Temperature dependence of minority-carrier lifetime in iron-diffused p-type silicon wafers

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Minority-carrier recombination lifetime was measured with a noncontact laser/microwave method for nondiffused and iron-diffused p-type silicon wafers in the temperature range from 28 °C to 230 °C. The lifetime increased monotonically with temperature in nondiffused silicon, while the lifetime in iron-diffused silicon showed a broad peak around 110 °C and a depression around 170 °C. The temperature dependence of the lifetime in iron-diffused silicon was analyzed based on Shockley–Read–Hall statistics. The origin of the lifetime temperature dependence was attributed to the dissociation of iron-boron pairs. Our experimental data supported that an electron trap for an iron-boron pair at $E_c - 0.29$ eV was more effective as a recombination center than a hole trap at $E_v + 0.1$ eV. It was also shown that the effect of iron in concentrations as low as 1×10^{11} cm^{-3} on the lifetime can be detected with the noncontact laser/microwave method.

I. INTRODUCTION

Minority-carrier recombination lifetime is one of the most important parameters in evaluating silicon material and devices.[1] The kinetics of the recombination via deep levels has been well described by the Shockley–Read–Hall (SRH) model,[2,3] in which electrons and holes can recombine by successive capture into deep levels in the forbidden gap. Information about deep levels is generally obtained by means of deep level transient spectroscopy (DLTS),[4] Hall effect, and photoluminescence. From the view point of sensitivity and quantitative analysis, DLTS has been the most commonly used technique. However, it gives no information about the effectiveness of the level as a recombination center.[5,6]

The temperature dependence of minority-carrier recombination lifetime has been used to identify metallic impurities in silicon crystals.[7–9] Recently, this method has been further developed to identify the energy levels related to metallic impurities by means of noncontact laser/microwave DLTS which requires no electrode contact.[10]

In this paper, we report the temperature dependence of the minority-carrier lifetime for iron-diffused p-type silicon measured by a noncontact laser/microwave method. The results are analyzed based on the SRH statistics. Iron has been intentionally diffused since it is one of the most frequent contaminants occurring during device fabrication processes and it also greatly degrades the lifetime.[6] The properties of the deep levels related to iron obtained from this study are compared with the previous results.[5,9,11–13]

II. EXPERIMENT

A. Sample

The samples used in this study were (100) silicon wafers 100 mm in diameter, 525 μm thick, p-type (boron doped) with 10 Ω cm resistivity prepared from float-zone (FZ) and Czochralski (CZ) single crystals. The CZ wafers contained 1.44×10^{18} cm^{-3} of interstitial oxygen (ASTM F-121, 1979). After RCA cleaning,[14] different levels of iron contaminations were introduced onto the wafer surface by a spincoating method.[15] These wafers were then annealed at 1000 °C for 20 min in a dry oxygen ambient to diffuse iron into the bulk and also to reduce the surface recombination velocity by the formation of a thermally grown ~40 nm oxide layer. The samples were transported in and out of the furnace in a nitrogen ambient with a 5 min holding time at 1000 °C. The sample transport velocity was about 10 cm/min. No oxygen precipitation was observed in the CZ wafers after this heat treatment. The iron concentrations in the bulk measured by conventional DLTS are listed in Table I.

B. Measurement

Minority-carrier recombination lifetime was measured with a noncontact laser/microwave (LM) method (LIFETECH-88, SEMITEX Co., Ltd.).[9] Electron-hole pairs were generated by excitation with laser pulses (910 nm, pulse width 100 ns). The decay of excess carriers was observed by monitoring the decay of the microwave (14 GHz) reflection intensity. We measured the lifetime in the temperature range from 28 °C to 230 °C at intervals of about 6 °C. One complete temperature scan required about 70 min. The wafers were divided into two pieces after confirming that the lifetime at room temperature (RT) was uniform. One piece was used to measure the temperature dependence of the lifetime, and the other to measure the iron concentration by conventional DLTS.

In a photoconductive decay method, the measured lifetime (τ_M) is generally given by

$$1/\tau_M = 1/\tau_B + 1/\tau_S. \tag{1}$$

TABLE I. Carrier-trap parameters of the samples used in this study.

Sample	[Fe][a] (cm^{-3})	$\tau_{n0(FeB)}$[b] (μsec)	$\tau_{n0(Fei)}$[b] (μsec)	$\tau_{n0(Fei)}$[b] (μsec)
PFZ01	1×10^{11}	1.2×10^{2}	4.4×10^{1}	5.2×10^{1}
PFZ02	2×10^{11}	8.3×10^{1}	2.9×10^{1}	3.3×10^{1}
PCZ02	2×10^{11}	7.2×10^{1}	3.1×10^{1}	3.0×10^{1}
PFZ03	4×10^{11}	4.4×10^{1}	1.7×10^{1}	1.6×10^{1}
PFZ04	3.9×10^{12}	5.9×10^{0}	2.3×10^{0}	2.5×10^{0}
PFZ05	1.4×10^{13}	1.7×10^{0}	4.9×10^{-1}	7.8×10^{-1}
PFZ06	5.4×10^{13}	4.6×10^{-1}	1.5×10^{-1}	2.8×10^{-1}

[a]Iron concentrations measured by DLTS using the energy level at $E_v + 0.1$ eV.
[b]Calculated from the least-squares fitting using Eqs. (13)–(22) at 300 K.

where τ_B is the bulk lifetime and τ_S is the lifetime due to surface recombination. To obtain the bulk lifetime, the $1/\tau_S$ term must be subtracted from the $1/\tau_M$ term. For some of the samples, we compared the lifetime measured by a noncontact laser/microwave method with a constant flux surface photovoltage (SPV) method[16] (CMS-II DZ AUTO, Semiconductor Diagnostics Inc.) at RT. When the minority-carrier diffusion length ($\propto \tau^{1/2}$) was smaller than one-third of the thickness of the test sample, the SPV method can directly measure the bulk lifetime, neglecting the surface recombination velocity.[17] Fairly good agreement between the two methods was obtained as shown in Fig. 1. In the noncontact laser/microwave method, the lifetime was measured by taking the time difference between e^{-1} and e^{-2} of the peak intensity in the decay curve.[9]

III. RESULTS

The temperature dependence of the minority-carrier recombination lifetime is shown in Fig. 2 for different iron concentrations listed in Table I. The concentrations were measured by conventional DLTS using energy level at $E_v + 0.1$ eV[5,11,12] for the iron-boron (Fe$_i$B$_s$) pair hole trap. In a standard sample without iron-diffusion, the lifetime
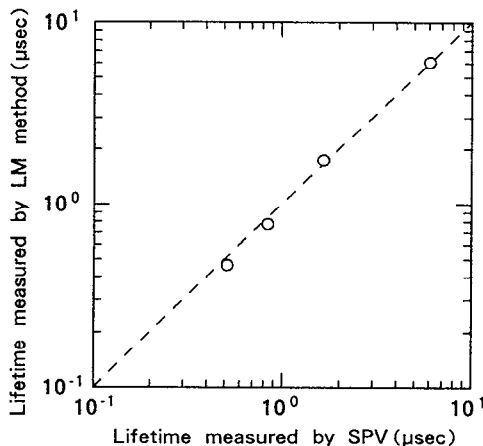

FIG. 1. Comparison of the lifetime measured by the SPV method and the laser/microwave method.
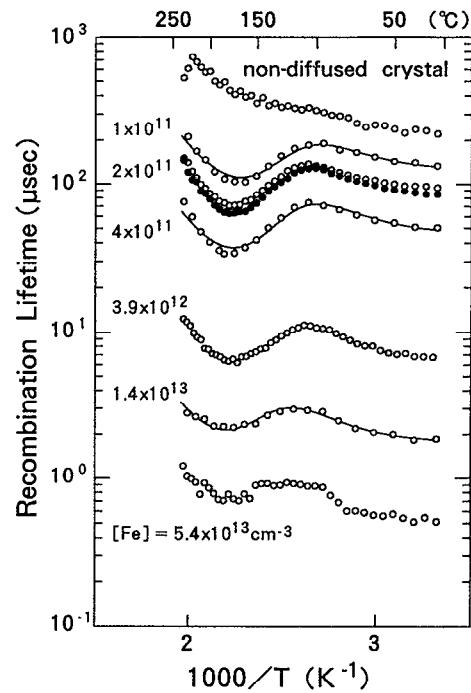

FIG. 2. Temperature dependence of minority-carrier recombination lifetime in iron-diffused p-type silicon crystals. O:FZ; ●:CZ . The solid line represents the temperature dependence of the lifetime calculated from Eq.(20) assuming that the effective recombination center for an Fe$_i$B$_s$ pair is located at $E_c - 0.29$ eV.

increased monotonically with temperature, whereas, in irondiffused samples, the lifetime showed a temperature dependence which has a minimum around 170 °C. There was no difference between FZ and CZ wafers when oxygen was not precipitated. It was also shown that the effect of iron in concentrations as low as 1×10^{11} cm^{-3} on the lifetime can be detected with the noncontact laser/microwave method.

As seen in Fig. 2, the lifetime curve for the sample with [Fe] = 5.4×10^{13} cm^{-3} has a less well defined depression. This is attributed to the precipitation of super-saturated iron. Evidence for the precipitation for iron concentrations above 1×10^{13} cm^{-3} arises from a reduced lifetime at RT after a temperature scan.

IV. DISCUSSION

In the case of low level excitation and a single deep level with energy level E_t within the band gap, the minority-carrier recombination lifetime (τ_{SRH}) via the deep level is defined by the Shockley–Read–Hall (SRH) model[2,3] as

$$\tau_{SRH} = \tau_{p0}[(n_0 + n_1)/(p_0 + n_0)]$$
$$+ \tau_{n0}[(p_0 + p_1)/(p_0 + n_0)], \tag{2}$$

where

$$\tau_{p0} = (C_p N_t)^{-1}, \tag{3}$$

$$\tau_{n0} = (C_n N_t)^{-1}, \tag{4}$$

$$p_0 = N_v \exp[(E_v - E_F)/(kT)], \tag{5}$$

$$n_0 = N_c \exp[(E_F - E_c)/(kT)], \tag{6}$$

$$p_1 = N_v \exp[(E_v - E_t)/(kT)], \tag{7}$$

$$n_1 = N_c \exp[(E_t - E_c)/(kT)], \tag{8}$$

$$C_p = \sigma_p v_{\text{th}}, \tag{9}$$

$$C_n = \sigma_n v_{\text{th}}. \tag{10}$$

For convenience, each symbol employed with its physical meaning is listed as follows: p_0 is the hole concentration in the valence band in thermal equilibrium; n_0 is the electron concentration in the conduction band in thermal equilibrium; p_1 and n_1 are the concentrations of holes and electrons related to the E_t level, respectively; C_p is the capture coefficient for holes; C_n is the capture coefficient for electrons; N_t is the trap density; N_v is the effective density of states in the valence band; N_c is the effective density of states in the conduction band; σ_p is the capture cross section for holes; σ_n is the capture cross section for electrons; v_{th} is the average thermal velocity. In the following discussions, we adopted the numerical values as: $N_v = 2.19 \times 10^{15} T^{3/2}$ cm^{-3}; $N_c = 5.57 \times 10^{15} T^{3/2}$ cm^{-3}; $v_{\text{th}} = 1.93 \times 10^7 (T/300)^{1/2}$ cm s^{-1}; the acceptor concentration $N_A = 1.3 \times 10^{15}$ cm^{-3} from the resistivity data (ASTM F-723, 1982).

Under the assumption that $n_0 \ll p_0$ and $n_1 \ll p_1$ for p-type silicon, Eq. (2) reduces to

$$\begin{aligned}
\tau_{\text{SRH}} &= \tau_{n0}(1 + p_1/p_0) \\
&= \tau_{n0}[1 + \exp\{[(E_v - E_t) \\
&\quad - (E_v - E_F)]/(kT)\}].
\end{aligned} \tag{11}$$

It has been generally accepted that iron in p-type silicon results in deep levels at $E_v + 0.1$ eV and $E_v + 0.37$ eV for Fe$_i$B$_s$ pairs and interstitial iron (Fe$_i$), respectively.[5] Assuming that all iron atoms in p-type silicon are either associated with boron, i.e., Fe$_i$B$_s$, or remain as Fe$_i$, we may obtain the lifetime τ_{FeB} and τ_{Fei}, respectively, as follows;

$$\tau_{\text{FeB}} = \tau_{n0(\text{FeB})}\{1 + \exp[(E_F - 0.1)/(kT)]\}, \tag{12}$$

$$\tau_{\text{Fei}} = \tau_{n0(\text{Fei})}\{1 + \exp[(E_F - 0.37)/(kT)]\}, \tag{13}$$

where

$$E_F = -kT \ln(N_A/N_v). \tag{14}$$

It is also known that an Fe$_i$B$_s$ pair is formed by Coulomb attraction and dissociates at an elevated temperature[5,11–13,18] according to the following equations;

$$\text{Fe}_i\text{B}_s \rightleftharpoons \text{Fe}_i + \text{B}_s, \tag{15}$$

$$N_{\text{FeB}}/(N_{\text{Fei}}N_{\text{Bs}}) = 10^{-23}\exp[U/(kT)], \tag{16}$$

where N represents the concentrations of respective species shown with the subscript. U is the pair binding energy of 0.5 to 0.67 eV.[11,13,18] Under the assumption that the sum of the concentrations of Fe$_i$ and Fe$_i$B$_s$ is constant in the measured temperature range,[19,20] the sum of the molar fractions of Fe$_i$ (X_{Fei}) and Fe$_i$B$_s$ (X_{FeB}) is unity;
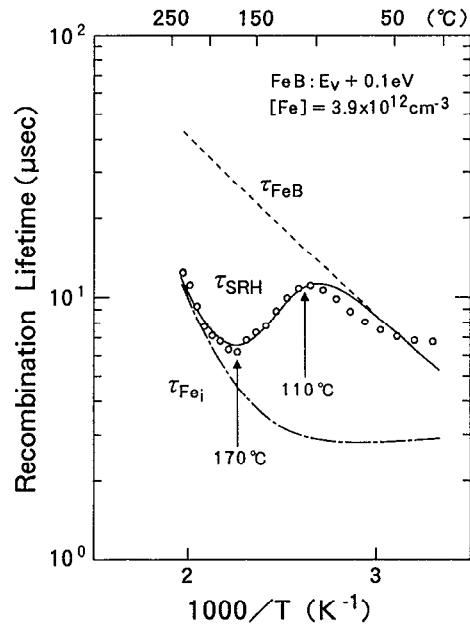

FIG. 3. Temperature dependence of the lifetime in iron-diffused p-type silicon. The solid line represents Eq. (20) assuming that the effective recombination center for an Fe$_i$B$_s$ pair is located at $E_v + 0.1$ eV, the dashed line represents Eq. (12) and the dash-dotted line represents Eq. (13).

$$X_{\text{Fei}} + X_{\text{FeB}} = 1, \tag{17}$$

where

$$X_{\text{Fei}} = N_{\text{Fei}}/(N_{\text{Fei}} + N_{\text{FeB}}), \tag{18}$$

$$X_{\text{FeB}} = N_{\text{FeB}}/(N_{\text{Fei}} + N_{\text{FeB}}). \tag{19}$$

From the above equations, we may obtain the lifetime in iron-diffused p-type silicon, as;

$$1/\tau_{\text{SRH}} = X_{\text{FeB}}/\tau_{\text{FeB}} + X_{\text{Fei}}/\tau_{\text{Fei}}. \tag{20}$$

Substituting Eqs. (12)–(19) into Eq. (20) and using the experimentally obtained value of $U = 0.68$ eV, the result of the least-squares fitting of Eq. (20) for the sample with [Fe] $= 3.9 \times 10^{12}$ cm^{-3} is shown as the solid line in Fig. 3. Above 110 °C, the calculation agrees with the experimental data quite well, however, it deviates below 110 °C.

Next, we assumed that an Fe$_i$B$_s$ pair forms an effective recombination center at $E_c - 0.29$ eV, instead of $E_v + 0.1$ eV, as proposed by Brotherton, et al.[5] In this condition $p_1 \ll n_1$ and $n_0 \ll p_0$; therefore Eq. (2) reduces to

$$\begin{aligned}
\tau_{\text{SRH}} &= \tau_{p0}(n_1/p_0) + \tau_{n0} \\
&= \tau_{n0} + \tau_{p0}(N_c/N_v)\exp\{[(E_t - E_c) \\
&\quad - (E_v - E_F)]/(kT)\}.
\end{aligned} \tag{21}$$

Now the lifetime dominated by Fe$_i$B$_s$ pair is given by

$$\begin{aligned}
\tau_{\text{FeB}} = \tau_{n0(\text{FeB})} &+ \tau_{p0(\text{FeB})}(N_c/N_v) \\
&\exp[(E_F - 0.29)/(kT)].
\end{aligned} \tag{22}$$

The result of the least-squares fitting using Eq. (22), instead of Eq. (12), for the sample with [Fe] $= 3.9 \times 10^{12}$
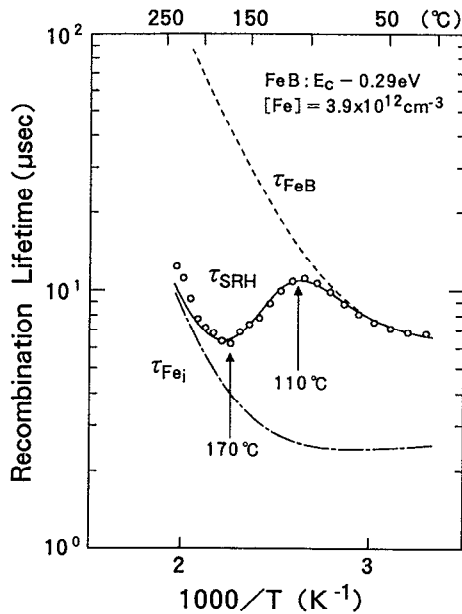
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FIG. 4. Temperature dependence of the lifetime in iron-diffused p-type silicon. The solid line represents Eq. (20) assuming that the effective recombination center for Fe_iB_s pair is located at $E_c - 0.29$ eV, the dashed line represents Eq. (22) and the dash-dotted line represents Eq. (13).
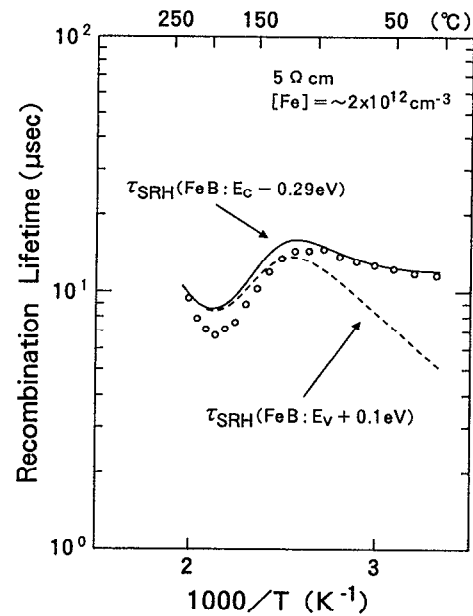

FIG. 5. Temperature dependence of the lifetime in iron-diffused p-type silicon having the resistivity of 5 Ω cm. The solid and dashed lines are deduced from the result of the 10 Ω cm sample assuming that the effective recombination center for an Fe_iB_s pair is located at $E_c - 0.29$ eV and $E_v + 0.1$ eV, respectively.

cm^{-3} is shown in Fig. 4. In spite of neglecting the temperature dependence of the capture cross section and the band gap,[21] better agreement with the experimental data was obtained. In our experimental condition, the temperature dependence of the capture cross section[7] is relatively smaller than that of the exponential function in Eqs. (12), (13), and (22). Under the assumptions that the iron related deep levels are pinned to the valence band ($E_v + 0.1$ eV and $E_v + 0.37$ eV) or the conduction band ($E_c - 0.29$ eV) like the gold-acceptor level,[22] and the inequalities are valid for carriers, the temperature dependence of the band gap does not affect that of the lifetime.

To confirm the validity of an energy level at $E_c - 0.29$ eV as a recombination center, we measured the temperature dependence of the lifetime for an iron-diffused sample with a different N_A, i.e., having the resistivity of 5 Ω cm. From Eqs. (12), (14), and (22), the lifetime around RT strongly depends on N_A when the effective recombination center is located at $E_v + 0.1$ eV rather than $E_c - 0.29$ eV. In Fig. 5, we compared the experimental data with the theoretical forecast from the least-squares fitting of the 10 Ω cm sample. When the energy level at $E_c - 0.29$ eV was postulated as the effective recombination center, good agreement was obtained. This means that the dissociation of Fe_iB_s pairs dominates the temperature dependence of the lifetime, and the energy level at $E_c - 0.29$ eV is the effective recombination center for an Fe_iB_s pair. The solid lines in Fig. 2 represent the temperature dependence of the lifetime deduced from the least-squares fitting assuming a recombination center at $E_c - 0.29$ eV. The calculated values of $\tau_{p0(FeB)}$, $\tau_{n0(FeB)}$ and $\tau_{n0(Fei)}$ at 300 K are listed in Table I.

It was also found that there was no difference between

FZ and CZ wafers as long as oxygen was not precipitated. This means that interstitial oxygen does not affect the electrical behavior of iron in p-type silicon. Comparing the temperature dependence of the lifetime for sample P4 in Ref. 9 with our sample with [Fe] = 5.4×10^{13} cm^{-3} in Fig. 2, we find good agreement between both samples. This indicates that the states of iron and iron complexes do not depend on whether iron is doped directly into the silicon melt[9] or diffused from the crystal surface. As reported by one of the authors,[9] our result shows the existence of the recombination center due to Fe_i up to 230 °C,[19] which is contrary to the annealing behavior of iron reported by others.[11,12] This discrepancy may be attributed to the differences in iron concentration, annealing time, or annealing ambient.

V. SUMMARY

In summary, we have studied the temperature dependence of minority-carrier recombination lifetime by means of a noncontact laser/microwave method for nondiffused and iron-diffused p-type silicon wafers in the temperature range from 28 °C to 230 °C. The lifetime increased monotonically with temperature in nondiffused standard p-type silicon, while the lifetime in iron-diffused silicon showed a broad peak and a depression around 110 °C and 170 °C, respectively. The temperature dependence of the lifetime in iron-diffused p-type silicon was analyzed based on SRH statistics. The increases in lifetime at low and high temperatures were attributed to Fe_iB_s pairs and Fe_i, respectively. The decrease in lifetime between 110 °C and 170 °C was dominated by the Fe_iB_s pair dissociation to Fe_i. Our exper-

imental data supported that an electron trap for an Fe_iB_s pair at $E_c - 0.29$ eV was more effective as a recombination center than a hole trap at $E_v + 0.1$ eV. Finally, it was also shown that the effect of iron in concentrations as low as 1×10^{11} cm^{-3} on the lifetime can be detected with the noncontact laser/microwave method.

ACKNOWLEDGMENTS

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