Positron probing of phosphorus-vacancy complexes in silicon irradiated with 15 MeV protons

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Abstract. Defects in phosphorus-doped silicon samples of floating-zone material, $n$–FZ–Si(P), produced under irradiation with 15 MeV protons at room temperature are studied by positron annihilation lifetime spectroscopy over the temperature range of ~ 30 K – 300 K and by low-temperature Hall effect measurements. After annealing of $E$–centers and divacancies, we detected for the first time high concentrations of positron traps which had not been observed earlier. These defects are isochronally annealed over the temperature interval of ~ 320 °C – 700 °C; they manifest themselves as electrically neutral deep donor centers in the material of $n$-type. A long-lived component of the positron lifetime, $\tau_2(I_2 \leq 60\%) \sim 280$ ps, attributed to these centers, suggests a relaxed configuration involving two vacancies. The enthalpy and entropy of annealing of these centers are $E_a \sim 1.05(0.21)$ eV and $\Delta S_m \approx 3.1(0.6)$ k$B$, respectively. It is argued that the microstructure of the defect consists of two vacancies, $VV$, and one atom of phosphorus, P. The split configuration of the VPV complex is shortly discussed.

1. Introduction
It is widely believed that accumulation of defects in $n$–FZ–Si(P) material takes place similarly under irradiation with fast electrons and protons of MeV energies, and the phosphorus-vacancy pairs ($E$–centers), together with divacancies, are believed to be dominant acceptor-type defects responsible for degrading $n$–type conductivity of silicon wafers at low doses of irradiation. However, this similarity vanishes under proton irradiation, and the generally adopted model of dominating formation of $E$–centers appears to be inadequate for interpreting experimental data [1]. It has been revealed that electrically neutral defects trapping positrons are formed in $n$–FZ–Si(P) material as a result of proton irradiation [2]. The microstructure of these defects is still an unresolved problem. Below we present some new data on their positron probing and analyze their possible configurations.

2. Experimental
Samples cut from Si crystal grown by the floating-zone technique were studied. They were subjected to irradiation with 15 MeV protons at room temperature. Two doses of proton irradiation, $4 \cdot 10^{13}$ and $8 \cdot 10^{13}$ protons/cm$^2$, were used. According to data of IR spectroscopy, the concentration of oxygen in...
Isochronal annealing leads to decreasing the average positron lifetime (\(\tau_{av}\)). Thermally stable electrically neutral positron traps: phosphorus-multivacancy complexes

The rate of annealing was \(\tau_{av} = 0.16 \text{ cm}^2 \text{ s}^{-1}\). The thickness of samples was \(\lesssim 900 \mu\text{m}\), which is much less than the stopping range of the protons (\(-1500 \mu\text{m}\)). We have conducted Hall effect measurements as a complementary method to that of positron annihilation lifetime; in a similar way this material was studied in [2]. Data on the average positron lifetime \(\tau_{av}\) (AT \(\approx 30–300 \text{ K}\)) were used for obtaining the shorter \(\tau_1\) and longer \(\tau_2\) values of lifetime: \(\tau_{av} = \tau_1 I_1 + \tau_2 I_2\); the intensities are \(I_1 + I_2 = 1\) (LT9 and LT10 programs were applied for data processing). The ratio \(I_2/I_1\) was used for estimating the positron trapping rate \(k\) (see equation (1)).

The irradiated samples were isochronally annealed over the temperature range of 80°C–700°C. The rate of annealing was \(\alpha = h^{-1} \text{ s}^{-1}\) (\(h = 10\text{ min.} \approx 20°\)). For convenience, we use the temperature units K and °C while discussing the data of measurements and isochronal annealing, respectively.

### 3. Thermally stable electrically neutral positron traps: phosphorus-multivacancy complexes

Isochronal annealing leads to decreasing the average positron lifetime (i) proportionally to the dose of irradiation: the ratios of \(\tau_{av}\) (100K)\(_{\text{irr.}}\) values obtained before annealing (shown by arrows in figure 1) and after annealing at 300°C \(\tau_{av}\) (100K)\(_{\text{irr.}}\) (anneal. at 300°C) are 1.039 and 1.078 at doses \(4 \times 10^3\) and \(8 \times 10^3\) protons/cm\(^2\), respectively. This proportionality suggests (ii) that the thermally stable defects of a vacancy type are formed as a result of irradiation rather than in the course of isochronal annealing.

A clearly seen correlation between a decrease in the average positron lifetime \(\tau_{av}\) and an efficiency of restoration of electrical activity of phosphorus atoms shown in [2] points out the involvement of phosphorus atoms in the microstructure of these defects: their concentration is estimated to be (iii) \(N_{DD} \sim 10^{15} \text{ cm}^{-3}\) and \(\sim 5 \times 10^{14} \text{ cm}^{-3}\) for the higher and lower doses of proton-irradiation, respectively.

The conclusions (i)-(iii) indicate that the defects survive at earlier stages of annealing when \(E\)-centers and divacancies are annealed in the temperature intervals of ~100°C–160°C and ~180°C–280°C, respectively. As we should expect for the carbon-lean \(n\)-FZ-Si(P) material [1, 2], any oxygen-related centers have not manifested themselves in neither electrical nor positron annihilation data.

Being deep donors with their levels \(E_{DD} > E_c \sim 0.24\) eV, the centers turned out to be electrically neutral (or even, perhaps, electrically inactive) in the investigated material of \(n\)-type [1]. However, owing to an open volume related to the presence of vacancies in their microstructure, the deep donors are effective positron traps in the irradiated material [2]: the positron trapping cross-section for these defects is estimated to change from \(\sim 5.7 \times 10^{-14}\) cm\(^2\) (230 K) to \(\sim 3 \times 10^{-12}\) cm\(^2\) (66 K). According to the data of Hall effect measurements, the isochronal annealing of these defects is finished at ~650°C–700°C [1]; by means of PAL spectroscopy they have been detected up to ~500°C (figure 1).
4. Open volume of thermally stable phosphorus-vacancy complex: a split VPV configuration

If trapped, positrons live longer in the states related to structural defects and this fact indicates the presence of vacancies in their configurations. The positron lifetime calculated \textit{ab initio} for the open volume of a vacant site is longer than the one for the regular crystal lattice of silicon; at a divacancy the positron lives still longer [3, 4, 5]: its lifetime is getting somewhat shorter owing to the relaxation effects [6, 7]. The lifetime of the long-lived component, \( \tau_2 (100K) \), proves to be \( \sim 280 \) ps at the both doses of proton irradiation (see figure 2): the value of \( \tau_2 \) depends on both the temperature of annealing and measurement and it covers a range of \( \sim 275 – 305 \) ps, i.e. the one close to that being characteristic of a divacancy. As seen from figure 2, the calculated positron lifetime associated with the divacancies and the lifetime \( \tau_2 \sim 280 \) ps, related to the phosphorus complexes of a vacancy type, are in the range of \( \sim 242 – 300 \) ps, thus inviting us to conclude that the phosphorus-related complex under discussion should also contain two vacancies. There is no information on \textit{ab initio} calculations of the positron lifetime for such complexes in the literature so far. A possible atomic configuration of the complex as a VPV combination [1] is depicted in figure 4. The position of the central atom (P) may be most likely distorted because of a relaxation of the surrounding atoms. Earlier, a similar atomic configuration has been considered for the \( E \)-centre containing one full vacancy split into two semi-vacancies, i.e. 0.5V–P–0.5V [8]. We think that the thermally stable phosphorus-vacancy complex having two full vacancies may be configurated similarly, with a distortion of VPV configuration, which may provide suitable positron lifetime, \( \sim 250 \) ps \( \leq \tau \leq \sim 280 \) ps, which corresponds to a pair of vacancies involved in the defect (see figure 2). \textit{Ab initio} calculations of the structural parameters in both configurations, VVP and VPV, might shed light on this point. In this connection it will be noted a model of the tin-vacancy pair in which tin atom resides in a position halfway between two normal silicon atom sites (i.e. tin atom is in the center of a “divacancy” [14]).

5. Enthalpy and entropy of annealing of thermally stable phosphorus-multivacancy complexes

Below we consider just a part of the data obtained at \( T_{\text{meas}} = 115 \) K for a low dose of irradiation (4·10\(^{13}\) protons/cm\(^2\)), when the positron trapping is still effective (see figure 3): isochronal annealing of the defects under study is described by the equation of quasi-chemical reaction of the 1\(^{\text{st}}\) order:

\[
\ln \frac{k_i - k_{i+1}}{k_{i+1}} \equiv A - \frac{E_a}{k_B T_{\text{ann}}},
\]

where the positron trapping rate \( k_i (T_{\text{meas}}) \) is derived at the annealing temperature \( T_i \) from the average positron lifetime [9, 11]; \( E_a \) is the enthalpy of annealing; \( A \approx K_0 h \alpha^2 \). Factor \( K_0 \) was estimated making use of a generalized approach [10]; \( K_0 \approx 4\pi r_0^2 \cdot N_{DD} \cdot \beta \cdot (a/2)^2 \cdot (\alpha \cdot r_0 \cdot \exp (\Delta l_{\text{att}} \alpha / k_B)), \) where \( r_0 \approx 10^{-8} \) cm; \( \beta \approx \ldots \)
1. $a \approx 2.35 \cdot 10^{-8}$ cm (the interatomic distance in the crystal lattice of silicon); $v_0 \leq 10^{13}$ s$^{-1}$ is the characteristic frequency of atomic vibrations; $\Delta S_{m}/k_B$ is the change of entropy due to dissociation of the vacancy-impurity complex ($k_B$ is the Boltzmann constant). The positron trapping rate was estimated by well-known formula [9]: $k_i \approx \lambda_b \cdot I_2 / I_1 \approx \mu \cdot N_{DD}$ ($\mu$ is the positron trapping coefficient; see also, e.g., [11] for details). Using equation (1) we have evaluated the enthalpy of annealing and the configurational entropy $\sim 1$ < 4 is close to the one discussed for a short-range distortion around point defects in the cubic crystal lattice of diamond type. This conclusion is also supported by the positron lifetime value $\tau_2 \leq 280$ ps which we attribute to the thermally stable divacancy-phosphorus-impurity complex, i.e. to the point defect (see also sections 3 and 4). The entropy estimated is known to characterize the effective frequency of oscillations of the atoms in the defect towards a saddle point where the defect dissociation is most probable (for more detail see, e.g., [10]). Values of $\Delta S_m \sim 2–3k_B$ include implicitly a contribution related to the distortion of the crystal lattice around the defect; an assessment of this contribution is a challenge, so knowledge of these $\Delta S_m$ values is indispensable for elucidating a role of entropy in thermal decomposition of the complexes: which configuration, a non-split PVV or a distorted VPV, is preferable, will be discussed elsewhere.

6. Conclusion
Thermally stable vacancy complexes including an impurity atom of phosphorus have been revealed in $n$–FZ–Si(P) material irradiated by 15 MeV protons. These defects are believed to be deep donors at $E_{DD} > E_c \sim 0.24$ eV. Isochronal annealing of these complexes in the interval of $\sim 300 \degree C – 650 \degree C$ leads to the restoration of electrical activity of phosphorus impurity atoms as shallow donors. The enthalpy of annealing ($\sim 1$ eV) and the configurational entropy ($2–3k_B$) estimated on the basis of data of the positron lifetime measurements suggest a dissociation process of the complexes consisting of one phosphorus atom and two vacancies, most likely, in a split (distorted) VPV configuration.

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