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Minority carrier lifetime of p-type silicon containing oxygen precipitates: influence of injection level and precipitate size/density

M. Porrini [a,*], P. Tessariol [b,1]

[a] *MEMC Electronic Materials SpA, Via Nazionale 59, 39012 Merano BZ, Italy*
[b] *INFM UdR di Padova at Dipartimento di Fisica, Università di Padova, Via Marzolo 8, 35131 Padova, Italy*

Abstract

The behaviour of minority carrier lifetime in p-type Czochralski silicon containing various concentrations of oxygen precipitates has been investigated in relationship to precipitate size, which is estimated by means of the reduction of interstitial oxygen concentration and injection level. The latter is varied in a wide range by comparing surface photovoltage technique, which operates at low injection, and microwave probed photoconductive decay technique, which operates at high injection. It is shown that at high injection level, the experimentally observed lifetime dependence on precipitate density and size can be explained, assuming that the recombination process takes place via silicon–precipitate interface states. However, at low injection, it is necessary to also take into account the effect of a fixed positive charge at the silicon–precipitate interface, which creates a depletion region around the precipitate, thus increasing its 'effective capture size'. A model is presented, based on these mechanisms, which is in good agreement with the experimental data.

Keywords: CZ silicon; Lifetime; Oxygen precipitate; Surface photovoltage technique; Microwave probed photoconductive decay technique; Injection level

1. Introduction

An accurate control of oxygen precipitate density and distribution in silicon wafers is essential for the achievement of good ultra-large-scale-integration device yield, where an effective gettering of metallic impurities is required. At the same time, precipitates and other defects must be absent in the near-surface device active region. The need for a tight control of oxygen precipitation in silicon has stimulated the research of innovative methods for its characterization. Lifetime techniques, which take advantage of oxygen precipitate activity as recombination centres for minority carriers [1,2], are receiving increasing attention. Examples of the use of lifetime techniques for monitoring the evolution of oxygen precipitation during the complex heat treatment sequences of device fabrication processes are beginning to appear in the literature [3]. In spite of the large number of works on electrical properties of oxygen precipitates [2], a full understanding of the mechanism at the basis of their recombination activity has not yet been achieved. In this contribution, the results of lifetime measurements with microwave-probed photoconductive decay (μ-PCD) [4] and surface photovoltage (SPV) [5] techniques of samples with various densities and size of oxygen precipitates are reported. A simple extension of a model proposed by Hwang and Schroder [6] to explain the different behaviour of precipitates in p- and n-type silicon is proposed here to explain the strong dependence of the measured lifetime on minority carrier injection level. This model, which is based on recombination at the silicon/precipitate interface, is shown to be in good agreement with experimental results.

2. Experimental

Samples used in this work are 0.6 mm thick, 150 mm diameter Czochralski-grown silicon wafers. The samples are boron doped and the resistivity is about 13

* Corresponding author. Tel.: +39-0473-333192; fax: +39-0473-333270.
E-mail address: mporrini@memc.com (M. Porrini)
[1] Present address: ST Microelectronics, 20041 Agrate Brianza, Via C. Olivetti 2, Italy.

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Ω·cm. The initial interstitial oxygen concentration (O_i) is subdivided in three groups: high oxygen samples with $O_i = (8.012 \pm 0.147) \times 10^{17}$ cm^{-3}, medium oxygen samples with $O_i = (7.078 \pm 0.057) \times 10^{17}$ cm^{-3} and low oxygen samples with $O_i = (6.113 \pm 0.142) \times 10^{17}$ cm^{-3}. Oxygen content was measured by Fourier transform infrared spectroscopy (FTIR) according to the ASTM F121-83 standard method. Carbon concentration is below the FTIR detection limit. Samples were preannealed at 1000°C for 15 min to dissolve the grown-in precipitate nuclei and provide a homogeneous starting condition for the successive precipitation steps. For the nucleation and growth of various densities and sizes of oxygen precipitates, the samples were submitted to a three-step thermal treatment for various temperatures and times, as summarized in Table 1.

The amount of precipitated oxygen (ΔO_i) was determined as the difference between the oxygen concentration before and after the thermal cycle. The density of oxygen precipitates (bulk micro defects (BMD)) was determined by cleaving and etching the sample with Schimmel solution and counting the etch pits by a Nomarski microscope. The minority carrier lifetime or diffusion length was measured by μ-PCD with Semilab WT-85XL equipment or by SPV with SDI CMS 4000 equipment. The μ-PCD technique operates at a high injection level (estimated to be about 10^{16} cm^{-3} [7]), whereas SPV operates at a very low injection level (estimated to be below 10^{9} cm^{-3} [8]). Before lifetime measurement, the sample surface was chemically polished by dipping the samples in an acid mixture of HNO_3 and HF. This type of surface finish is characterized by a surface recombination velocity (S) of about 4000 cm s^{-1} [9], corresponding in our case to a surface lifetime contribution τ_S of about 15 μs. τ_S is given by Eq. (1) [10], where L is the sample thickness and D the diffusion coefficient of minority carrier:

$$\tau_S = \frac{(SL + 2D)^2}{\pi^2 S^2 D} \quad (1)$$

3. Results and discussion

For our samples and thermal treatments, the measured BMD density covers five orders of magnitude, from 3×10^6 to 3×10^{11} cm^{-3}, while the amount of precipitated oxygen, ΔO_i, is in the range of 4×10^{15}–3×10^{17} cm^{-3}. The relationship between ΔO_i and BMD density is shown in Fig. 1. The exponential relationship with a power of about 2 between BMD and ΔO_i shows that oxygen precipitates tend to become smaller as their density increases.

In Fig. 2, lifetime is plotted as a function of BMD density for all examined samples. As expected, lifetime decreases as the BMD density increases. Moreover, the decrease is much more pronounced in the case of SPV than in the case of μ-PCD, showing that at low injection level (SPV), the 'recombination efficiency' of BMD is larger than at high injection (μ-PCD).

Measured minority carrier lifetime (τ_m) is the result of two parallel processes: bulk recombination (dominated by the Shockley–Read–Hall recombination mechanism) and surface recombination, and is often expressed as:

$$\tau_m = \left(\frac{1}{\tau_b} + \frac{1}{\tau_S}\right)^{-1} = (\sigma(\Delta n) v_{th} N_T + 1/\tau_S)^{-1} \quad (2)$$

where N_T is the recombination centre density, v_{th} is the carrier mean thermal velocity and $\sigma(\Delta n)$ is the injection level dependent cross-section. This equation predicts a decrease in lifetime at increasing recombination centre density N_T with a slope of -1 in the logarithmic scale, with saturation to a value equal to τ_S as N_T tends to zero. The SPV technique being essentially insensitive to surface recombination, this saturation is expected only in the case of μ-PCD, as is indeed observed (see Fig. 2).

Comparing Eq. (2) with the experimental results of Fig. 2, it is evident that the assumption of a recombination centre density N_T simply proportional to the BMD concentration cannot explain the existence of two different slopes: -1 in the case of SPV, in agreement with Eq. (2), and about $-1/3$ in the case of μ-PCD. A more realistic assumption, recently verified by DLTS studies of Koizuka and Yamada-Kaneta [11], is that silicon–precipitate interface states are recombination centres for minority carriers, as proposed by Hwang and Schroder in their model which describes the different impact of BMD on lifetime in p- or n-type silicon [6]. Following their proposal, it is assumed here that oxygen precipitates can be described as spherical silica (SiO_2) particles with radius r_0 in the silicon bulk, and that the silicon–silica interface is characterized by a certain surface density of recombination centres. The precipitate radius r_0 can be calculated from the reduction of interstitial oxygen ΔO_i as:

Table 1
Thermal treatments

Step	Temperature (°C)	Time (h)	Environment
Nucleation	450–550–650	2–8–32	N_2 (10 l min^{-1})
Growth (first step)	800	4–16	O_2 (1 l min^{-1})+N_2 (10 l min^{-1})
Growth (second step)	1000	16	O_2 (2 l min^{-1})

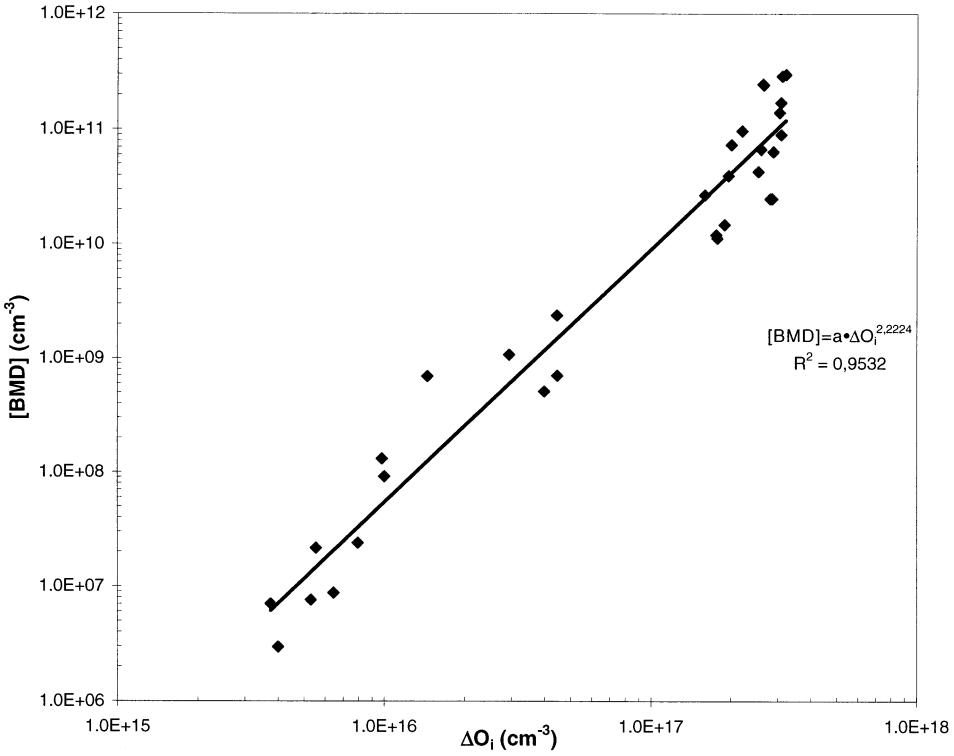

Fig. 1. Precipitate density versus interstitial oxygen reduction.

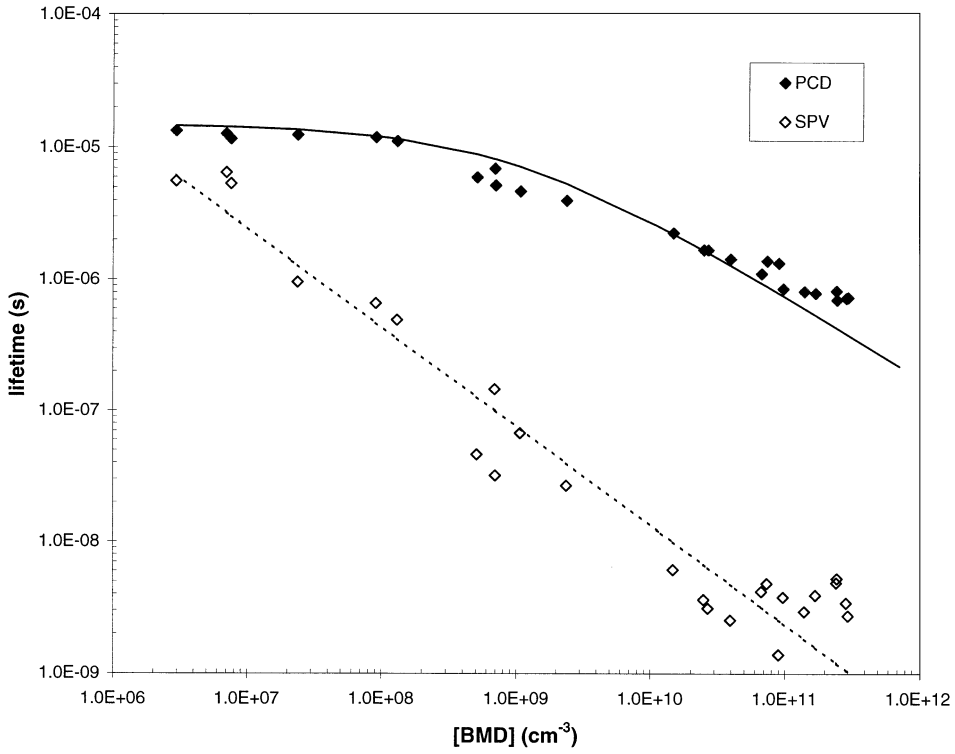

Fig. 2. Recombination carrier lifetime determined with μ-PCD and SPV as a function of oxygen precipitate density [BMD]. Solid line, theoretical prediction of Eq. (2), with τ_b given by Eq. (4); dashed line, theoretical prediction of Eq. (6) for $Q_f = 10^{12}$ cm^{-2} and for a mean value of [B] $= 1.03 \times 10^{15}$ cm^{-3}.

$$r_0 = 1.73 \times 10^{-8}(\Delta O_i/[BMD])^{1/3} \quad (3)$$

The bulk lifetime component due to these spherical particles having a surface recombination velocity s_{eff} is now given by (if we neglect the diffusion term [6]):

$$\tau_b = \frac{1}{4\pi r_0^2 [BMD] s_{eff}} \quad (4)$$

The lifetime predicted by this simple 'geometrical' model is shown as solid line in Fig. 2 and fits the μ-PCD data quite well. In order to explain the strong injection level dependence and the SPV values, it is necessary to further refine the model, taking into account the effect of band bending around the precipitate and the presence of a positive fixed charge due to silicon dangling bonds. In p-type silicon, this well-known phenomenon induces a depletion region around each precipitate, thus enlarging the minority carrier capture volume of the precipitate and increasing its recombination efficacy (see Fig. 3).

In order to estimate the size of the depletion region, we can impose the condition of neutrality, considering a fixed positive charge density at BMD surface given by Q_f and the dopant concentration [B]. In this way, the depletion region radius r_d is given by:

$$r_d = (r_0^3 + 3Q_f r_0^2/[B])^{1/3} \quad (5)$$

The depletion region radius r_d can be considered as an 'effective' precipitate size, and the minority carrier lifetime is given, in this case, by:

$$\tau_m = \frac{1}{4\pi s_{eff} [BMD] r_d^2} \quad (6)$$

The lifetime predicted by Eq. (6) is shown as dashed line in Fig. 2, and is in good agreement with the experimental data obtained at low injection.

The high carrier injection occurring during μ-PCD measurements produces an accumulation layer near the silicon–precipitate interface and compensates the positive charge density effect. In this n-type-like condition, band bending can be neglected and Eq. (6) is reduced to the simpler 'geometrical' model of Eqs. (3) and (4), by simply assuming $Q_f = 0$. On the contrary, for low injection measurements, it is necessary to take into account the positive charge effect in order to explain both the slope and the absolute values of Fig. 2. It is worth noticing that the hypothesis that the larger precipitate recombination efficacy at low injection is due to the injection level dependence of s_{eff} can be discarded, since it would lead, by data fitting, to a value of s_{eff} larger than the mean thermal velocity for free electrons.

Fig. 4 shows the good agreement between calculated and measured lifetime, supporting the validity of the proposed model. Values of surface recombination velocity extracted from experimental data fit are: $s_{eff} = (1.5 \pm 0.9) \times 10^5$ cm s^{-1} from μ-PCD data using the geometrical model (flat band approximation), and $s_{eff} = (5 \pm 3) \times 10^5$ cm s^{-1} for SPV data by the 'electrical enlarged' model, assuming a positive fixed charge density $Q_f = 10^{12}$ cm^{-2}. The latter is a typical value for the Si–SiO_2 structure, and similar values are reported in other works on silicon–silicon oxide interface recombination property [12,13].

Further support to this model is given by the results of variable injection level μ-PCD measurements on samples containing oxygen precipitates. As is shown in Fig. 5, the μ-PCD lifetime clearly increases with increasing injection level, as predicted by the present model, due to the progressive shrinking of the space-charge region around the precipitate.

4. Conclusion

In this work, a good correlation was found between BMD density, determined by the traditional etch and count technique, and minority carrier lifetime, measured with low (SPV) and high (μ-PCD) injection level techniques. Results presented here support the model proposed by Hwang and Schroder for the recombination behaviour of BMD, reinforcing the hypothesis that the interface states at the Si–BMD interface play a primary role in the recombination mechanism of excess minority carriers. An explanation is proposed for the

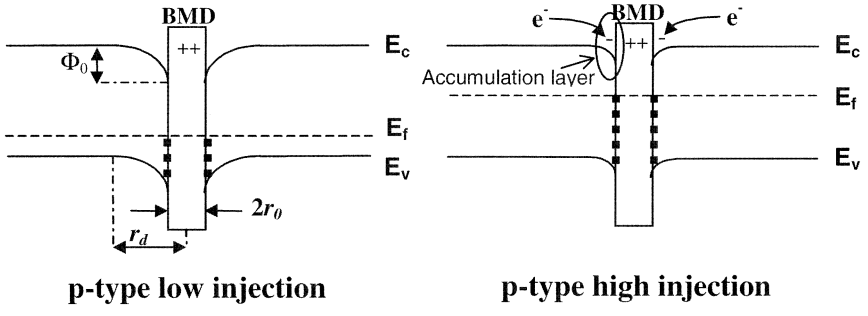

Fig. 3. Band bending diagrams in the case of low (left) and high (right) injection level. Φ_0 is the band banding, E_c the lower limit of the conduction band, E_v the upper limit of the valence band and E_f the Fermi level position.

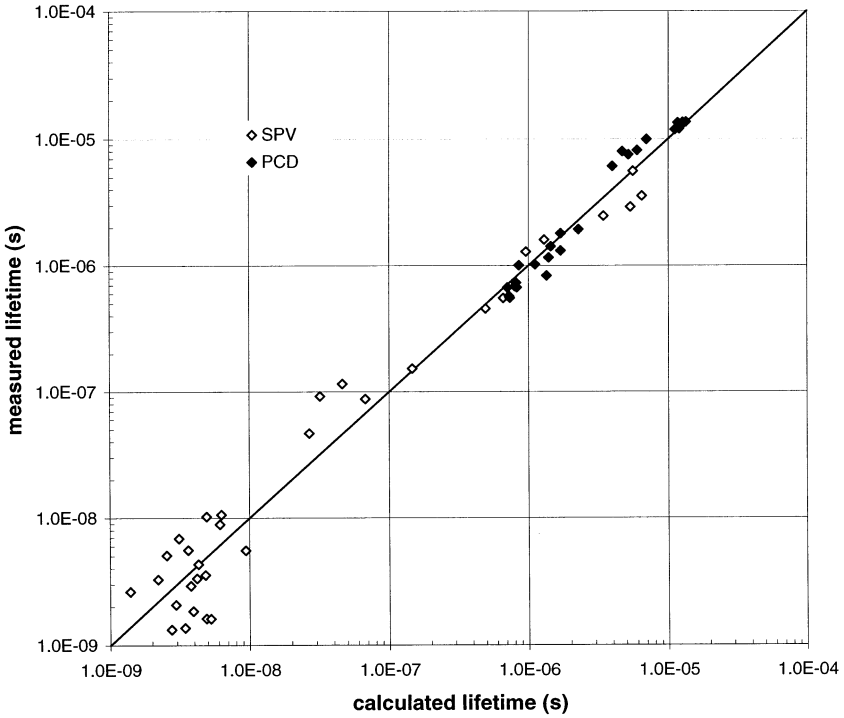

Fig. 4. Measured lifetime versus calculate lifetime in geometrical model (μ-PCD at high injection level), and electrical enlarged precipitate model (SPV at low injection level) for $Q_f = 10^{12}$ cm^{-2}.

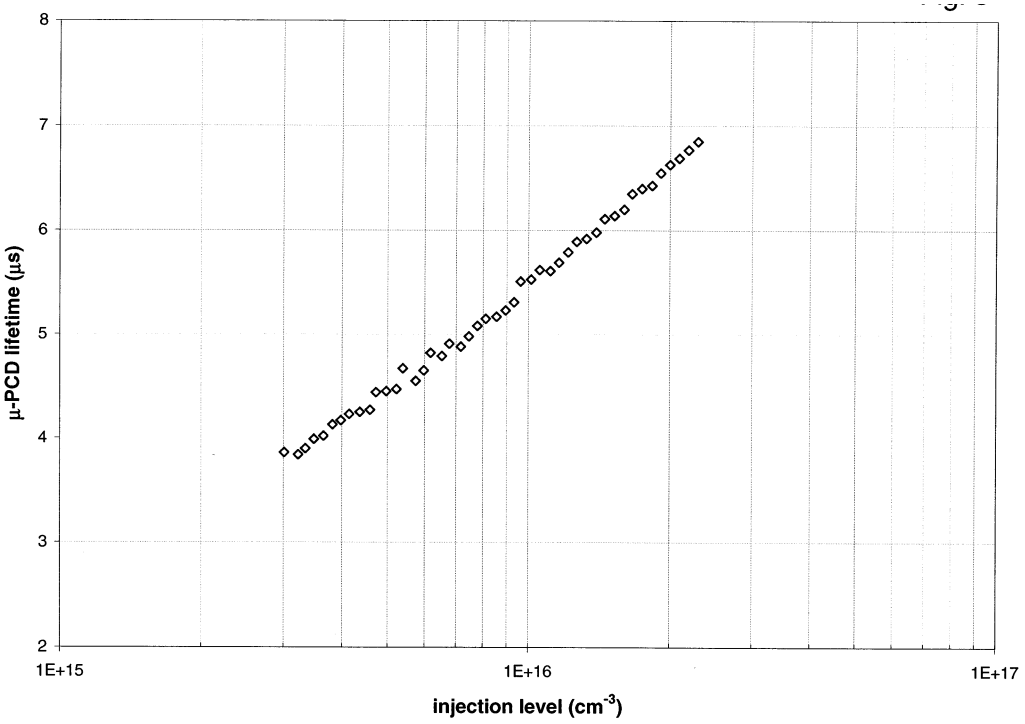

Fig. 5. Measured μ-PCD lifetime versus injection level for a sample with medium precipitate density ([BMD] about 10^9 cm^{-3}).

strong injection level dependence of measured lifetime, based on the hypothesis of an 'electric enlargement' of the BMD in p-type silicon. Low injection techniques are confirmed to be more sensitive to BMD density in comparison with high injection techniques, in agreement with model predictions.

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