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POSITRON ANNIHILATION STUDIES OF CZOCHRALSKI-GROWN SILICON ANNEALED UNDER PRESSURE

G.P. KARWASZ^{a,b}, R.S. BRUSA^a, A. MISIUK^c AND A. ZECCA^a

^aInstituto Nazionale per la Fisica della Materia, Universita' di Trento, 38050 Povo, Italy

^bInstytut Fizyki, WSP Słupsk, Arciszewskiego 22b, 76-220 Słupsk, Poland

^cInstytut Technologii Elektronowej, Al. Lotników 32/46, 02-668 Warszawa, Poland

Two positron techniques have been applied to study dynamics of oxygen precipitation in Czochralski-grown silicon, annealed under high (up to 1.4 GPa) pressure. Lifetime measurements were performed with 180 ps resolution; Doppler broadening with a variable-energy slow-positron beam. Different thermal treatments rise the mean lifetime of positrons from 222 ps in as-grown samples up to 227 ps. In samples with a high (up to 85%) amount of oxygen precipitated, an intermediate (550–800 ps) lifetime is observed.

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1. Czochralski-grown silicon

Positron lifetime studies of silicon system is a difficult task. Theoretical calculations indicate that the lifetime in bulk, defect-free silicon (221 ps [1]) lies close both to the lifetime of monovacancies (250 ps) as well as to SiO₂ phase [2]. Existing experimental results for Si bulk lifetime show a large span of almost 10 ps. Studies of defects are usually performed in on-purpose prepared samples, e.g., by electron [3] or neutron irradiation [4].

Czochralski-grown silicon, due to the preparation method by melting in SiO₂ crucible, contains high ($4-10 \times 10^{17} \text{ cm}^{-3}$) amounts of interstitial oxygen, an order of magnitude more than floating zone Si. Thermal treatment of Cz-Si leads to complex phenomena, like appearance of thermal donors (450°C), creation of nucleation centers (600–900°C) and oxygen precipitation. The amount of oxygen precipitated and the form of precipitates depend strongly both on pre-annealing history as well as the final annealing (800–1100°C) temperatures. Prolonged annealing at temperatures above 1150°C causes dissolving of precipitates [5].

In the present work massive oxygen precipitation was obtained by three-phase annealing: nucleation at about 450°C, primary precipitation at 650°C, oxygen clusters grown at 950–1050°C. An additional factor enhancing the precipitation is the use of high (up to 1.4 GPa) hydrostatic pressure during the final annealing. In

particular, the amount of oxygen removed from interstitial sites at 950°C rises by a factor of 3 if a hydrostatic pressure of 1 GPa is applied [6]. In some of the presently studied samples as much as 85% of interstitial oxygen has precipitated. Pressure annealing at lower temperatures (450°C) rises the number of donors. Different typology of defects is seen by optical microscopy after selective chemical etching. The total surface density of these defects is almost constant at about $3 \times 10^6/\text{cm}^2$. Populations of defects depend on the annealing history, say, saucer pits and prismatic dislocation loops dominate in samples with the highest amount of oxygen precipitated.

All samples were 0.6 mm thick and unless stated differently obtained from a single (001) oriented *p*-type wafer with an initial oxygen concentration $10\text{--}11 \times 10^{17} \text{ cm}^{-3}$. Before annealing the hole concentration was $1 \times 10^{15} \text{ cm}^{-3}$. For the most significant cases, samples with lower ($8 \times 10^{17} \text{ cm}^{-3}$) oxygen contents were also examined. More than 60 samples were measured. Annealing times, apart from those for treatments under pressure, were usually 20 h; inert atmosphere (Ar) was used. "As grown" refers to the same type Si, without thermal treatment. As "reference" sample Cz-Si, *p*-type, 5 Ω cm resistivity, 0.6 mm thick pieces from Thompson SGS, Milan were used.

2. Apparatus

Previously described [7] lifetime apparatus based on BaF₂ scintillators and fast Hamamatsu R2083Q photomultipliers were used. Na²²Cl source of approximately 2 μCi was encapsulated in 7.5 μm kapton foils. Several measurements were undertaken to preserve good time resolution and stability of apparatus like: room temperature stabilisation, relatively low (30–50/s) counting rate, frequent calibration checks using defect-free metal monocrystals, precise source component determination, several (4–30) independent runs with about 1×10^6 counts each. This allowed us to achieve an overall run-to-run repeatability of τ_1 within 2 ps. The time resolution was 180 ps. The fit parameter χ^2 was usually below 1.1.

3. Analysis

PATFIT was used in data analysis. For all samples a free-run, two-component analysis was performed. A theoretical source contribution at 382 ps for the given kapton thickness is 6.5%. However, the apparatus calibration for metals gave this component by 5.4–6.2% higher. A minimum of χ^2 value for 1- and 2-component analysis is observed at about 11.5–12.5%. However, for some samples the free-run analysis with 12% source contribution was diverging. Therefore, we preferred to underestimate slightly the source component at 11%. This obviously yields the presence of a long component in all spectra. We note that unless a real long component appears, say in pressure annealed samples, the artificial τ_2 due to the source component is usually in the 1.1–15 ns range with intensity 0.2–0.3%.

4. Short lifetime component

Positron lifetime data reproduce well changes in oxygen precipitation and the dynamics of oxygen-related defects. As-grown sample, in repetitive measurements

showed a slightly higher τ_1 (222.6 ps) than in the reference sample (221.6 ps). Generally, different thermal treatments causing oxygen precipitation usually increase this lifetime. The τ_1 remains unchanged if only one thermal treatment is performed, compare Table I.

Similarly, no change in τ_1 , within the error bar, can be distinguished in samples without the intermediate, 650°C nucleation step (i.e., with only one, 450°C/20 h preannealing), see Table II. Second annealing, at 650°C, increases τ_1 , see Fig. 1.

TABLE I

Short lifetime component (in ps) in one-step annealed Cz-Si.

T_1/t_1	450°C/20 h	650°C/20 h	727°C/5 h
τ_1	221.8 ± 1.1	222.6 ± 1.6	223.7 ± 0.7

TABLE II

Short lifetime component in two-step annealed Cz-Si.
 $T_1/t_1 = 450^\circ\text{C}/20\text{ h}$.

T_2/t_2	957°C/5 h	1050°C/5 h
τ_1	223.8 ± 1.5	221.9 ± 1.0

Fig. 1. Dynamics of defects related to primary oxygen precipitation after nucleation (450°C/20 h). The first point is the τ_1 value in the sample subjected only to nucleation.

TABLE III

Short lifetime component (in ps) in three-step annealed Cz-Si.
Preannealing at (450°C/20 h + 650°C/20 h).

$T_3/$	1050°C/	1050°C/	1050°C/	1127°C/
t_3/p	20 h/1 bar	3 h/100 bar	3 h/10 kbar	5 h/10 kbar
τ_1	224.4 ± 0.9	225.8 ± 0.8	225.2 ± 0.6	225.9 ± 0.5

The 650°C treatment seems to be essential for formation of defects. Similar lifetime $\tau_1 = 225.5$ ps was measured both for samples with the preliminary and final 650°C annealing (450°C/20 h + 650°C/20 h) and (650°C/20 h + 1127°C/5 h). The same rise of τ_1 is also well visible in samples after a complete, 3-stage annealing, both with and without pressure, see Table III.

In neither of the samples we have found the very short (80–100 ps) lifetimes observed by Dannefaer and Kerr [8] in high-oxygen contents ($13 \times 10^{17} \text{ cm}^{-3}$) Cz-Si.

5. Pressure treatments

No pressure influence at the nucleation stage (450°C, 20 h) is observable in τ_1 , see Table IV.

At the nucleation stage (650°C/20 h) in the samples after prenucleation (450°C/20 h) it seems that the pressure inhibits migration of oxygen. τ_1 remains in the 222 ps range after 650°C annealing under pressure but rises if annealed without pressure, see Table V.

TABLE IV

Short lifetime component in one-step (450°C, 20 h) pressure-treatment Cz-Si.

p	1 bar	30 bar	11 kbar
τ_1	221.8 ± 1.8	221.3 ± 1.5	222.1 ± 0.8

TABLE V

Short lifetime component in pressure-treated Cz-Si (650°C, 20 h). Preannealing 450°C, 20 h.

p	1 bar	30 bar	10 kbar
τ_1	225.6 ± 1.2	222.2 ± 0.3	222.5 ± 0.4

A certain rise of τ_1 is observed if the third stage of a complete annealing cycle is performed under pressure, compare Table I. However, for samples in Table III, the pressure-induced precipitation may be compensated by annealing at longer periods of time without pressure.

Tendentiously, the intensity of τ_2 (1.1–0.15 ns) rises slightly (from 0.2 to above 0.5%) with high pressures applied. Strong influence of pressure is observed for samples with third annealing at 900–950°C (see the next paragraph).

6. Nanovoids

An intermediate (500–800 ps) lifetime component has been distinguished in all samples subjected to two-step preannealing (prenucleation at 450°C and nucleation at 650°C) and the final annealing under high pressure (1–1.4 GPa) at 870–950°C. The intensity of this component decreases with oxygen initial contents and with decreasing annealing pressure. An error bar on τ_2 (one standard deviation of a single run) is typically 10%; for some samples it is less than 5%.

This lifetime is substantially different from long σ -Ps lifetimes and resembles that for multivacancy defects in Si. From theoretical calculations it follows, that a rising number of vacancies in vacancy clusters causes an asymptotic rise of τ up to 600 ps. Therefore, we suppose that presently observed lifetimes are due to positron annihilation in extended vacancy-like defects, say prismatic dislocation loops, surrounding oxygen precipitates. Multi-atom microvoids have been also postulated in the SiO_2 phase [8].

We note also that PATFIT program produces a kind of artificial coupling between τ_2 and I_2 , maintaining the product $\tau_2 I_2$ almost constant, see Fig. 2. Particular samples form distinct parts of this “universal” curve. A hypothesis could be formulated that smaller (and more numerous) oxygen clusters show shorter τ_2 , in

Fig. 2. τ_2 vs. I_2 correlation plot for samples preannealed at 450°C/20 h + 650°C/20 h and annealed under pressure at different temperatures. For sample numbers, see Table VI.

TABLE VI

Lifetime analysis of samples with high oxygen precipitation. Initial oxygen contents $10\text{--}11 \times 10^{17} \text{ cm}^{-3}$, sample No. 44, $8 \times 10^{17} \text{ cm}^{-3}$, pre-annealing ($450^\circ\text{C}/20 \text{ h} + 650^\circ\text{C}/20 \text{ h}$).

Sample No.	Temp. [$^\circ\text{C}$]	Pressure [atm]	τ_1 [ps]	τ_2 [ps]	I_2 [%]
2	900	10 k	221.0	530	4.0
13	950	10 k	223.1	640	2.1
41	957	100	221.0	570	3.2
44	900	10 k	223.7	790	1.1
54	957	1	227.5	800	1.4
71	957	12 k	224.9	810	0.9

analogy with free-volumes analysis in polymers, for example. Doppler-broadening studies with a variable-energy positron beam show depth inhomogeneities in pressure annealed samples. A decrease in the S -parameter at near-to-surface depth (20–50 nm) with a rising pressure at 957°C can be interpreted as the presence of SiO_x phase. This phase does not appear in a sample annealed under pressure at 1127°C .

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