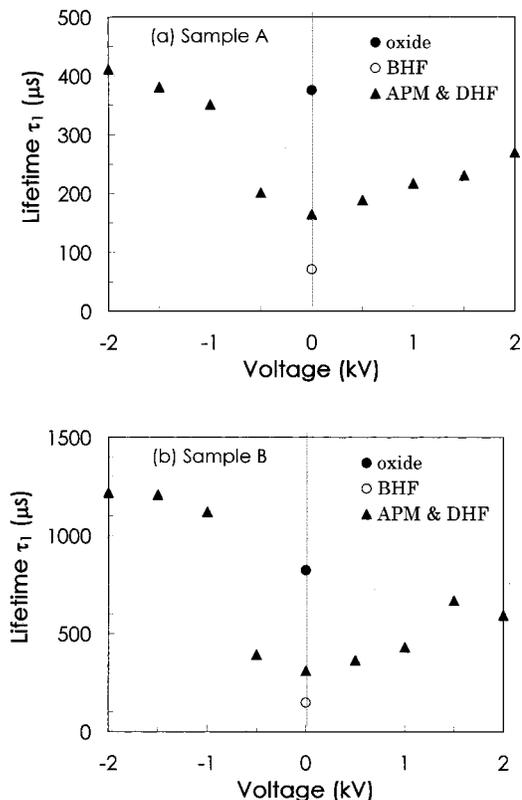


FIG. 3. Variation of the primary-mode lifetime with the voltage applied to the electrode for (a) sample A and (b) sample B after the oxide removal and the APM–DHF treatment. Lifetime values before (“oxide”) and just after the oxide removal (“BHF”) are also shown.

recombination completely for any wafer. For sample A, the saturation is not complete although a tendency toward it is observed. Somewhat larger voltage may be necessary for practical application.

In the present experimental setting shown in Fig. 1, the electric field is applied to only one of the wafer surfaces. Therefore, the measured lifetime may be influenced by recombination at the other surface. To suppress the surface recombination on both sides, the electrode should be placed under the wafer also, and the voltage should be applied between the wafer and the two electrodes. The sheet resistance of the bottom electrode needs to be high enough so that the microwave transmission is not affected.

The  $\mu$ -PCD measurements were performed about 30 min after the chemical treatment. The lifetime of the APM–DHF-treated wafers decreases gradually with time, decreases by a factor of 1.5–2, 3 h after the treatment. For sufficient passivation effects, the measurement should be done within 30 min after the treatment.

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