Positron diagnostics of phase transitions in a system formed by SiC, nitrogen, and vacancy defects

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Measurements of the positron lifetimes revealed the influence of nitrogen impurities on the processes of formation and evolution of vacancy clusters representing phase transitions in a system consisting of the SiC host lattice, impurities, and vacancy defects. Similar phase transitions occur in multicomponent nonequilibrium systems.

1. INTRODUCTION

Investigations of structural[1-3] and particularly of radiation,[4-6] defects in semiconductor materials are of fundamental importance for physics of semiconductors. Among the enormous number of known semiconductor materials the compound silicon carbide (SiC) is distinguished by an extremely desirable combination of mechanical, thermal, optical, and electrophysical properties[7,8] which make this material promising for applications in nuclear reactor construction, as well as in microelectronics and optoelectronics. Silicon carbide is highly stable under the influence of hard radiation and also exhibits certain special properties which extend potential applications of this wide-gap semiconductor. For example, some of the radiation defects created in SiC act as effective recombination centers, which have been used in the development of SiC diodes emitting green and light blue light.[9] However, the nature of many radiation centers has not yet been identified. Additional information can be obtained by applying not only conventional techniques, but also new methods that allow selective investigation of different types of structure defects.

Recent years have seen extensive utilization of the positron annihilation method, which is very sensitive and can be applied selectively to vacancy-type defects.[10] The data obtained by this method[11-13] and their correlation with the results of other investigation have demonstrated the great promise of the positron annihilation technique in the diagnostics of structure defects in semiconductor materials.

We shall report and analyze the results of positron investigations of vacancy-type defects formed as a result of irradiation of silicon carbide by various types of penetrating radiation, and the evolution of these defects in the course of thermal annealing of the irradiated samples. These results reveal the fundamental role of the nitrogen impurity in the clusterization of vacancy defects as a result of phase transitions in the host lattice–impurity–vacancy system. The results given below have been reported partially in communications on structure defects in SiC single crystals irradiated with reactor neutrons,[14,15] heavy ions,[16] and fast electrons.[17]

We determined the positron lifetime spectra as a function of the fluence (dose) of high-energy particles and as a function of the temperature of isochronous annealing of samples which received various fluences. An analysis of the results obtained for identical objects using different types of radiation has made it possible to draw conclusions on the mechanisms of defect formation and evolution of defects during annealing of irradiated silicon carbide samples and on the capabilities of the positron annihilation method in the observation of phase transitions in multicomponent systems of the host–impurity–vacancy type characterized by small values of the order parameter.

2. EXPERIMENTAL METHOD

We investigated single crystals of semiconducting silicon carbide in the form of the 3C, 6H, 4H, and 15R polytypes. The positron lifetime spectra of these polytypes were practically identical, so that all further investigations were carried out on 6H-SiC crystals because of their ready availability and because of their industrial applications. We investigated p- and n-type single crystals grown by the Lely method at temperatures 2600–2700°C. The n-type conduction was imparted by doping with nitrogen, while boron or aluminum was used to obtain p-type samples. The investigated range of impurity concentrations was (2×10^{17})–(1×10^{20}) cm^{-3}.

A linear accelerator provided fast ($E_e = 4$ MeV) electrons which were used to bombard samples at various temperatures. The electron fluence (dose) range was (1×10^{15})–(3×10^{18}) cm^{-2}. Irradiation with reactor neutrons (with the fraction of neutrons of energy in excess of 10 keV amounting to $\sim10\%$) took place at a temperature not exceeding 90°C; the fluence range was (3×10^{15})–(1×10^{21}) cm^{-2}. We also used $^{129}Xe^{+}$ ions of energy 124 MeV provided by the Y-300 accelerator at the Nuclear Reactions Laboratory of the Joint Nuclear Research Institute (Dubna); the temperature of the sample was less than 50°C. In this case the fluence range was (5×10^{10})–(5×10^{14}) cm^{-2}.

The positron lifetime spectra were determined at room temperature using apparatus for fast–fast coincidences with a working resolution corresponding to a full width at half-maximum (FWHM) of 380 ps (Ref. 18). The positron source was radioactive ^{22}NaCl evaporated on a Mylar film and covered from above by an identical film. The activity of the source was $\sim10\ \mu$Ci. The fraction of the component of the source utilized in calibration experiments on annealed ($p < 10^{-3}$ Pa) samples of nickel, iron, titanium, and dislocation-free single-crystal silicon amounted to $\sim11\%$. All the experimental spectra were analyzed, after subtraction of the components of the source, using the POSITRONFIT EXTENDED program[19], which yielded one or both compo-

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nents. In many cases it was not possible to carry out a component analysis of the spectra and they were then described by the average positron lifetime $\bar{\tau}$ defined as the first-order moment of the experimental spectrum.

Isochronous annealing ($t_a = 10$ min, in steps of 50 or 100°C) took place in air (temperature range $T_a = 50$–1000°C) or in an atmosphere of pure argon ($T_a = 1050$–2300°C). The annealing temperatures were constant to within ± 2 and ± 10°C, respectively.

3. EXPERIMENTAL RESULTS

The positron lifetime spectra of the original samples of all the n-type SiC polytypes investigated included one component with a lifetime of 157 ± 2 ps, whereas in the case of p-type samples or samples grown at temperatures well below 2600°C the positron lifetime was somewhat longer and could reach ~ 167 ps. Hence, we assumed that the lifetime due to annihilation of quasifree positrons in the host crystal lattice was $\tau_b = 157 \pm 2$ ps.

Figures 1, 2, and 3 give typical dose dependences of the average positron lifetime $\bar{\tau}$ in 6H-SiC irradiated with reactor neutrons, electrons, and xenon atoms. All samples exhibited a monotonic rise of $\bar{\tau}$ as a function of the fluence and a saturation region in which $\bar{\tau}$ remained practically constant in spite of a further increase of the fluence. In the neutron irradiation case the saturation of the average positron lifetime occurred at $\Phi_n = 2.5\times 10^{17}$ cm^{-2} and in the saturation region (up to $\Phi_n = 1\times 10^{20}$ cm^{-2}) the value of $\bar{\tau}$ was 225 ± 2 ps, whereas the experimental positron lifetime spectra were described by one time component (the χ^2 statistical fit criterion was at least 1.07). When the reactor neutron fluence reached 1×10^{21} cm^{-2}, the value of $\bar{\tau}$ rose further to 238 ± 3 ps.

Irradiation with fast electrons also increased the average positron lifetime when the fluence Φ_e was increased. However, the saturation value of $\bar{\tau}$ reached at $\Phi_e = 1\times 10^{18}$ cm^{-2} amounted to 198 ± 2 ps and was considerably less than the corresponding value in the case of the neutron-irradiated samples.

The dependence of the average positron lifetime $\bar{\tau}$ on the xenon ion fluence reached saturation at $\Phi_i \approx 5\times 10^{11}$ cm^{-2} and remained constant at $\tau = 170 \pm 2$ ps, within the limit of experimental error. The 124-MeV xenon ions penetrated a silicon carbide crystal to a depth of ~ 4.5 mg/cm^2 (Ref.16), whereas positrons from the ^{22}Na radioactive isotope reached a depth of ~ 25 mg/cm^2. The positrons thermalized in the damaged surface layer were captured by defects and were annihilated on them in a time τ_d exceeding τ_b.

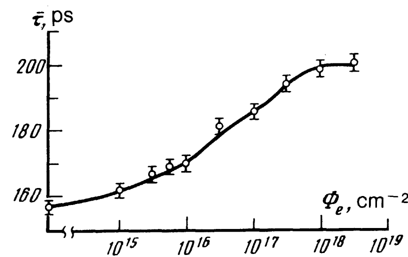

FIG. 2. Dependence of the average positron lifetime $\bar{\tau}$ on the fluence Φ_e of reactor neutrons.

Special measurements with a high-resolution spectrometer (FWHM = 250 ps) made it possible to separate the long-lived component with $\tau_d = 220$–230 ps in the ion-irradiated samples; the intensity of this component was $I_d = 13$–17%. The value of τ_d agreed with the positron lifetime in neutron-irradiated samples and the intensity represented the fraction of the positrons which were slowed down in the ion-damaged layer.

Figures 4, 5, and 6 give the results of determining the average positron lifetime in the course of isochronous annealing of silicon carbide samples irradiated with neutrons, electrons, and ions. Depending on the nature and fluence of the radiation, and on the impurity composition of a specific sample, we were able to identify between one and four of the following stages of annealing of positron-sensitive defects:

The low-temperature stage observed in the case of electron-irradiated n-type (temperature range $\Delta T_a = 150$–500°C) and p-type ($\Delta T_a = 100$–250°C) samples with different dopant concentrations, as well as in crystals irradiated with small ($\Phi_n \leqslant 1\times 10^{17}$ cm^{-2}) reactor neutron fluences;

The "negative" annealing stage resulting in an increase in the average positron lifetime with increasing the isochronous annealing temperature T_a in the range $\Delta T_a = 1000$–1200°C in the case of electron-irradiated and $\Delta T_a = 500$–1000°C in the case of neutron- or ion-irradiated crystals;

The high-temperature stage of defect annealing in the range $\Delta T_a = 1300$–1600°C, typical of samples which received low fluences of all the radiations we employed;

The high-temperature stage $\Delta T_a = 1300$–1500°C observed for those crystals which received high electron ($\Phi_e \geqslant 1\times 10^{18}$ cm^{-2}), neutron ($\Phi_n = 1\times 10^{20}$ cm^{-2}), and ion ($\Phi_i \geqslant 5\times 10^{13}$ cm^{-2}) fluences;

The high-temperature stage $\Delta T_a = 1600$–1950°C typical of strongly irradiated SiC single crystals irrespective of the type of radiation;

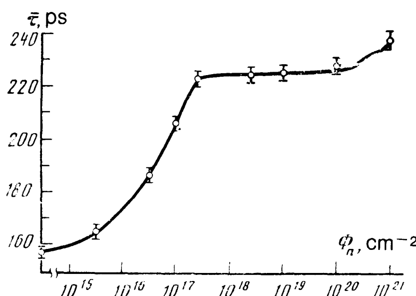

FIG. 1. Dependence of the average positron lifetime $\bar{\tau}$ on the fluence Φ_n of reactor neutrons.

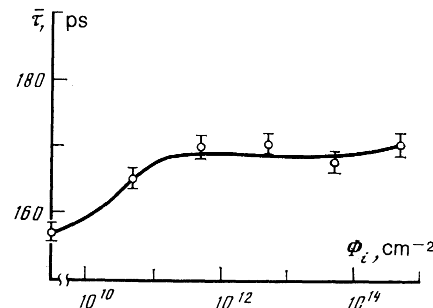

FIG. 3. Dependence of the average positron lifetime $\bar{\tau}$ on the fluence of Φ_i of xenon ions.

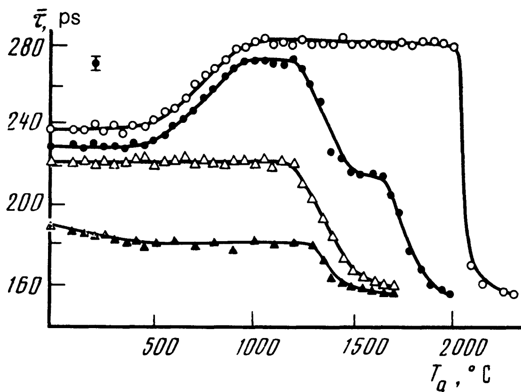

FIG. 4. Dependence of the average positron lifetime $\bar{\tau}$ on the temperature T_a of isochronous annealing of neutron-irradiated samples: ▲) $\Phi_n = 3\times10^{16}$ cm^{-2}; Δ) $\Phi_n = 1\times10^{19}$ cm^{-2}; ●) $\Phi_n = 1\times10^{20}$ cm^{-2}; O) $\Phi_n = 1\times10^{21}$ cm^{-2}.

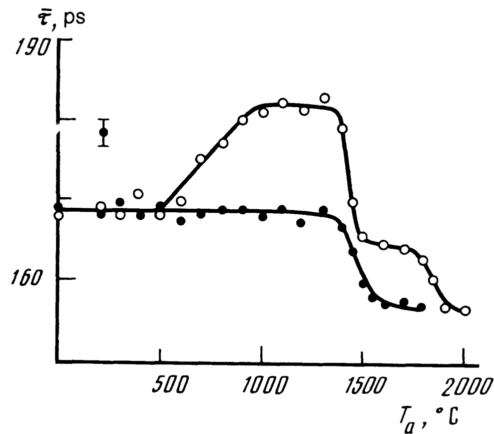

FIG. 6. Dependence of the average positron lifetime $\bar{\tau}$ on the temperature T_a of isochronous annealing of samples irradiated with xenon ions: ●) $\Phi_i \leqslant 5\times10^{12}$ cm^{-2}; O) $\Phi_i \geqslant 5\times10^{13}$ cm^{-2}.

The high-temperature stage $\Delta T_a = 2000$–2300°C observed only for samples irradiated with neutrons up to $\Phi_n = 1\times10^{21}$ cm^{-2}.

The values of the migration energy for each of these stages were reported in Refs. 15, 16, and 17.

4. DISCUSSION OF RESULTS

The main result of the interaction between a high-energy particle and atoms in a crystal is the formation of primary structure defects in the form of Frenkel pairs consisting of vacancies and interstitial atoms. Depending on the irradiation conditions (temperature, nature and energy of the particles, dose rate, etc.),the components of the resultant pair can be stable or mobile. Stable pairs are suitable for observation by the positron method: vacancies then can capture positrons and increase the positron lifetime. If the interstitial atoms are mobile, then the diffusion causes them to escape to sinks or it results in pair recombination in encounters with vacancies. If the vacancies (which are of more interest to us)

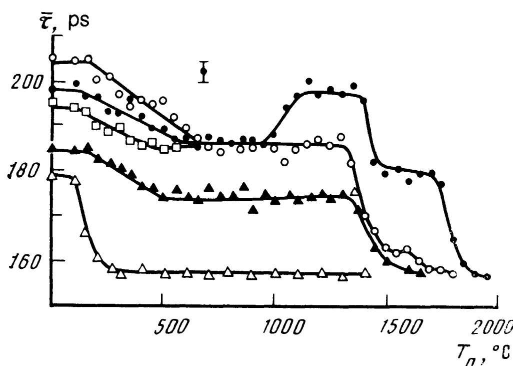

FIG. 5. Dependence of the average positron lifetime $\bar{\tau}$ on the temperature T_a of isochronous annealing of electron-irradiated samples: Δ) samples doped to $N_A - N_D = 5\times10^{19}$ cm^{-3} and irradiated by the fluence $\Phi_e = 1\times10^{18}$ cm^{-2}; ▲) samples doped to $N_D - N_A = 3\times10^{18}$ cm^{-3} and irradiated by the fluence $\Phi_e = 1\times10^{17}$ cm^{-2}; O) samples doped to $N_D - N_A = 3\times10^{17}$ cm^{-3} and irradiated by the fluence $\Phi_e = 1\times10^{18}$ cm^{-2}; ●) samples doped to $N_D - N_A = 2\times10^{18}$ cm^{-3} and irradiated by the fluence $\Phi_e = 1\times10^{18}$ cm^{-2}; □) samples doped to $N_D - N_A = 2\times10^{19}$ cm^{-3} and irradiated by the fluence $\Phi_e = 1\times10^{18}$ cm^{-2}.

are mobile, secondary defects may form with the participation of vacancies (for example, divacancies or vacancy–impurity complexes). In the case of silicon carbide, possible types of behavior of the simplest defects are complicated by the presence of two sublattices.

In any case the concentration of stable vacancy-type defects is governed by the number of primary knocked-out (PKO) atoms, which is proportional to the fluence of the high-energy particles employed. The coefficients of proportionality can be calculated for fast electrons, neutrons, and ions.[20] Such calculations were used in Fig. 7 to plot the dependence of the average positron lifetime $\bar{\tau}$ on the relative concentration of the PKO atoms. In the case of xenon ions the values of $\bar{\tau}$ are corrected for the thickness of the damaged layer which exceeds the positron range (for details see Ref. 21). Figure 7 demonstrates the identity of the defect-formation mechanisms in the case of neutrons and ions, on the one hand, and a major difference in the case of fast electrons, on the other. An elastic collision between a fast particle and a crystal atom is accompanied by the transfer of a kinetic energy to the atom, and the average value of this energy $\bar{E}_a$ is very different for light and heavy incident particles. In the case of electrons of energies amounting to several MeV the value of $\bar{E}_A$ is slightly higher than the threshold energy E_d for the displacement of an atom, so that the Frenkel pairs generated by electron bombardment are distributed uniformly throughout a crystal. On the other hand, in the case of fast neutrons and ions we have $\bar{E}_A \gg E_d$, which results in the formation of displacement cascades, which are local regions with a high concentration of the PKO atoms. Within such a region the probability of formation of secondary defects containing vacancies is high.

We shall analyze our experimental data on the positron lifetime in 6H-SiC samples on the basis of these general ideas about the processes of formation and behavior of radiation defects in samples which received different fluences of neutrons, ions, and electrons and were then annealed in a wide range of temperatures.

4.1. Neutron and ion irradiation

In describing the dependence of the average positron lifetime $\bar{\tau}$ on the relative fraction F of PKO atoms in the case

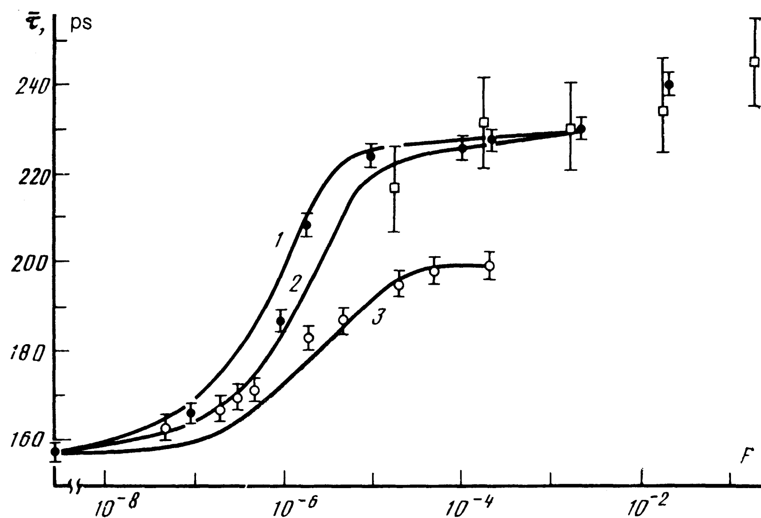

FIG. 7. Dependence of the average positron lifetime $\bar{\tau}$ on the relative concentration of primary knocked-out atoms: ●) neutron irradiation; ○) electron irradiation; □) ion irradiation; 1) curve calculated for $R_k = 20$ Å; 2) curve calculated for $R_k = 30$ Å; 3) curve calculated for $\sigma = 3\times10^{-15}$ cm^2.

of neutron and ion irradiation (Fig. 7), we use the cascade model of defect formation and the diffusion mechanism of positron capture. We assume that if a thermalized positron reaches a cascade region (which is a sphere of radius R_k) by diffusion, it is certain to become localized in defects and becomes annihilated by a process characterized by the lifetime $\tau_d = 225 \pm 3$ ps. If the cascade concentration is N_k, the rate of positron capture by these cascades is

$$k_k=4\pi N_k D R_k, \qquad (1)$$

where D is the positron diffusion coefficient.

The positrons that have escaped capture become annihilated at a rate $\lambda_b = 1/\tau_b$. Consequently, the probability of positron annihilation and defects is $p_k = k_k/(k_k + \lambda_b)$, so that the average lifetime of positrons can be described by

$$\bar{\tau} = p_k\tau_d + (1-p_k)\tau_b. \qquad (2)$$

If the concentration of cascades is not too high, so that the average distance between them is $r \approx 1/N_k^{1/3} \gg R_k$, we can easily demonstrate the validity of the relationship

$$R_k = r(N_d/n_d)^{1/3}, \qquad (3)$$

where n_d and N_d are, respectively, the concentration of defects in a cascade and its average value in the irradiated part of a sample. According to Ref. 23, the concentration of defects in a cascade is independent of the radiation fluence and of the energy of the PKO atom, but is governed exclusively by the parameters of the material

$$n_d = \eta c_V T_m / E_d, \qquad (4)$$

where c_V and T_m are the atomic specific heat and the melting point of the material. The coefficient η allows for the reduction in the concentration of the "surviving defects" (compared with the concentration of PKO atoms) in the case of fast ($\sim 10^{-12}$ s) annealing of the cascade region; it amounts to $\eta \approx 10^{-2}$ (Ref. 24).

Substituting in Eq. (4) the tabulated values of the parameters of SiC taken from Ref. 25 and assuming that E_d amounts to 17–30 eV (Ref. 6), we obtain $n_d \approx 3\times10^{19}$ cm^{-3}. At such high defect concentrations the rate of capture of positrons by the defects ($\sim 8\times10^{10}$ s^{-1}) is much higher than $\lambda_b = 6.4\times10^9$ s^{-1} (for the capture cross section taken from Ref. 15). This is a quantitative confirmation of the above conclusion that the capture of a positron by a cascade implies its preferential annihilation in a defect.

The average concentration of defects in the interior as a function of the relative concentration of the PKO atoms F can be found from $N_d = \eta F N_0$, where $N_0 = 9.6\times10^{22}$ cm^{-3} is the concentration of atoms in SiC.

The room-temperature diffusion coefficient of positrons in SiC can be assumed to be $D \approx 1$ cm^2/s by analogy with some other semiconductors.[26]

We can now calculate the fluence dependence of $\bar{\tau}$ using Eqs. (1)–(4) and employing R_k as the fitting parameter. The calculated curves 1 and 2 in Fig. 7 correspond to values of B_k amounting to 20 and 30 Å, respectively,. We can see that the experimental values obtained for neutrons and ions in the region of rise and saturation of $\bar{\tau}$ lie between these curves. Consequently, the average cascade radius can be estimated to be $R_k = 20$–30 Å. This value is in good agreement with the available experimental data for other semiconductors: in the case of GaAs the optical measurements gave $R_k = 25$ Å (Ref. 27), electron microscopy of Si yielded $R_k = 20$ Å (Ref. 28), whereas the positron method yielded the cascade radius amounting to 15 and 15 Å in n- and p-type Ge, respectively.[31]

We shall follow Refs. 14 and 15 and assume that defects and cascades are divacancies (which implies $\tau_{2V} = \tau_d = 225 \pm 3$ ps). This naturally does not exclude the existence of single vacancies or of their complexes formed with impurity or host interstitial atoms.

4.2. Electron irradiation

An analysis of the fluence dependence of $\bar{\tau}$ carried out for various irradiation temperatures[17] in combination with isochronous annealing curves shows that electron irradiation of n-type SiC samples creates at least two types of vacancy defect. One type of defect, stable up to ~ 150°C, is due to the presence of Frenkel (V–I) pairs. The much more stable defects of the second type should be regarded as complex-

es consisting of a vacancy and a nitrogen impurity atoms, as postulated in Ref. 17. Positrons captured by defects of both types become localized finally in vacancies, where they are annihilated. We can see from Fig. 7 that in the $F \approx 10^{-4}$ range there is saturation in the rise of $\bar{\tau}$, which is clearly due to the capture of practically all the positrons by V–I pairs and vacancy–impurity complexes. Since, according to the results of Ref. 12, the five types of positrons localized at vacancies and at vacancy–impurity complexes are practically identical, the saturation level of $\bar{\tau}$ manifested by curve 3 in Fig. 7 should represent the lifetime of a positron localized at a vacancy, i.e., $\tau_{1V} \approx 200$ ps. It should be pointed out that the numerical value of the ratio $\tau_{1V}/\tau_b \approx 1.27$ is in good agreement with similar values for our semiconductor materials.[11,29,30]

Following Eq. (2), we find that the average lifetime of positrons $\bar{\tau}$ is given by

$$\bar{\tau} = p_V \tau_{1V} + (1 - p_V) \tau_b, \tag{5}$$

where $p_V = k_V/(k_V + \lambda_b)$ is the probability of annihilation in a vacancy.

The kinetic expression for the rate of capture of positrons by defects of two types (labeled by the indices 1 and 2) is[29]

$$k_V = (N_1 \sigma_1 + N_2 \sigma_2) v, \tag{6}$$

where N and σ are the concentration of defects and the positron-capture cross section of the defects; $v \approx 10^7$ cm/s is the velocity of a thermalized positron.

For simplicity, we shall assume that the cross sections σ_1 and σ_2 are the same and equal to σ,and that the sum of the defect concentrations N_1 and N_2 is $N_0 F$, the concentration of the PKO atoms. It then follows from Eq. (6) that the rate of capture is given by

$$k_V = N_0 F \sigma v, \tag{7}$$

which together with Eq. (5) can be used in the calculation of $\bar{\tau}(F)$ by selecting the value of σ,so as to obtain the best description of the experiments. The calculated curve 3 in Fig. 7 corresponds to $\sigma \approx 3 \times 10^{-15}$ cm^{-2} and it describes satisfactorily the experimental results in the range $F \geqslant 10^{-5}$. At lower values of F the experimental points lie well above the calculated curve, indicating a considerable increase in the positron-capture cross section at low defect concentrations ($F \leqslant 10^{-6}$). We can assume that an increase in the concentration of the investigated defects changes the charge state of vacancies which occur in a Fresnel pair or in a complex, for example, in the case of a doubly charged negative Frenkel pair, it becomes singly charged or even neutral. There is a corresponding reduction in the effective radius of the Coulomb attraction of positrons to negatively charged vacancies and, consequently, the positron-capture cross section decreases. The Coulomb nature of the interaction underlying the positron capture is supported by the large value of the estimated capture cross section: even in the range $F \approx 10^{-5}$ it exceeds $\sim 10^{-15}$ cm^2, whereas for $F \leqslant 10^{-6}$, it should be even greater (in the case of a neutral vacancy, e.g., in silicon, we have $\sigma \approx 2 \times 10^{-16}$ cm^{-2}; see Refs. 29 and 30).

4.3. Annealing of irradiated SiC samples

Isochronous annealing of irradiated samples provides additional experimental information on the nature of radiation defects and on their behavior, particularly on the interaction between defects and between them and impurity atoms as the annealing temperature is increased.

1. The low-temperature annealing stage. This stage was observed for electron-irradiated n- and p-type SiC samples (Fig. 5) and samples irradiated with low reactor-neutron fluences ($\Phi_n \leqslant 3 \times 10^{16}$ cm^{-2}, Fig. 4). The results obtained at different electron irradiation temperatures indicated[17] that the low-temperature stage is associated with annealing of genetic Frenkel pairs (i.e., pairs consisting of components generated in one event): an increase in temperature results in recombination of "close" pairs (those separated by short distances between the components), whereas "distant" pairs dissociate into free vacancies V and interstitials I. It is interesting to note that an electron-irradiated p-type sample with a boron impurity concentration $N_A - N_D \approx 5 \times 10^{19}$ cm^{-3} exhibited a narrower stage shifted toward lower temperatures ($\Delta T_a = 100$–250°C, Fig. 5). The value of $\bar{\tau}$ corresponding to the preannealing state was much lower than for n-type samples and low-temperature annealing stored the initial positron lifetime. All this indicated that electron irradiation of p-type samples resulted in the formation of just one type of defect stable at room temperature: Frenkel pairs that were annealed totally at $T_a \approx 250$°C.

It is clear from Fig. 4 that the low-temperature stage was not manifested by the annealing curves of the samples irradiated by neutron fluences ($\Phi_n \geqslant 1 \times 10^{17}$ cm^{-2}). Clearly this was not due to the absence of Frenkel pairs as a result of strong neutron interaction, but to the predominance of the capture of positrons by cascades (and then by divacancies, forming these cascades). In fact, at low neutron fluences when the concentration of cascades was low [and, consequently, the average distance r between the cascades exceeded the positron diffusion length $\Lambda = (D\tau_b)^{1/2}$], the low-temperature stage was manifested by the isochronous annealing curves (Fig. 4).

2. The "negative" annealing stage was observed only for n-type samples with a fairly high dopant concentration ($N_D - N_A \geqslant 1 \times 10^{18}$ cm^{-3}) and irradiated with fairly high fluences ($\Phi_n \geqslant 1 \times 10^{20}$ cm^{-2}, $\Phi_i 5 \times 10^{13}$ cm^{-2}, $\Phi_e \geqslant 1 \times 10^{18}$ cm^{-2}). An increase in the average positron lifetime during this stage yielded a much higher value in the case of neutron or ion irradiation than after electron irradiation. A similar behavior of $\bar{\tau}$ was observed with increasing neutron fluence from 10^{20} to 10^{21} cm^{-2} (Fig. 4). The negative annealing stage was undoubtedly associated with the formation of vacancy clusters in which the lifetime of localized positrons was considerably longer than τ_b, τ_{1V}, or τ_{2V}. A component analysis of the spectra made it possible to distinguish, during the stage of negative annealing of neutron-irradiated samples, a long-lived component with $\tau_2 = 360 \pm 15$ ps and $\tau_2 = 463 \pm 18$ ps for the reactor-neutron fluences of 10^{20} and 10^{21} cm^{-2}, respectively. This in turn made it possible to estimate the dimensions of the resultant clusters: in these two cases they consisted of 5–8 vacancies and more than 20 vacancies. The maximum intensity of the long-lived component indicated that the cluster concentration reached a value of the order of 10^{18} cm^{-3}. Similar parameters were obtained also for the vacancy clusters formed as a result of thermal annealing of SiC samples irradiated with heavy ions.

In the case of the electron-irradiated samples we were

unable to separate the long-lived component in the positron lifetime spectra because of the relatively small increase in $\bar{\tau}$ during the negative annealing stage. Hence, we concluded that the clusters were then smaller or their concentration was lower (or both).

As pointed out already, the negative annealing was not observed for p-type electron-irradiated samples (Fig. 5) and there was no such stage in the case of neutron-irradiated (to a fluence of 1×10^{20} cm^{-2}) p-type SiC crystals. Hence, we concluded that the nitrogen impurity played a fundamental role in the clusterization of vacancy defects. This was supported also by the isochronous annealing curves obtained for n-type electron-irradiated SiC samples doped with nitrogen in various amounts (this is supported by the relevant curves in Fig. 5 and by the results in Ref. 17). It is worth drawing attention to the published information indicating that group V impurities can cause clusterization of vacancies in other semiconductors.[31] It follows from our data that the initial structures necessary for the clusterization process are complexes of vacancies containing group V impurity elements (in our case nitrogen atoms). The existence of complexes of this type can account for the considerable increase in the value of $\bar{\tau}$ above the initial value for an unirradiated crystal, which is observed in the case of n-type electron-irradiated samples after completion of the low-temperature annealing stage (this increase in $\bar{\tau}$ is not exhibited by p-type samples doped with boron to concentrations $N_A - N_D = 5\times10^{19}$ cm^{-3}). Moreover, we demonstrated earlier[17] that there is a critical concentration of complexes ($\sim10^{18}$ cm^{-3}) below which clusterization cannot take place. This critical concentration could be reached if, on the one hand, the doping is sufficiently heavy and, on the other, the radiation fluence is sufficiently high.

It follows that the experimental results given in the present subsection demonstrate convincingly that, in the case of silicon carbide doped with nitrogen to a relatively high concentration and irradiated with a sufficiently high fluence of high-energy particles, there are some critical situations in which the system comprising the host crystal, the impurity, and the radiation-generated vacancies becomes unstable as a result of thermal annealing. This instability gives rise to phase transitions which modify the vacancy subsystem (cause vacancy clusterization).

3. High-temperature stages. At high annealing temperatures ($T_a \geqslant 1200$°C) there are one or two stages of annealing of structure defects governed by the radiation fluence and by the nature of the impurity. In the case of SiC single crystals irradiated with reactor neutrons and ions in low fluences there is only one stage of annealing of defects forming cascades. When the neutron fluence reaches $\sim1\times10^{20}$ cm^{-2}, the high-temperature annealing occurs in two stages and a component analysis of the spectra shows that in the annealing temperature range $\Delta T_a = 1200$–1900°C the lifetime of the long-lived component $\tau_2 \approx 360$ ps remains constant within the limits of experimental error. It is possible that the first high-temperature stage causes annealing of "loose" clusters followed by compact cluster configurations.[15] Irradiation with neutron fluences up to $\sim1\times10^{21}$ cm^{-2} generates vacancy clusters (formed during the negative annealing stage), which are much more stable: they are annealed in one stage in the temperature range $\Delta T_a = 2000$–2300°C. This is a demonstration of a high thermal stability of large vacancy clusters which, as mentioned above, consist of 20 or more vacancies.

In the case of SiC samples subjected to weak electron irradiation the only high-temperature stage is associated with the annealing of vacancy–impurity complexes.[17] In the case of strongly irradiated crystals doped with nitrogen to high concentrations there is a stage of annealing of these complexes and also a stage resulting in dissociation of vacancy clusters. Since the temperature range of this stage is close to the similar annealing stage in the case of neutron- and ion-irradiated samples, we cannot exclude the possibility that the neutron annealing of neutron- and electron-irradiated SiC crystals results in the creation of vacancy clusters of similar sizes, but the concentrations are very different.

5. CONCLUSIONS

The present investigation demonstrates that annealing of silicon carbide samples exposed to high radiation fluences and doped heavily with nitrogen can exhibit critical situations resulting in an instability of the system formed by the host crystal, the impurity, and the radiation-generated vacancies. The development of this instability results in phase transitions, representing formation of vacancy clusters when the size, concentration, and thermal stability of these clusters are functions of the radiation fluence. Such phase transitions, typical of multicomponent systems containing vacancies and impurity atoms, are observed in metals, alloys, and semiconductors.

For example, it is shown in Ref. 32 that when the concentrations of quenching vacancies are the same in Al–Li samples, there is a critical concentration of lithium atoms which ensures that during annealing a negative stage in which vacancy clusters form. In this case the lithium atoms play a role similar to the nitrogen impurity in silicon carbide and the interaction of these atoms with the quenching-generated vacancies gives rise to phase transitions in the aluminum–lithium–vacancy system manifested by clusterization of lithium–vacancy complexes during annealing. It was reported in Ref. 33 that the tellurium dopant concentration is of decisive importance in the behavior of gallium arsenide irradiated with fast electrons. At high tellurium concentrations ($\sim4.5\times10^{18}$ cm^{-3}) there was a negative stage during isochronous annealing. According to our ideas, this stage is due to the formation of vacancy clusters and corresponds to a phase transition in the system formed by gallium arsenide, tellurium, and radiation-generated vacancies.

The development of an instability in a system supersaturated with vacancies by the formation of a new phase (vacancy clusters) has been considered on a number of occasions (see, for example, Refs. 34 and 35). As demonstrated in Ref. 36 and 37 the presence of impurity atoms in the irradiated material can under certain conditions make the interaction in a "gas" of vacancies an attractive effect.

The results obtained demonstrate the usefulness of the positron method in the analysis of radiation of the positron method in the analysis of radiation defects in silicon carbide. When heavy particles (neutrons, ions) are used, the fluence dependences of the average positron lifetime are described well by the cascade defect-formation model. A numerical estimate is obtained of the size of the displacement cascade ($\sim$40–60 Å) formed mainly by clustering of divacancies

with a local concentration of $\sim 3 \times 10^{10}$ cm^{-3}. Irradiation with fast electrons creates Frenkel pairs which are stable up to ~ 150°C, as well as vacancy–impurity complexes. In the case of n-type crystals these complexes act as effective positron-capture centers and they initiate the clusterization processes. In p-type crystals such vacancy–impurity complexes exhibit donor properties (they have a positive charge) and are therefore not detected by the positron method.

It follows that the positron annihilation method allows us to investigate the dynamics of phase transitions in systems with a small order parameter, i.e., in those cases when the formation of a new finely disperse phase consisting of vacancy clusters with dimensions of several angstroms is practically impossible to diagnose by such methods as electron microscopy or x-ray spectroscopy.

[1] J. H. Crawford Jr. and L. M. Slifkin (eds.), *Point Defects in Solids, Vol. 1, General and Ionic Crystals,* Plenum Press, New York (1972); *Vol. 2, Semiconductors and Molecular Crystals,* Plenum Press, New York (1975).

[2] V. V. Emtsev and T. V. Mashovets, *Impurities and Point Defects in Semiconductors* [in Russian], Radio i Svyaz', Moscow (1981), p. 248.

[3] V. S. Vavilov, A. I. Kiv, and O. R. Niyazova, *Mechanisms of Formation and Migration of Defects in Semiconductors* [in Russian], Nauka, Moscow (1980), p. 368.

[4] J. Bourgoin and M. Lannoo, *Point Defects in Semiconductors: II, Experimental Aspects,* Springer Verlag, Berlin (1983) [Springer Series in solid-State Sciences, Vol. 35].

[5] V. L. Vinetskiĭ and G. A. Kholodar', *Radiation Physics of Semiconductors* [in Russian], Naukova Dumka, Kiev (1979), p. 335.

[6] V. S. Vavilov, N. P. Kekelidze, and L. S. Smirnov, *Effects of Radiation on Semiconductors* [in Russian], Nauka, Moscow (1988), p. 106.

[7] S. A. Dobrolezh, S. M. Zubkova, V. A. Kravets, *et al., Silicon Carbide* [in Russian], Kiev (1963), p. 315.

[8] K. L. More, J. Ryu, C. H. Carter Jr. J. Bentley, and R. F. Davis, Cryst. Lattice Defects Amorphous Mater. **12**, 243 (1985).

[9] Y. M. Tairov and Y. A. Vodakov, in: *Electroluminescence* (ed. by J. I. Pankove), Springer Verlag, Berlin (1977), p. 31 [Topics in Applied Physics, Vol. 17].

[10] P. Hautojärvi (ed.), *Positrons in Solids,* Springer Verlag, Berlin (1979) [Topics in Current Physics, Vol. 12].

[11] G. Dlubek and R. Krause, Phys. Status Solidi A **102**, 443 (1987).

[12] S. Dannefaer, Phys. Status Solidi A **102**, 481 (1987).

[13] J. C. Bourgoin, H. J. von Bardeleben, and D. Stievenard, Phys. Status Solidi A **102**, 499 (1987).

[14] A. I. Girka, A. D. Mokrushin, E. N. Mohov, *et al., Proc. Eighth Intern. Conf. on Positron Annihilation* (ed. by L. Dorikens-Vanpraet, M. Dorikens, and D. Segers), World Scientific, Singapore (1989), p. 458.

[15] A. I. Girka, V. A. Kuleshin, A. D. Mokrushin, *et al.,* Fiz. Tekh. Poluprovodn. **23**, 1270 (1989) [Sov. Phys. Semicond. **23**, 790 (1989)].

[16] A. I. Girka, A. Yu. Didyk, A. D. Mokrushin, *et al.,* Pis'ma Zh. Tekh. Fiz. **15**, (12), 24 (1989) [Sov. Tech. Phys. Lett. **15**, 464 (1989)].

[17] A. I. Girka, V. A. Kuleshin, A. D. Mokrushin, *et al.,* Fiz. Tekh. Poluprovodn. **23**, 2159 (1989) [Sov. Phys. Semicond. **23** (1989)].

[18] I. A. Repin, S. V. Svirida, and A. N. Semenikhin, Prib. Tekh. Eksp. No. 6, 28 (1985).

[19] P. Kirkegaard and M. Eldrup, Comput. Phys. Commun. **8**, No. 7, 401 (1974).

[20] G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids,* Interscience, New York (1957).

[21] A. I. Girka, E. B. Klopikov, V. A. Skuratov, and A. V. Shishkin, Fiz. Tekh. Poluprovodn. **23**, 328 (1989) [Sov. Phys. Semicond. **23**, 202 (1989)].

[22] W. Brandt, Appl. Phys. **5**, 1 (1974).

[23] Yu. N. Devyatko, A. A. Makletsov, and A. E. Petrov, Preprint No. 116 [in Russian], Leningrad Electrophysics Institute (1987).

[24] A. A. Makletsov, Author's Abstract of Thesis for Candidate's Degree [in Russian], Salaspils (1989), p. 8.

[25] Proc. Intern. Conf. on Silicon Carbide, University Park, PA, 1968 (ed. by H. K. Henisch and R. Roy), Pergamon Press, Oxford (1969).

[26] H. H. Jorch, K. G. Lynn, and T. McMullen, Phys. Rev. B **30**, 93 (1984).

[27] G. Dlubek, A. Dlubek, R. Krause, and O. Brummer, Phys. Status Solidi A **107**, 111 (1988).

[28] R. F. Konopleva, V. L. Litvinov, and N. A. Ukhin, *Characteristics of Radiation Damage to Semiconductors by High-Energy Particles* [in Russian], Atomizdat, Moscow (1971), p. 176.

[29] S. Dannefaer, G. W. Dean, D. P. Kerr, and B. G. Hogg, Phys. Rev. B **14**, 2709 (1976).

[30] W. Fuhs, U.Holzhauer, F. W. Richter, R. Sturm, and S. Mantl, Phys. Status Solidi B **89**, 69 (1978).

[31] A. K. Pustovoĭt, R. F. Konopleva, A. I. Kupchishin, and K. M. Mukashev, Fiz. Tekh. Poluprovodn. **23**, 257 (1989) [Sov. Phys. Semicond. **23**, 160 (1989)].

[32] H. P. Leighly, P. G. Coleman, and R. N. West, *Proc. Eighth Intern. Conf. on Positron Annihilation* (ed. by L. Dorikens-Vanpraet, M. Dorikens, and D. Segers), World Scientific, Singapore (1989), p. 470.

[33] M. Stucky, C. Corbel, and G. Geffroy, *et al., Proc. Fourteenth Intern. Conf. on Defects in Semiconductors,* Paris, 1986, (ed. by H. F. von Bardeleben), in: Mater. Sci. Forum 10–12, Part II, 265 (1986).

[34] I. M. Lifshits and V. V. Slezov, Zh. Eksp. Teor. Fiz. **35**, 479 (1958) [Sov. Phys. JETP **8**, 331 (1959)].

[35] L. A. Maksimov and A. I.Ryazanov, Radiat. Effects **33**, 1 (1977).

[36] Yu. N. Devyatko and V. N. Tronin, Dokl. Akad. Nauk SSSR **269**, 97 (1983) [Sov. Phys. Dokl. **28**, 259 (1983)].

[37] Yu. N. Devyatko and V. N. Tronin, Fiz. Met. Metalloved. **63**, 635 (1987).

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