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Laser Infrared Photothermal Radiometric and ELYMAT Characterizations of p-Si Wafers Annealed in the Presence of an External Electric Field

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Laser infrared photothermal radiometry (PTR) was used as an analytical technique to measure the electronic transport parameters of p-Si wafers oxidized and thermally annealed under positive or negative external bias applied to the back surface. It was found that, following Fe contamination and recombination lifetime τ_e, degradation in the oxidation and thermal-anneal furnace, both polarities of the external field result in significant minority carrier lifetime improvement, as well as in strong changes in the front-surface recombination velocity S_1, of the samples, compared to a zero-bias annealed reference sample. A qualitative model involving the passivating action of positive mobile ions (protons) trapped at the oxide–Si interface was advanced to explain the relative relations $S_1^{(+)} > S_1^{(0)} > S_1^{(-)}$. The lifetime relations $\tau_e^{(+)} > \tau_e^{(-)} > \tau_e^{(0)}$ obtained through both PTR and electrolytical metal tracer (ELYMAT) measurements were explained in terms of the relative abilities of positive and negative applied electric fields to prevent heavy metal ions from diffusing into the Si bulk and compromising the lifetime.

1. Introduction

The major sources of contamination in a diffusion furnace consist of heavy metal diffusion from (or through) the process tube walls, out-diffusion from the cantilever or boats, and impurities in the process gas. To minimize contamination an externally controlled electric field can be applied to product wafers. Ambient yield-limiting metallic impurities (mostly positive ions, Fe, Ni, Cu, Cr, etc. [1, 2]) under the applied electric field can thus migrate toward, or away from, the external electrode. The benefits of applying an electric field during a thermal process include: reduction of added contamination during annealing processes; clean oxidation resulting in highly clean oxide layers without the use of chlorine; improvement of the minority-carrier diffusion length after the high temperature anneal, since fewer contaminants are incorporated into the wafers; and the possibility of extended operation at higher temperatures, resulting in cleaning of the boat/cantilever and thus minimizing out-diffusion of metal contaminants to process wafers [3]. In this work, the effects of an applied electric field on the transport parameters of oxidized p-type Si wafers have been studied by means of laser infrared photothermal radiometry (PTR) combined with a multi-parameter computational technique [4]. The electrolytical metal tracer (ELYMAT) [5] technique was also used for comparison and the PTR photoexcited-carrier lifetimes were found to be consistent with ELYMAT lifetime measurements.

2. Experimental

The experimental arrangement of our PTR instrument for Si wafer diagnostics has been reported earlier [4, 6]. Previously unoxidized, boron doped (100) Si single crystal wafers with a low-resistivity of 6 Ωcm, 6" in diameter and 650 μm thick, were used as samples for the present study. All heat treatments were carried out in a horizontal mini-furnace with radiation heating by quartz lamps. The furnace was equipped with a 10" diameter tube-reactor and pedestal, which were made from semiconductor purity quartz. The samples were positioned on standard silicon carbide holders (boats) produced by the Norton Corporation. Heating for oxidation and thermal annealing was carried out by quartz-lamp radiation. The experimental schematic is presented in Fig. 1. An external bias was applied to the Si wafers in the SiC boat at potentials $\Phi = 0$ V, +1000 V, or −500 V. An electric field normal to the surface plane of our wafers was created by the voltage Φ between the external metallic electrode (grounded) and the standard silicon carbide (SiC) boat, on which the Si wafers were positioned in such a manner that their backsides only (not the frontsides) were contacting vertically the SiC boat. Therefore, the back surface of the wafers during the oxidation process was always at a potential Φ with respect to ground. Additional unbiased Si "shield" wafers were positioned vertically on standard quartz boats manufactured by Heraeus inside the quartz-tube reactor, Fig. 1. These wafers prevented direct contact of the cool O_2 gas flow with the heated sample wafers inside the SiC boat and were only used as O_2 gas flow dispersion devices. Samples were heated using quartz lamps as radiation heaters. Oxidation was performed for 1 h at 1000 °C at atmospheric pressure. The three p-Si wafers, grown by the magnetic CZ method with low initial Fe content (average initial carrier recombination lifetime of 358 μs as measured by the ELYMAT method, corresponding to a bulk iron concentration of approximately 3×10^{10} cm^{-3}), were Fe-con-

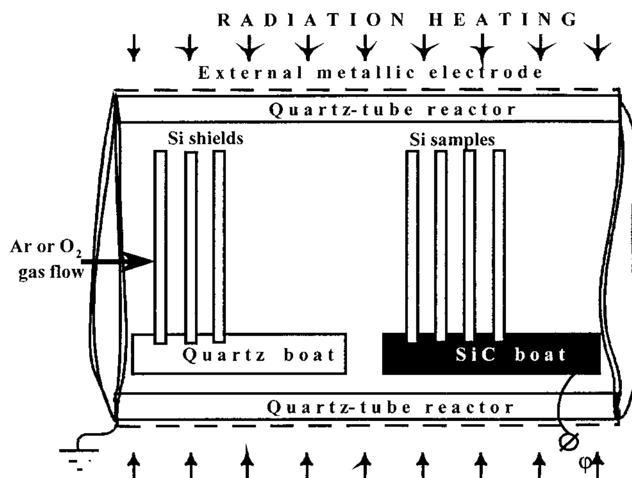

Fig. 1. Schematic of installation/furnace for heat-treatment of Si wafers in presence of various electric fields. The electric field normal to the plane of the wafer was created by a potential difference Φ between the external grounded metallic electrode and the SiC boat (Φ = −500, 0, +1000 V). Si shields positioned in a quartz boat prevented interaction of a cool gas flow (O_2 or Ar) with the heated wafers. Samples were heated by quartz-lamp irradiation

Table 1
Thermoelectronic values for samples annealed in the presence of an external electric field

wafer/potential/position	τ (s)	S_1 (cm/s)	D_n (cm^2/s)	α (cm^2/s)
p-Si #1: Φ = 0 V				
A	28	2900	3.6	0.35
B	28	2500	3.6	0.35
C	33.5	3500	7.0	0.47
D	33.5	3500	7.0	0.55
back surface	32	3000	5.0	0.55
p-Si #2: Φ = +1000 V				
A	53	4300	10	0.70
B	54	4200	10	0.70
C	52	4200	10.4	0.75
D	51	4200	10.4	0.70
back surface	38	4500	6	0.40
p-Si #3: Φ = −500 V				
A	45	2200	8.3	0.65
B	46	1800	7.5	0.65
C	45	1700	7.5	0.65
D	44	1900	7.5	0.65
back surface	44	3200	6.0	0.50

taminated as a result of the high-temperature processing (oxidation). Sample p-Si #1 was thermally oxidized without an electric field, sample p-Si #2 was oxidized under an electrostatic potential of +1000 V applied to the Si back surface, and sample p-Si #3 was oxidized under a similarly applied electrostatic potential of −500 V. Control p-Si wafers of the same origin as the foregoing wafers were also oxidized for 1 h at 1000 °C at atmospheric pressure with the same values of the applied electric field (+1000 V, 0 V, −500 V).

Further thermal annealing was performed at standard pressure and O_2 flow rate of 500 cm^3/min, at 1050 °C for 70 min. Following the high temperature heat treatments, the three sample wafers were examined under the PTR probe at four radial positions perpendicular to, and in the middle of, the [110] flat from center to edge at 1.8 cm intervals across the front surface (see inset Fig. 2b), and at one position located near the center of the back surface. Some non-uniformities in the radial distributions of both the carrier recombination lifetime and the surface recombination velocities were observed as reported earlier [4]. Table 1 shows that the variation of these parameters across individual wafers at the four radial positions A (center)–D (edge), see inset Fig. 2b, is much narrower than the changes effected by the application of external dc bias.

3. Results

The following average ELYMAT lifetime values were obtained after oxidation: τ_e(+1000 V) = 224 μs, τ_e(−500 V) = 199 μs, and τ_e(0 V) = 160 μs. The drastic decrease in the ELYMAT lifetime value under zero external bias from 358 to 160 μs is consistent with heavy metal contamination inside the quartz-tube furnace, and with Fe-contamination in particular, as determined with vapor-phase decomposition combined with total reflection X-ray fluorescence (VPD/TXRF) analysis of the oxide layers. It is clear that

the presence of an electric field across the wafer thickness hinders metal ion transport into the wafer during thermal oxidation in a contaminated furnace.

Figures 2a and b show the PTR signal amplitude and phase of sample p-Si #3 (Φ = −500 V), for the positions A–D, plus the back-surface centerpoint, respectively. The continuous lines represent the best-fit results using our three-dimensional PTR model [7] and the multi-parameter fit of the theory to the data to extract a unique set of transport parameters [4]. The same procedures were applied to wafers p-Si #1 and p-Si #2. The standard deviation for all three wafers was on the order of the size of the symbols used in Fig. 2. The thermal and electronic ("thermoelectronic") transport parameters obtained at these positions, as well as at the center of the back surface, carrier de-excitation or recombination lifetime τ, minority carrier (electrons) diffusion length D_n, front surface recombination velocity S_1, and thermal diffusivity α are presented in Table 1. It was further found that our samples did not exhibit significant transient behavior under low-fluence laser excitation, as was the case with some bare silicon wafers reported earlier [6]. *The absence of PTR transients is a very useful diagnostic indication that the oxidation and thermal annealing processes can achieve an electronically stable* SiO_2*–Si interface.* The D_n values determined by the multi-parameter fit are lower than usually quoted values of this parameter [4]. The reason for the apparent discrepancy is the very short optical absorption depth in Si at 514 nm ($\sim$1 μm), which yields measurements of the near-surface carrier diffusivity value [4]. Due to contamination this value can be much lower than bulk values measured by optical transmission methods using

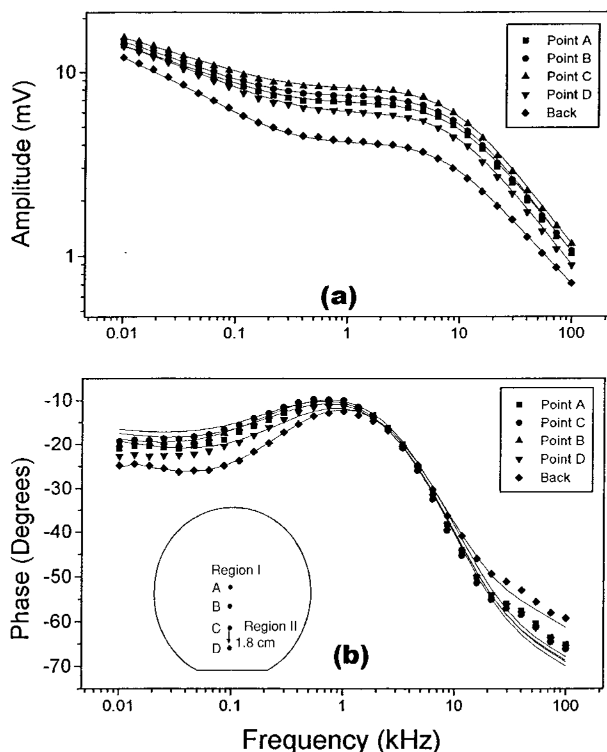

Fig. 2. Experimental PTR frequency scans and theoretical multi-parameter fits to the data for wafer p-Si #3. a) Amplitude and b) phase. The inset shows the radial locations of points A–D

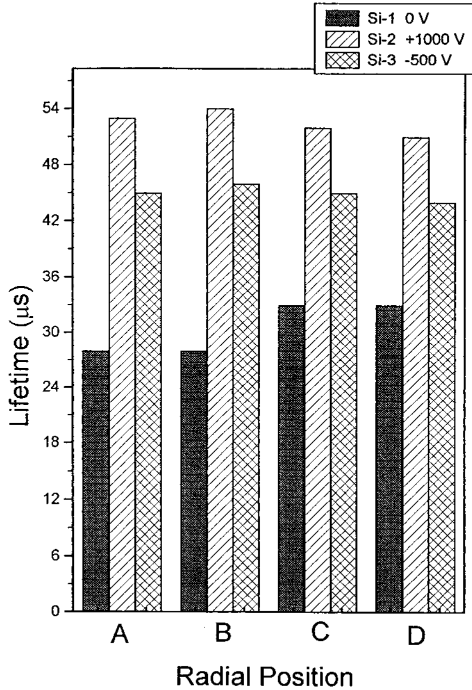

Fig. 3. Photoexcited minority-carrier (electron) lifetime histogram for radial wafer locations A–D of the three p-Si wafers

more transparent wavelengths. Preliminary PTR measurements reported with a 860 nm output semiconductor laser diode [8] on a 250 Ωcm Si wafer were consistent with the value of D_n = 34.4 cm^2/s, which lies within the broadly accepted bulk value range [4, 9] between 30 and 37 cm^2/s for D_n.

Figure 3 is a compact histogram of all PTR lifetimes measured with or without an applied electric field to the Si back surface as functions of radial position (A–D). The effect of experimental error in the calculation of lifetime values, Table 1, is on the order of ±1.5 μs. The lifetime improvement for both wafers thermally annealed in the presence of an electric field of either sign is remarkable. Between the two polarizations of the electric field, the positive bias was most effective in increasing the recombination lifetime.

Figure 4 is a compact histogram of all front surface recombination velocities measured without or with the applied electric field corresponding to Fig. 3. The most striking trends here are the significant increase of S_1 for the positive polarity of the field, and the also significant decrease for the negative polarity, both with respect to the zero-field case. It should be recalled that surface recombination velocity (SRV) is a phenomenological parameter that measures the electronic quality

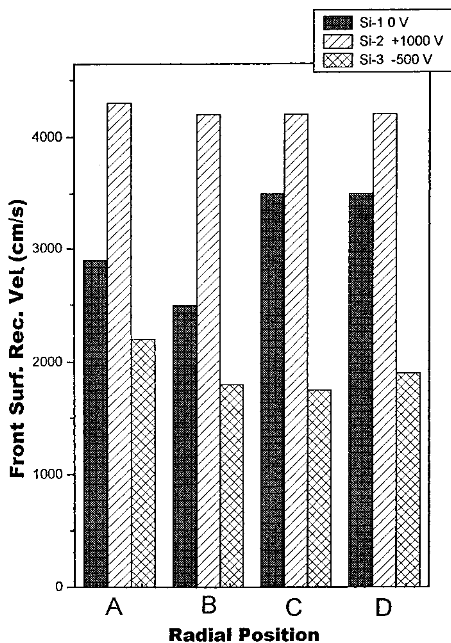

Fig. 4. Photoexcited minority-carrier (electron) surface recombination velocity histogram for radial wafer locations A–D of the three p-Si wafers

of wafer surfaces in terms of the structure and density of traps and surface/interface states, which act as recombination sites. The range of values reported in the literature for the front surface recombination velocity of n- and p-silicon is between 0.25 cm/s, for a very passivated surface [10, 11] and 10^7 cm/s for highly doped p-silicon [10–13]. A typical value of the front SRV ($\sim$100 cm/s) for p-silicon represents a moderately passivated surface. Therefore, the front and back SRV values measured in all our samples formally correspond to non-passivated (active) surfaces. This result is consistent with the relatively small D_n measured for the respective locations on the wafers.

4. Discussion

Relatively little work has been reported on the effects of externally applied electric fields on Si processing, mainly within the context of controlling the rate of oxide growth [14–17]. Qualitatively, trends observed in Figs. 3 and 4 may be explained consistently by analogy to the well-known mechanism of the corona-oxide-semiconductor (COS) technique [18]. In this technique, negative charges are deposited on oxidized p-Si wafers to bias the substrate into accumulation, followed by smaller area positive charge driving the sample into deep depletion. It is possible that positively charged ions (protons) at the Si–SiO_2 interface of p-Si introduced by the oxidation neutralize interface-trapped charges. In particular, it is known that most of the interface-trapped charge can be neutralized (passivated) by low-temperature (450 °C) hydrogen annealing [19]. Since in our experiments the interface H^+ concentration in the oxide depends on the electric field polarity, it is reasonable to assume that a positive bias applied to the back surface repels the positive charges away from the interface, while a negative bias attracts them. As a result, the interface is most passivated in the case of the application of a negative bias, and it is least passivated in the case of a positive bias, with the zero-bias case lying in between. Therefore, we expect for the front-surface recombination (or trapping) velocities

$$S_1^{(+)} > S_1^{(0)} > S_1^{(-)}, \tag{1}$$

as was found experimentally through the PTR probe. The details of the trapping of laser photo-excited minority carriers (electrons) into the charged Si–SiO_2 interface states remain unclear and will be the subject of a future investigation. Specifically, the role of positive mobile oxide charges (protons) in decreasing the rate of carrier trapping on the SiO_2 side of the interface, or in mediating electron–hole recombination on the Si side remains unknown. Besides, it is well known that the application of an external electric field influences the oxidation rate of Si [14–17]. It is plausible that applied fields affect the process of interface trap generation and thus the degree of passivation. In comparison, it is known that COS negative charging, followed by positive charge driving (deep depletion), reduces the SRV in p-Si, a process which is electrostatically similar to negative biasing of the Si back surface. From the surface recombination results of our experiments it may be concluded that the minimum of the SRV is reached under -500 V bias to the back surface, when (positive) mobile ion concentration at the SiO_2–Si interface reaches its maximum (maximum passivation). The maximum SRV is attained under $+1000$ V bias, which results in minimum interfacial positive mobile ion concentration (minimum passivation).

The PTR lifetime results of Fig. 3 can be examined by considering the effects of an applied bias on the diffusion probability of heavy metallic contaminants, such as Fe_i^+, incorporated in the wafer from the gas ambient in the oxidation furnace [20]. Under a

positive substrate bias, the diffusion of positive heavy metal ions from the oxide into the Si is impeded, thus decreasing the bulk concentration of the efficient electronic trap [Fe_i^+] and leading to bulk lifetime increase

$$\tau_e^{(+)} > \tau_e^{(0)} \tag{2}$$

as observed in our experiments through the PTR probe. On the other hand, a straightforward explanation of the relative values of lifetimes under zero and negative bias

$$\tau_e^{(0)} < \tau_e^{(-)} \tag{3}$$

is not as apparent. Nevertheless, the same inequality was obtained from measurements using the ELYMAT technique under the condition that Fe_i^+ was the major lifetime-limiting impurity, validated through the VDP/TXRF analysis. A tentative hypothesis involves the effective neutralization of the heavy ions diffusing to the SiO_2–Si interface through trapping of photo-generated minority electrons, which accumulate at the interface under a negative bias. The observed order of inequalities, Fig. 3,

$$\tau_e^{(+)} > \tau_e^{(-)} > \tau_e^{(0)} \tag{4}$$

also implies that the blocking effect (positive bias) is more efficient than neutralization through interfacial trapping (negative bias) in preventing heavy metal ions from reaching the bulk Si. For instance, Fe_i^+ is a deep donor with an energy level [20] at $E_V + 0.4$ eV.

Once again, it should be emphasized that the foregoing physical model is not meant to be species specific, but rather general, aimed at explaining the observed trends in the measured parameters qualitatively, and based on the fact that PTR probes the free-photoexcited minority-carrier density (here electrons) under medium injection conditions. As seen, the three PTR lifetime relations, inequalities (3), are consistent with ELYMAT lifetime relations among the identically oxidized control p-Si wafers: $\tau_e(+1000\ \text{V}) = 224\ \mu\text{s} > \tau_e(-500\ \text{V}) = 199\ \mu\text{s} > \tau_e(0\ \text{V}) = 160\ \mu\text{s}$, albeit without absolute-value agreement. This can be attributed to the different experimental parameters of the two metrologic methodologies. Specifically, the laser source used with ELYMAT was a semiconductor diode emitting at 905 nm, thus affording an optical penetration depth in Si of ~30 μm. This is much deeper than the Ar-ion laser penetration depth used for the PTR experiments, and is capable of sampling the true bulk value of the lifetime. Earlier comparison between 514 nm and 1.06 μm laser excitation using a Nd-YAG laser has shown significant increase in the respective PTR lifetimes [21] for 1.06 μm excitation. Furthermore, actual differences in the physics of signal generation between the ELYMAT and the PTR techniques cannot be ruled out. Such differences have lead to differences in the lifetime values measured by several semiconductor metrologic techniques and have been documented for Surface Photovoltage (SPV), Microwave Photoconductivity (μ-PCD), and ELYMAT [22–24]. A comparison between PTR and ELYMAT is currently under investigation.

5. Conclusions

In conclusion, PTR metrology was found capable of measuring the electronic transport properties of p-Si wafers oxidized and thermally annealed in the presence of an applied electric field. It was found through ELYMAT lifetime measurements that the thermal treatment of p-Si wafers in a contaminated quartz-tube reactor/furnace decreases substantially the carrier recombination lifetime, however, application of a positive bias to the

back surface of the wafer yields a substantial restoration/increase of the lifetime value (up to double the zero-field value), presumably due to effective hindering of metal ion transport from the contaminated furnace walls across the oxide–Si interface by the applied electric field. The positive bias also increases substantially the value of the front surface recombination velocity (SRV). The application of a negative bias to the back surface of the wafer also increases the value of the minority carrier lifetime, but not as much as the positive bias. Substantial decrease of the SRV below the zero-field value was also observed. The SRV trends were qualitatively explained in terms of a model of the oxide–Si interface, which invokes the effects of external applied electrostatic fields on the passivating action of positive mobile ions (protons) trapped at the oxide–Si interface. The lifetime trends were explained in terms of the relative abilities of positive and negative applied electric fields to prevent heavy metal ions from diffusing into the Si bulk and becoming lifetime killers. The lifetime relations among the biased and non-biased wafers were similar to those obtained from ELYMAT measurements.

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References

[1] B. O. Kolbesen and H. P. Strunk, VLSI Electron. Microstruct. Sci. **12,** 143 (1985).
[2] H. R. Huff and F. Shimura, Solid State Technol. **28**, 103 (1985).
[3] I. Ziman and A. Sergienko, U.S. Patent # 5770000, Sizary Ltd., Migdal Tefen Israel.
[4] M. E. Rodríguez, A. Mandelis, L. Nicolaides, J. Garcia, G. Pan, and Y. Riopel, J. Electrochem. Soc. **147**, 687 (2000).
[5] V. Lehmann and H. Föll, J. Electrochem. Soc. **135**, 2831 (1988).
[6] M. E. Rodríguez, A. Mandelis, J. Garcia, and Y. Riopel, Appl. Phys. Lett. **74**, 2429 (1999).
[7] T. Ikari, A. Salnick, and A. Mandelis, J. Appl. Phys. **85**, 7392 (1999).
[8] S. Sheard and M. Somekh, in: Non-Destructive Evaluation, Progress in Photothermal and Photoacoustic Science and Technology, Vol. 2, Chap. 5, Ed. A. Mandelis, PTR Prentice-Hall, Inc., Englewood Cliffs (N.J.) 1994.
[9] T. Yoshida and Y. Kitagawara, Electrochem. Soc. Proc. Vol. **96-13**, 450 (1996).
[10] T. Yoshida and Y. Kitagawara, Electrochem. Soc. Proc. Vol. **96-13**, 455 (1996).
[11] E. Yablonovich, D. L. Allada, C. C. Chang, T. Gmitter, and T. B. Bright, Phys. Rev. Lett. **57,** 249 (1986).
[12] E. Yablonovich, R. M. Swanson, W. D. Eades, and B. R. Weinberg, Appl. Phys. Lett. **48**, 245 (1986).
[13] D. A. Ramappa and W. B. Henley, Appl. Phys. Lett. **72**, 2298 (1998).
[14] P. J. Jorgensen, J. Chem. Phys. **37**, 874 (1962).
[15] J. R. Ligenza, J. Appl. Phys. **36**, 2703 (1965).
[16] D. O. Raleigh, J. Electrochem. Soc. **113**, 782 (1966).
[17] F. C. Collins and T. Nakayama, J. Electrochem. Soc. **114**, 167 (1967).
[18] D. K. Schroder, M. S. Fung, R. L. Verkuil, S. Pandey, W. C. Howland, and M. Kleefstra, Solid State Electron. **42**, 505 (1998).
[19] D. K. Schroder, Semiconductor Material and Device Characterization, Chap. 6, Wiley, New York 1998.
[20] G. Zoth and W. Bergholtz, J. Appl. Phys. **67**, 6764 (1990).
[21] A. Mandelis, R. Bleiss, and F. Shimura, J. Appl. Phys. **74**, 3431 (1993).
[22] M. L. Polignano, F. Cazzaniga, A. Sabbadini, G. Queirolo, A. Cacciato, and A. di Bartolo, Mater. Sci. Eng. B **42**, 157 (1996).
[23] G. Zoth, in: Recombination Lifetime Measurements in Silicon, ASTM STP 1350, Eds. D. C. Gupta, F. R. Bacher, and W. M. Hughes, Am. Soc. Test. Mat. 1998 (p. 30).
[24] R. Falster and G. Borionetti, ibid (p. 226).