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Defects in FZ-silicon after neutron irradiation—A positron annihilation and photoluminescence study

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Float-zone (FZ) Si irradiated with 1 MeV neutrons was investigated by means of positron annihilation lifetime spectroscopy and photoluminescence. Three types of defects were observed: di-vacancies, small vacancy clusters and an unknown defect with the defect-related lifetime of (285 ± 5) ps that contribute to positron trapping only at low temperatures. Two annealing stages were observed: one at 350°C and another at 500°C. While the former is due to the annealing of divacancies, the latter is caused by the annealing of vacancy clusters and the unknown defect. © *2004 Kluwer Academic Publishers*

1. Introduction

Despite a great number of experimental studies devoted to the investigation of the influence of neutron irradiation on electrical and optical properties of silicon crystals, the irradiation-induced defect structure still remains a subject of both scientific and technological interest. Floating zone Si is used to produce fast-particles detectors, which are implemented in colliding experiments, exposed to high dose neutron irradiation. It was observed, that the electrical properties of these detectors become worse under the long-time irradiation. The understanding of the nature of induced defects is a key point to find a way to avoid such deterioration.

Since a variety of point defects is introduced during neutron irradiation, it is impossible to characterize all of them using a single experimental technique. The positron annihilation lifetime spectroscopy (PALS) has been proved to be a convenient tool to investigate vacancy-type defects. Although many positron works have been done on this field, there are still open questions concerning the identification of the observed vacancies or vacancy complexes. In the first positron studies on neutron-irradiated silicon by Dannefaer *et al.* [1] the detected defect-related lifetime of about 325 ps was attributed to divacancies. The same defect was found also for neutron irradiated Cz Si [2] showing an annealing stage at 600°C. This contradicts the EPR study of defects in electron-irradiated silicon [3] where the annealing stage at 350°C for divacancies was found. Relatively new theoretical calculations of vacancy clusters in Si using self-consistent charge-density functional-based tight-binding method gives values of 295 and 325 ps for the isolated divacancies and trivacancies [4], respectively. This also contradicts most of the experimental results [5–8].

Although many positrons studies about neutron-irradiated FZ Si exist, only in few of them temperature-dependent positron lifetime measurements were applied. As our presented work shows, it is very important to investigate the temperature dependence of annihilation parameters in order to interpret the experimental results, since different defects may have different temperature-dependent positron trapping activity.

PALS uses defect-related positron lifetime to identify the defect structure. This lifetime represents the time the trapped positron survives in the defect, till its annihilation. But sometimes, the exact identification of defects from the results of positron annihilation alone is impossible, when several defects or defect-complexes have close lifetimes. In such cases the combination of PALS with other experimental techniques, which can give us additional information about the defect structure, is necessary.

The paper presents the results of our investigation of neutron-irradiation defects in FZ Si studied by temperature-dependent PALS measurements in correlation with photoluminescence experiments.

2. Experimental

We investigated intentionally undoped Si samples grown by the float-zone technique (slightly p-type, resistivity 3 kΩcm). The concentration of oxygen and carbon was about 10^{15} cm^{-3}. The samples were irradiated with 1 MeV neutrons with 4 doses: 2.4×10^{15}, 3.5×10^{15}, 4.5×10^{15} and 5.0×10^{16} cm^{-2}. In the text below the samples are referred to as number 1, 2, 3 and 4, respectively. The irradiation was performed at room temperature at the reactor facility of Lubliana. Afterwards the samples were stored in a refrigerator at −6°C to prevent the possible annealing of the irradiation-induced defects. A piece of unirradiated boron-doped Si was used as reference and exhibits no positron traps.

For each sample, temperature-dependent positron lifetime measurements were performed in the temperature interval from 20 to 300 K. For PALS measurements, two spectrometers were used with time resolution of 232 and 240 ps. Around 3×10^6 counts were collected for each spectrum and stored in 400 channels in a multi-channel analyzer, the channel width was 25.7 and 25.5 ps, respectively.

After source and background corrections, the positron lifetime spectra $n(t)$ were fitted according to the positron trapping model with a sum of exponential decay components

$$N(t) = \sum_{i=1}^{k+1} I_{\text{i}}/\tau_{\text{i}} \exp(-t/\tau_{\text{i}}), \tag{1}$$

where k is the number of deferent type of defects contributing to the positron trapping. In present paper only one defect type was assumed in analyzing, i.e., 2 component decompositions of spectra were performed. From the decomposition the average lifetime was obtained as

$$\tau_{\text{av}} = \sum_i I_{\text{i}}\tau_{\text{i}}, \tag{2}$$

which is not sensitive to the uncertainties of numerical fitting.

As a check whether the chosen model, i.e., number of the positron lifetime components assumed, is correct one can compare the experimentally determined positron bulk lifetime τ_{bulk} with the calculated bulk lifetime determined from the decomposition $\tau_{\text{bulk}}^{\text{TM}}$

$$\tau_{\text{bulk}}^{\frac{1}{\text{TM}}} = \sum_i \frac{I_{\text{i}}}{\tau_{\text{i}}} \tag{3}$$

If the model assumptions are correct, $\tau_{\text{bulk}}^{\text{TM}}$ agrees with τ_{bulk}. If the values differ significantly, more components should be taken into account.

Photoluminescence (PL) was excited by an Argon-ion laser at 514.5 nm using an excitation power of 20 mW. The luminescence was dispersed with a dual-grating spectrometer and detected with a liquid-nitrogen cooled Germanium photodiode using a standard lock-in technique. For all measurements, the sample was maintained at 20 K.

Samples 3 and 4 were used for studying the annealing behavior of the induced defects. Sample 4 was isochronally annealed for 30 min in the temperature range 350–600°C in steps of 50 K. After each annealing step, the temperature-dependent PALS measurements were performed. A piece of the same material was used for isochronal annealing together with the PL measurements ($\Delta T = 100$ K, $\Delta t = 30$ min). Sample 3 was annealed at 325°C before the temperature-dependent PALS measurement.

3. Results and discussion

3.1. Vacancy-like defects

Fig. 1 presents the positron average lifetime as a function of temperature obtained as a result of a two-component spectra decomposition (i.e., one-defect trapping model [9]) for FZ Si irradiated at different integrated neutron flux. For comparison the curve of boron-doped reference Si, which shows no positron traps, is included. The bulk lifetime equals 219 ± 1 ps in agreement with the previous results in defect-free silicon [10], revealing no temperature dependence.

The average lifetimes for the irradiated samples are well above that of bulk silicon, indicating the presence of vacancy defects. The values of the average lifetime for the sample 4 are distinctly larger than for samples 1–3. This points to a higher concentration of irradiation induced defects, which one should expect, because the irradiation doses of sample 1–3 and sample 4 differ by one order of magnitude.

We have to state that the two-component one-defect trapping model, applied for the spectra decomposition, is actually not valid for the whole range of measurement temperatures. The calculated bulk lifetime ($\tau_{\text{bulk}}^{\text{TM}}$) in the case of sample 4 was significantly higher than τ_{bulk} for any measurement temperature. For the samples 1–3, $\tau_{\text{bulk}}^{\text{TM}}$ was close to 219 ps only at room temperature,

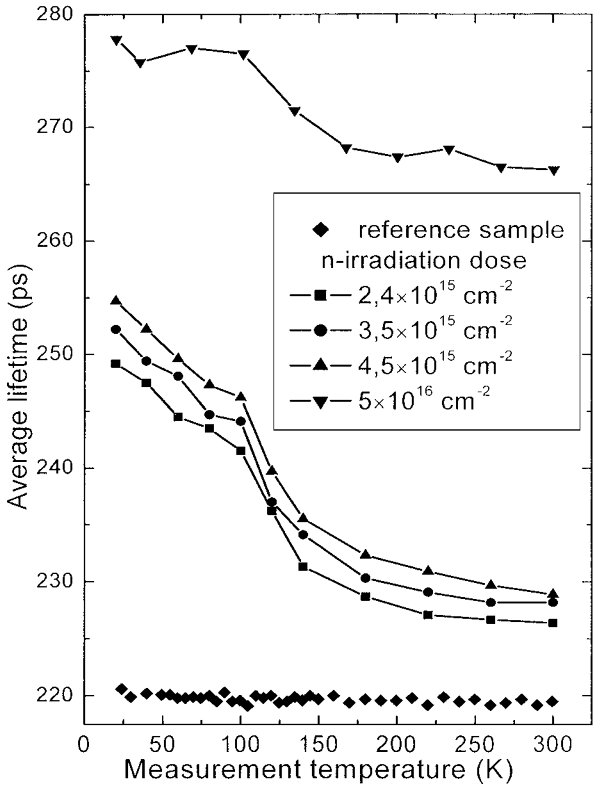

Figure 1 Positron average lifetime in FZ Si irradiated with neutrons at different doses.

while in the low temperature range, this value was much higher. The difference between the calculated and real bulk lifetimes points to the presence of more then one type of positron sensitive defects. This means, that the one-defect decomposition could be concerned as a correct one only for the spectra measured in samples 1–3 at room temperature. In the case of other spectra more than one defect contribute to positron trapping. However, the decomposition of the spectra into more than two components was impossible, because the lifetimes, related to different defects, did not differ sufficiently [11].

As the outcome of the spectra decomposition for the samples 1–3 at 300 K the defect-related lifetime (τ_2) of 320 ± 10 ps with the corresponding intensity (I_2) 10–20% was obtained. At low temperatures τ_2 was equal to 290 ± 5 ps with $I_2 = 70\%$. The fact that the defect-related lifetime is not constant within the measurement temperature interval is due to the trapping of positrons in at least two defects, each of them have different temperature dependence of the trapping rate. The second lifetime presents then a superposition of the lifetimes related to the different positron traps. As was mentioned earlier, according to the calculated bulk lifetime, the one-defect trapping model for the samples 1–3 is valid at room temperature, meaning that the trapping only in one defect with a positron lifetime of 320 ± 10 ps. This defect lifetime is attributed to the divacancy type defect according to many other [5–8]. In order to prove this assumption, sample 3 was heated for 1 h at the temperature of 300°C, at which only divacancy defects anneal. Fig. 2 demonstrates the average and defect-related lifetimes for sample 3 before and after this heating treatment. After annealing, the average lifetime decreases in the whole temperature interval. At temperatures higher than 200 K, it becomes close to the bulk lifetime, what means that no positron trapping occurs in this temperature interval. According to the decomposition (Fig. 2b) the decrease of the average lifetime corresponds to the annealing of the 320 ps defect, which therefore should be a divacancy type defect. One could see from the average lifetime curve that positrons are still trapped at low temperatures. This effect will be discussed later, when considering the low temperature positron trap defect.

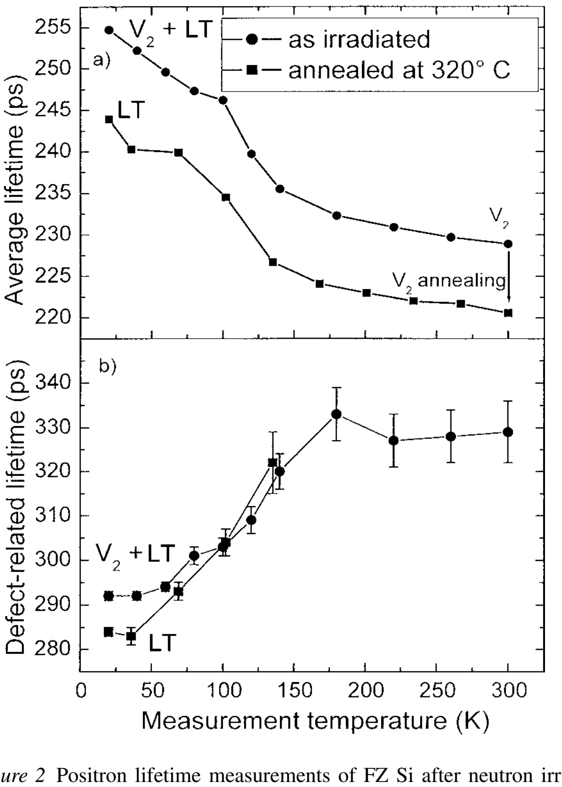

Figure 2 Positron lifetime measurements of FZ Si after neutron irradiation at a dose of 4.5 × 10^{15} cm^{-2} in as-irradiated state and after annealing at 320°C. (a) average positron lifetime and (b) defect-related lifetime versus measurement temperature. The defects contributing to positron trapping at different temperatures are noted: V_2—divacancy type, LT—low temperature positron trapping defect.

The interpretation of the experimental results in the case of the sample 4 is more complicated. Again it was impossible to decompose the spectra in more than two components. But according to the $\tau_{\mathrm{bulk}}^{\mathrm{TM}}$, the used one-defect trapping model is not valid at all measurement temperatures, what means, that there are more than one defects types, which trap positrons and have close defect lifetimes. In order to identify the observed defects we studied their thermal annealing behavior. The average lifetime measured as a function of sample temperature after each annealing step of sample 4 is presented in Fig. 3a. The dashed line at 219 ps represents the bulk lifetime. The lowering of the lifetime curves indicate gradual annealing of the defects. After the last step at 600°C the average lifetime is equal to the bulk value in the whole temperature interval, meaning that vacancy-like defects are no longer present.

Two annealing stages can be observed. The first already appears during the first annealing at 350°C and the second occurs at 500–550°C. To show the presence of these annealing stages more clearly it is better to present the average lifetime values measured at the highest and lowest measurement temperatures versus the annealing temperature (Fig. 3b). The bulk lifetime is again included as a dashed line. The annealing behavior is explained by the temperature evolution of two kinds of defects, each contributing to the annihilation at high or low temperatures. The first annealing stage is only visible at high measurement temperatures and represents the annealing of the defect responsible for the positron trapping at elevated temperatures. This defect anneals already at 350°C. The other defect, detectable only at low temperatures, is stable until the annealing step of 500°C, and completely vanishes after annealing at 600°C.

The second positron lifetime and it's intensity in as-irradiated state and after the annealing at 400°C are presented in Fig. 4. Before the annealing, the dominating positron trapping occurs at high temperatures with the intensity of 80% and second positron lifetime of (295 ± 5) ps. Taking into account that the two-component trapping model is not valid, more than one defect should contribute to positron trapping. We suppose that the mixture of the lifetimes realted to V_2 and V_2O defects, 320 ps and 270 ps respectively [12, 13], results in the observed second lifetime of 295 ps. The defects anneal during the first heating at 350°C, what coincides with the annealing stage of the divacancies, like in the sample 3. But the concentration of the V_2 and V_2O is probably high enough to form a larger vacancy

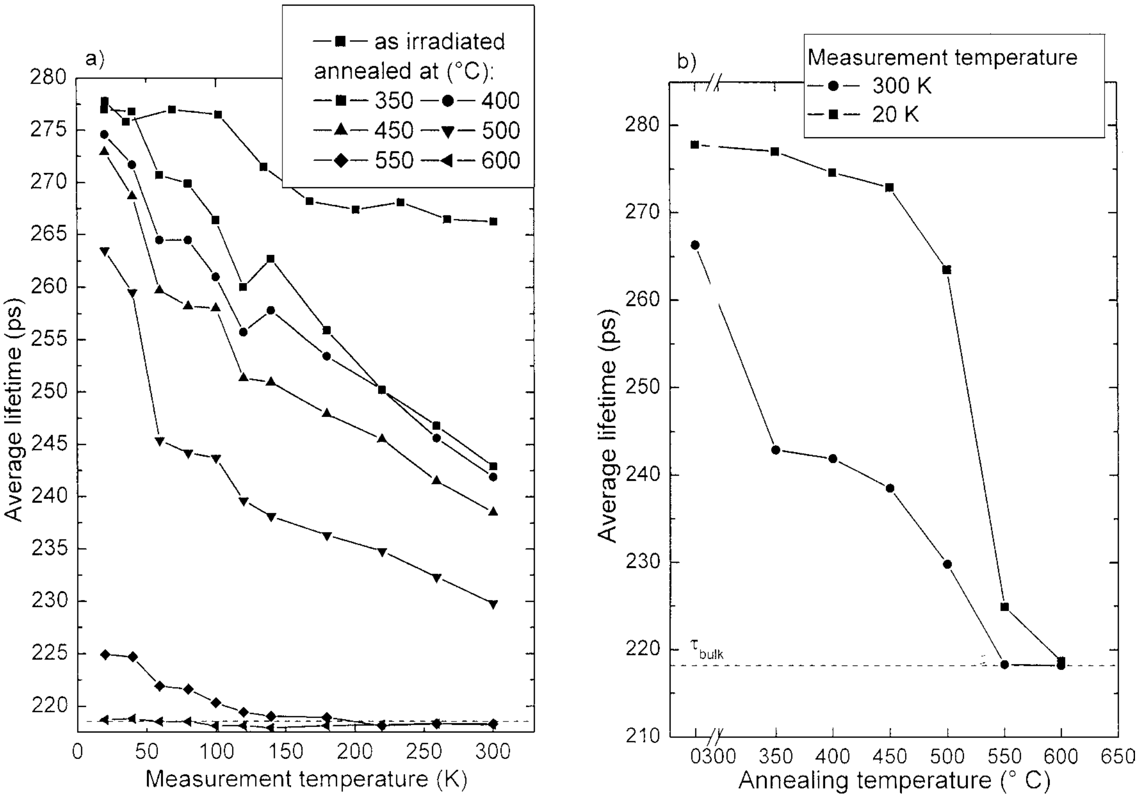

Figure 3 Positron average lifetime of undoped FZ Si irradiated with neutrons with a dose of 5 × 10^{16} cm^{-2}. (a) Average lifetime as a function of measurement temperature in as-irradiated state and after different annealing steps. (b) Average positron lifetime measured at 300 K and at 20 K as a function of annealing temperature.

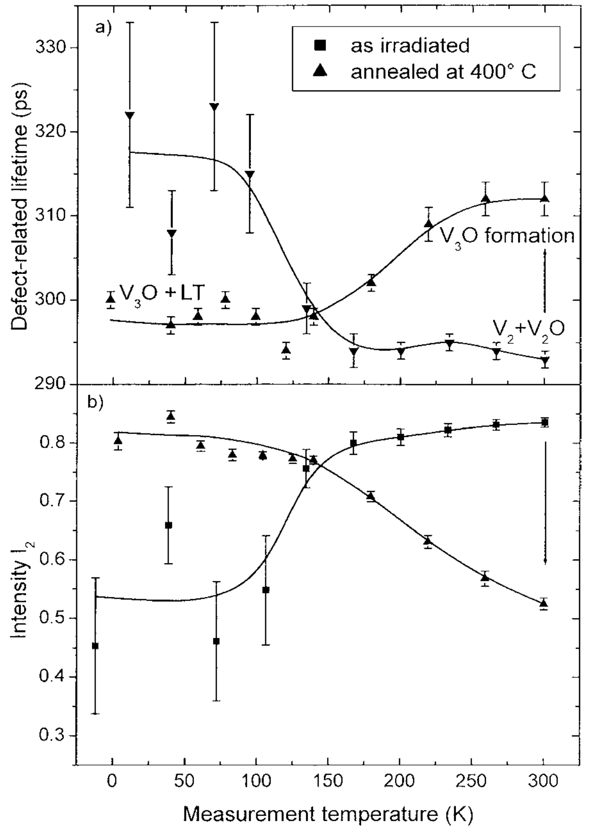

Figure 4 Positron lifetime measurements of FZ Si irradiated with neutrons with a dose of 5 × 10^{16} cm^{-2} in as-irradiated state and after annealing at 400°C. (a) Defect-related lifetime and (b) its intensity versus measurement temperature. The lines are drawn to guide the eye. The defect responcible for positron trapping are noted: (LT means low temperature positron trap).

cluster V_3O. The clustering effect is responsible for the increase of the second positron lifetime (Fig. 4a) and simultaneous decrease of it's intensity (Fig. 4b) which corresponds to the smaller concentration of the formed defect. It is worthy of note that after first annealing, the trapping model is valid at room temperature, but still not at low temperatures, similar to the samples 1–3.

The formation of the tri-vacancies was also observed in the photoluminescence experiment performed on the sample identical to the sample 4. The photoluminescence intensity versus annealing temperature is presented in Fig. 5. One can see the significant increase of the signal, which corresponds to the V_3 defects, after

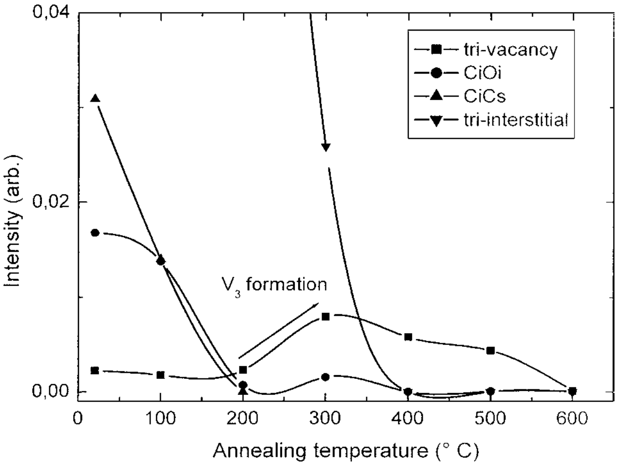

Figure 5 Photoluminescence intensity as a function of annealing temperature of the FZ Si irradiated with neutrons at a dose of 5 × 10^{16} cm^{-2}.

annealing at 300°C, which is in a good agreement with the PALS data.

3.2. Low temperature positron trapping defect

As was mentioned above the applied two-component one-defect trapping model is valid neither for samples 1–3 nor for sample 4 in the whole temperature range. In the case of samples 1–3 and annealed sample 4 the model gives correct $\tau_{\text{bulk}}^{\text{TM}}$ only at high temperatures, while at low temperatures the calculated bulk lifetime is much higher than the real one. This means that at low temperatures the trapping into more then one defect occurs. We propose that is addition to divacancy type defects, one more defect is introduced during the irradiation, which contributes to positron trapping only at low temperatures.

The presence of this defect is perfectly seen in the spectra decomposition of sample 3 (Fig. 2). After the annealing of divacancies at 320°C the average lifetime is close to the bulk lifetime at high temperatures but continuously increases towards low temperatures due to incremental positron trapping into the low temperature trap defect. Before the annealing, we could not decompose the spectra, measured at low temperatures, into two components, because of the presence of two types of positron sensitive defects: V_2 and the low temperature positron trap. But after the annealing, i.e., when the divacancies disappeared, the two-component trapping model for the low-temperature spectra was valid. This means, we deal only with one defect type in the annealed sample, which is "visible" at low temperatures and does not trap positrons at temperatures close to room temperature. The lifetime related to this defect, obtained from the decomposition at the lowest measurement temperature, is 285 ps (Fig. 2b).

Such trapping behavior is characteristic for shallow trap type defects [9]. The term "shallow" relates to the small positron binding energy (in the range of 20–50 meV). Generally it is accepted, that a shallow trap defect represents a negative ion, e.g., an acceptor-type impurity, which is able to trap positrons only at low temperatures due to it's shallow negative potential (Rydberg tail). Since there is no open volume associated with the negative ions, i.e., no missing atom core, the trapped positrons annihilate with the bulk lifetime. But the observed 285 ps lifetime is distinctly higher than the bulk one (219 ps). This value lies between the defect lifetimes corresponding to the mono- and divacancy type defects, 270 and 320 ps resprectively. Thus the observed low temperature positron trapping defect can not be related to a negative ion, but is associated with an open volume defect of the size of a monovacancy. No information regarding the nature of this defect was found in other positron works. As a possible candidate for it, the unusual so-called "zero"-defect, which represents the accumulation of interstitials inside vacancy agglomerate [14, 15], could be considered.

4. Conclusion

FZ silicon crystals irradiated by neutrons at different doses have been investigated by means of positron annihilation lifetime spectroscopy and photoluminescence. The temperature dependent PALS measurements revealed two types of defects introduced by irradiation: vacancy-like defect (V_2 and V_2O) and an unknown open-volume defect that contributes to annihilation only at low temperatures. The divacancies anneal at 300–350°C. In the case of high irradiation dose the concentration of V_2 is high enough to form larger vacancy complexes—probably V_3O, which are thermally stable up to 600°C. The formation of the trivacancy complex during the annealing has also been observed in photoluminescence measurement in very good agreement with the PALS data.

The exact nature of the low temperature positron trap could not be established. The positron lifetime related to the defect equals to 285 ps, which points to a size between of mono- and divacancy. However the defect is thermally stable up to 600°C, where neither mono- nor divacancies are usually observed.

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