Similarities and distinctions of defect production by fast electron and proton irradiation: moderately doped silicon and silicon carbide of n-type

© V.V. Emtsev¶, A.M. Ivanov, V.V. Kozlovski*, A.A. Lebedev, G.A. Oganesyan, N.B. Strokan, G. Wagner+

Ioffe Physicotechnical Institute, Russian Academy of Sciences,
194021 St. Petersburg, Russia
* St. Petersburg State Polytechnic University,
195251 St. Petersburg, Russia
+ Leibniz-Institute for Crystal Growth,
D-12489, Berlin, Germany

(Получена в Редакцию 22 октября 2011 г. Принята к печати 24 ноября 2011 г.)

Effects of irradiation with 0.9 MeV electrons as well as 8 and 15 MeV protons on moderately doped *n*-Si grown by the floating zone (FZ) technique and *n*-SiC $(4H)$ grown by chemical vapor deposition are studied in a comparative way. It has been established that the dominant radiation-produced defects with involvement of V group impurities differ dramatically in electron- and proton-irradiated *n*-Si (FZ), in spite of the opinion on their similarity widespread in literature. This dissimilarity in defect structures is attributed to a marked difference in distributions of primary radiation defects for the both kinds of irradiation. In contrast, DLTS spectra taken on electron- and proton-irradiated *n*-SiC $(4H)$ appear to be similar. However, there are very much pronounced differences in the formation rates of radiation-produced defects. Despite a larger production rate of Frenkel pairs in SiC as compared to that in Si, the removal rates of charge carriers in *n*-SiC $(4H)$ were found to be considerably smaller than those in *n*-Si (FZ) for the both electron and proton irradiation. Comparison between defect production rates in the both materials under electron and proton irradiation is drawn.

1. Introduction

Irradiations of semiconductors with fast electrons at several MeV allow one to get a deeper insight into the nature of intrinsic defects and their interactions with impurities. In this respect, silicon provides an excellent example; see for instance review paper [1]. Irradiation of Si with protons at MeV energies has also be used in defect studies, since it is widely believed that the both ways of defect production are very similar, mostly being distinct in their production rates [2,3]. Actually, this is true for proton irradiation at light doses over a range of $5 \cdot 10^{11} \le \Phi \le 5 \cdot 10^{12}\,\mathrm{cm}^{-2}$. From the other side, there is a pronounced difference in distributions of primary radiation defects produced at random by fast electrons and in cascades by protons. The difference is expected to become important at heavier doses of proton irradiation. However, this dose range has been scantily investigated, except for some optical and positron annihilation experiments on proton-irradiated Si [4,5]. It is clear that the first material to be used in such comparative studies of electrically active defects should be *n*-Si, because our knowledge of radiation-produced effects and defects in electron-irradiated materials can provide a reliable basis for revealing any distinction between two kinds of irradiation. Together with silicon, it could be reasonable to take a look at *n*-SiC, too, because of its prospects for semiconductor electronics [6]. Progress of the chemical-vapor deposition (CVD) technique for this material [7] has substantially improved high-voltage power and high-temperature characteristics of SiC devices, which can successfully replace similar silicon-based devices. Interest in SiC has been expressed for the development of detectors for high-energy nuclear particle detectors capable of prolonged operation in accelerators such as the Large Hadron Collider (LHC, CERN, Switzerland) [8]. Replacement of Si-based devices, in particular detectors, with SiC-based devices requires direct comparative studies on radiation defect production in the both materials. Use of published data for such a comparison is complicated by the fact that the materials studied and irradiation conditions chosen differ greatly in various experiments[9].

There is another point of keen interest while comparing radiation defect production processes in *n*-Si and *n*-SiC with similar concentrations of charge carriers. According to recent papers [10,11], the minimum threshold electron energies at which radiation defects are produced in SiC lie between 240 to 250 keV and 90 to 100 keV on the silicon and carbon sublattices, respectively. It means that the threshold energy for atomic displacement on the silicon sublattice in SiC is coincident well with the known values for silicon itself [12]. In other words, the threshold energies for atomic displacement of Si atoms in the both materials turned out to be close, $E_{\mathrm{th}} = 24$ to 25 eV.

This paper consists of two parts. In the first part electrical properties of *n*-Si and *n*-SiC $(4H)$ irradiated with electron irradiation at $E_e = 0.9$ MeV will be touched on. It is well known that fast electrons at this energy can knock out regular atoms from crystal lattice sites. The average energy imparted to a primary knocked-on atom is about 50 eV. Under these conditions, only point defects, first of all isolated Frenkel pairs, are generated for the most part, with negligibly small formation rates of complex defects, such as divacancies. Isolated Frenkel pairs differ in the distance between their components, i. e. between a self-

¶ E-mail: emtsev@mail.ioffe.ru

interstitial and its parent vacancy. Frenkel pairs, for which the probability of separation into isolated self-interstitials and vacancies upon annealing is markedly lower than the probability of their mutual recombination, commonly named "close" Frenkel pairs.

In the second part of this paper, the same materials are compared on being irradiated with heavier particles, protons at $E_p = 8$ and 15 MeV. In this case, the production of primary radiation defects becomes far more complicated. Radiation defects appear both as a result of direct interactions of impinging protons with lattice atoms as well as in cascades of atomic collisions triggered by high-energy recoil host atoms. It is apparent that under proton irradiation the energies of recoil atoms vary greatly, from several eV to hundreds keV. Energy distributions of recoil atoms can be assessed by numerical simulations.

While studying electrical properties of irradiated *n*-Si and *n*-SiC, it is also important to identify the defects responsible for changes in charge carrier concentration. In this respect, it would be instructive to establish whether the model of radiation defect formation suggested in [13,14] for oxygen-lean *n*-Si grown by the floating zone technique (FZ) and subjected to fast electron irradiation at room temperature, remains valid in the case of proton irradiation, too. This model is based on the predominant formation of electrically active E-centers, the complexes formed by trapping mobile vacancies at V group impurity atoms, in *n*-Si with low concentration of residual oxygen, a few $10^{16}\,\mathrm{cm}^{-3}$ [13,14].[1]

These complexes are deep acceptors at $E_T \approx E_c - 0.4\,\mathrm{eV}$. In this way, the formation of E-centers exerts two effects: a pronounced loss of shallow donor states together with compensation of electron conductivity by the acceptor levels of E-centers.

As to irradiated *n*-SiC $(4H)$, the concentration of charge carriers in this material is known to drop upon irradiation because of the usual compensation of shallow donors due to production of deep acceptor centers [16,17].

2. Experimental

Silicon samples were cut from n-Si wafers. The *n*-Si crystal grown by the floating zone technique was doped with phosphorus in concentrations of $(6-8)\cdot 10^{15}\,\mathrm{cm}^{-3}$. The residual concentration of oxygen did not exceed $5\cdot 10^{16}\,\mathrm{cm}^{-3}$. The thickness of samples for irradiation were of 400 to $900\,\mu$m, taking into account the energy bombarding particles.

The *n*-SiC $(4H)$ epitaxial layers $50\,\mu$m thick were grown in a commercial horizontal hot-wall CVD-system at the Leibniz Institute for Crystal Growth, Berlin, Germany. Commercial SiC (4H) wafers were used as substrates. The electron concentration due to uncompensated donors in these layers, $n = N_D - N_A$, did not exceed $2\cdot 10^{15}\,\mathrm{cm}^{-3}$. Schottky diode structures were fabricated on the grown SiC layers.

Irradiations of the *n*-Si (FZ) and *n*-SiC $(4H)$ with 8 MeV and 15 MeV protons were performed at a MGTs-20 cyclotron at room temperature. The stopping range of 8 MeV protons is $500\,\mu$m in Si and $350\,\mu$m in SiC, whereas this range for 15 MeV protons increases up to $\sim 1500\,\mu$m and $\sim 1000\,\mu$m in Si and SiC, respectively. The sample thickness was chosen to be shorter than the stopping range of the protons used, which eliminated the formation of hydrogen- related complexes. The stopping range of 8 MeV protons in *n*-Si only slightly exceeded the thickness of thin samples investigated and the defect distribution across the sample thickness is expected to be nonuniform. For the other proton-irradiated samples under consideration, this nonuniformity became insignificant. The current density of the incident proton beam was from 10 to 100 nA/cm^2.

The irradiation with 0.9 MeV electrons was carried out with the help of a resonant transformer accelerator on a target cooled with a water stream. The pulse repetition frequency was 490 Hz and the pulse duration was $330\,\mu$s. The stopping range of 0.9 MeV electrons is ~ 1.5 mm in Si and ~ 1.0 mm in SiC. The average current density of the electron beam was 0.5 to $5.0\,\mu$A/cm^2. The distribution of defects introduced by electron irradiation is believed to be uniform throughout the sample volume because the thickness of the Si and SiC samples being irradiated was substantially shorter than the stopping range of the fast electrons.

The concentration of primary radiation defects, i.e. Frenkel pairs, was calculated by the McKinley–Feshbach equation [18] in the case of fast electron irradiation, and by simulating the slowing-down of protons with the aid of the TRIM software [19] in the case of proton irradiation.

The charge carrier concentrations in *n*-Si (FZ) samples prior to and after irradiation were determined using Hall effect measurements in the Van der Pauw geometry. Electrical measurements were taken over a wide temperature interval of 25 to 300 K. In contrast to *n*-Si, the application of ohmic contacts to weakly doped *n*-SiC $(4H)$ presents great difficulties. Because of this, concentrations of uncompensated donors were measured with the help of the capacitance–voltage technique. Such $C-V$ characteristics at frequencies $f = 1$ kHz and 100 kHz were taken at $T = 300$ and 77 K, respectively. Additionally, deep-level transient spectroscopy (DLTS) was employed to determine the energy states associated with radiation defects.

3. Results and discussion

3.1. Electron Irradiation of *n*-Si (FZ)

Fast electron irradiation at MeV energies, the scattering cross-section is nearly independent of energy and can be

[1] A possible competitor to V group impurities in the formation of impurity–vacancy complexes is the oxygen forming oxygen-vacancy pairs, called the A-center. However, its role in moderately doped *n*-Si (FZ) is insignificant, taking into account that at comparable concentrations of P and O the cross-section of A-center formation is by two orders of magnitude smaller than that of E-centers [15].

Table 1. Average and maximum energies of primary knocked-on Si atoms (PKA) under irradiation with fast electrons at various energies. The threshold energy of atomic displacement in Si is taken at $E_{\text{th}} = 25\,\text{eV}$

E_c, MeV	$\langle E_{\text{PKA}}\rangle$, eV	$E_{\max}$, eV	$\nu = \langle E_{\text{PKA}}\rangle / 2E_{\text{th}}$
0.5	37	58	1.0
0.9	51	130	1.0
2	76	460	1.5
2.5	86	666	1.7
4	105	1530	2.1
8	135	5496	2.7

estimated by a simplified McKinley-Feshbach equation [18]:

$$\sigma_d = \frac{2\pi Z^2 e^4}{E_{\text{th}} M c^2}, \tag{1}$$

where c is the speed of light; e is the elementary charge; M and Z are the mass and nuclear charge of a host atom in the target, and E_{th} is the threshold energy for atomic displacement. For silicon, E_{th} was taken to be 25 eV, the value most frequently used in analyses and calculations in the literature [20]. For silicon carbide, comparatively new values of 24 eV and 18 eV were taken on the silicon and carbon sublattices, respectively [10,11].

At these threshold energies, the cross-sections of radiation defect production are 40 barns for silicon and ~ 23 barns for carbon. The production rate of Frenkel pairs η_{FP} is calculated as a product of the cross-section by the concentration of host atoms in the target. Accordingly, the production rate η_{FP} in SiC was obtained as the sum of the partial rates η_{FP} for silicon and carbon atoms. Then, the production rate η_{FP} is $\sim 2\,\text{cm}^{-1}$ for both Si host atoms in Si as well as Si atoms on the silicon sublattice in SiC. On the carbon sublattice in SiC, η_{FP} is equal to $\sim 1\,\text{cm}^{-1}$. It should be noted that the total production rate of Frenkel pairs in SiC on the both sublattices being $\sim 3\,\text{cm}^{-1}$ exceeds the production rate η_{FP} in Si. This is primarily due to the higher concentration of lattice atoms in such a binary compound like SiC, as compared to monoatomic Si.

Let us estimate the average energy received by primary knocked-on atoms (PKA), say, Si atoms, upon a collision with a relativistic electron. As in the case of bombardment with atomic particles, the number of host atoms primarily kicked out by a relativistic electron from their lattice sites is distributed approximately by the inverse-square energy law. In this case, the average energy received by the knocked-on atoms upon a collision with a relativistic electron can be calculated by the equation, derived for the elastic Rutherford scattering [21]:

$$\langle E_{\text{PKA}}\rangle = \frac{E_{\text{th}} E_{\max}}{(E_{\max} - E_{\text{th}})} \ln\left(\frac{E_{\max}}{E_{\text{th}}}\right) \tag{2}$$

where

$$E_{\max} = \frac{2E(E + 2mc^2)}{Mc^2}. \tag{3}$$

Here, m is the electron mass. Table 1 lists the average and maximum energies of recoil silicon atoms in relation to the energy of bombarding electrons. The same table presents the numbers ν of atomic displacements produced by recoil atoms (called the multiplication factor), estimated using the classical Kinchin–Pease equation [22]:

$$\nu = \frac{\langle E_{\text{PKA}}\rangle}{2E_{\text{th}}}. \tag{4}$$

It must be noted that equation (4) is deduced in the belief that the dependence of probability W for atomic displacement of an atom from a crystal lattice site on the received energy E has the form of a step function: $W = 0$ at $E < E_{\text{th}}$ and $W = 1$ at $E \geq E_{\text{th}}$.

It can be seen in Table 1 that for fast electrons at 0.9 MeV the multiplication factor equals 1. However, when comparing the results of this study with published data obtained at fast electron energies exceeding 2 MeV, we take the multiplication factor into account.

Electrical measurements on n-Si samples over a wide temperature range as indicated above made it possible to define temperature dependences of the charge carrier concentration, $n(1/T)$. Fig. 1 shows such $n(1/T)$ curves for the initial and electron-irradiated n-Si (FZ). These curves display a saturation plateau near room temperature, decreasing with increasing irradiation dose. This enables one to determine the rate of charge carrier removal from the conduction band, η_c. In the present study, it was found to be $\eta_c \approx -0.23\,\text{cm}^{-1}$. Taking into account that each E-center removes two electrons from the conduction band the production rate of free vacancies appears to be about $0.1\,\text{cm}^{-1}$, which is in good agreement with the published data [14] earlier obtained on the A-center production in oxygen-rich n-Si. Together with this, the contribution of divacancies to the conductivity compensation in irradiated n-Si can be disregarded, because their formation rate during 0.9 MeV

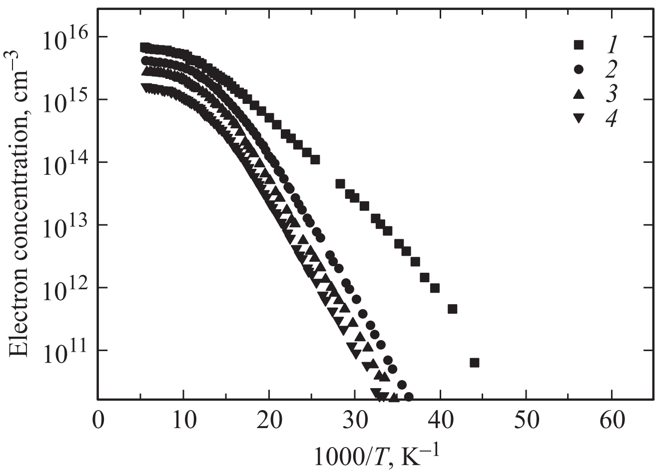

Figure 1. Temperature dependences of the charge carrier concentration in the n-Si:P (FZ) before (curve *1*) and after irradiation with 0.9 MeV electrons (curves *2–4*). Dose Φ, cm^{-2}: *1* — 0, *2* — 10^{16}, *3* — $2 \cdot 10^{16}$, *4* — $3 \cdot 10^{16}$.

electron irradiation is at least an order-of-magnitude lower than the formation rate of E- and A-centers [23].

At the same time, analysis of $n(1/T)$ curves using the relevant equations of charge balance in nondegenerate semiconductors under thermal equilibrium [24] makes it possible to separately determine the total concentration of shallow donor states of phosphorus impurity atoms, N_d, as well as the total concentration of compensating acceptors, N_a, in initial and irradiated materials. This is possible because the exponential part of these $n(1/T)$ curves at cryogenic temperatures defines the compensation ratio $K = N_a/N_d$, whereas a saturation plateau of a $n(1/T)$ curve around room temperature provides another relation $n_{\rm sat} = N_d - N_a$.

In this way, it was demonstrated that a decrease in the charge carrier concentration upon irradiation of moderately doped n-Si (FZ) with 0.9 MeV electrons is well described in the framework of the model with a predominant role of E-centers [13,14]. In actual fact, the data in Fig. 1 used to determine the removal rate of shallow donor states and the production rate of compensating acceptors, $\eta_{\rm SD} \approx -0.12\,{\rm cm}^{-1}$ and $\eta_a \approx +0.11\,{\rm cm}^{-1}$, respectively, point clearly to a 1 : 1 correspondence between them, which is true for the production of E-centers [23].

The removal rate of shallow donor states in n-Si (FZ) due to the E-center formation, $\eta_{\rm SD}$, at early stages of fast electron irradiation can serve as a measure of the production rate of loosely bound Frenkel pairs with widely separated components. Such Frenkel pairs are dissociated into isolated vacancies and self-interstitials at room temperature. As a result, the mobile vacancies are trapped at phosphorus impurity atoms, giving rise to the appearance of E-centers, whereas the mobile self-interstitials form interstitial-type complexes being electrically neutral in n-Si. Therefore, judging from the E-center formation rate one can estimate the production rate of isolated vacancies at $\eta_{\rm FP} = 0.12\,{\rm cm}^{-1}$. In other words, the fraction of separated Frenkel pairs could be about 6% taking into consideration that the production of primary radiation defects in Si during electron irradiation at 0.9 MeV is calculated to be $\eta_{\rm FP} = 2\,{\rm cm}^{-1}$. This lends considerable support to some conservative estimates of [25,26]. The fraction indicated above is thought to be underestimated because of the unknown contribution of mutual annihilation processes of mobile vacancies and self- interstitials as well as their trapping at internal sinks. However, this can be assessed based on the data obtained for heavily doped n-Si. For heavily doped n-Si with $n \approx 10^{19}\,{\rm cm}^{-3}$, in which the average distance between V group impurity atoms is only 30 Å and the trapping of vacancies at V group impurity atoms can be greatly enhanced, the removal rate of charge carriers η_c under irradiation with 1 MeV electrons turned out to be $1.1\,{\rm cm}^{-1}$ [27]. Therefore, the fraction $f_{\rm FP}$ of separated primary defects is equal to 25%, in the belief that the nature of dominating complexes remains the same. Therefore, in moderately doped material about 20% of vacancies liberated from Frenkel pairs can disappear due to mutual annihilation with self-interstitials and trapping at sinks. On the other hand, the fraction $f_{\rm FP}$ in heavily doped n-Si increases to 60%, as the energy of fast electrons is raised to 2.5 MeV [28]. Such an increase in the fraction of separated primary defects under irradiation gives clear evidence that even modest changes in the average energy of primary knocked-on atoms strongly affects the distribution of Frenkel pairs over the distance between their constituent defects, thus enhancing separation into isolated vacancies and self-interstitials.

3.2. Electron Irradiation of *n*-SiC $(4H)$

To determine the removal rate of charge carriers η_e, from the conduction band of n-SiC $(4H)$ under electron irradiation, the capacitance-voltage dependences were replotted as a function of the inverse capacitance $(1/C)$ on the square root of the sum $(U + V_c)$. Here U is the bias voltage and $V_c = 1.5\,{\rm V}$ was taken for the contact potential difference. In these coordinates, the dependences are linear with a slope determined by the space charge density of uncompensated donors $N_d - N_a$. Fig. 2 shows the resulting dependences of $(N_d - N_a)$ on the dose of fast electrons for two samples. A linear decay with the increasing electron dose is clearly observed. The slope of these dependences can be used to assess the removal rate of charge carriers, being $\eta_c \leq 0.1{\rm cm}^{-1}$. The rate η_e obtained for n-SiC $(4H)$ is nearly one half of that for n-Si (FZ) under the same irradiation conditions.

Spectra of deep levels introduced by radiation defects was studied by taking DLTS measurements on the samples prior to and after electron irradiation at a dose of $2.5 \cdot 10^{15}\,{\rm cm}^{-2}$. The main parameters of the deep levels determined in this study are listed in Table 2. Most of the levels are similar to the centers also observed in [29,30]. Based on the total concentration of radiation defects listed in Table 2 their effective production rate close to $\sim 0.13\,{\rm cm}^{-1}$. Of course, DLTS measurements at higher temperatures might have revealed additional radiation- induced deep levels.

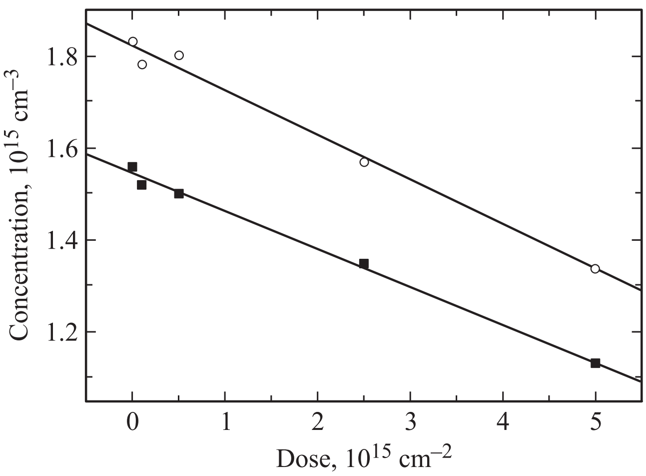

Figure 2. Dose dependences of the uncompensated donor concentration $(N_d - N_a)$ for the 2 n-SiC $(4H)$ samples subjected to irradiation with 0.9 MeV electrons.

Table 2. Energy levels, electron capture cross-sections, and concentrations of deep centers in the *n*-SiC (4*H*) samples before and after irradiation with 0.9 MeV electrons at a dose of $2.5 \cdot 10^{15}\,\mathrm{cm}^{-2}$. The rate of deep center production is $\eta = N/\Phi$, cm^{-1}

Deep centers	E, eV	N, cm^{-3}	σ_n, cm^2	η, cm^{-1}
E0,before irradiation	0.16	$7.0 \cdot 10^{12}$	$9.0 \cdot 10^{-16}$	
E1	0.24	$1.0 \cdot 10^{13}$	$9.0 \cdot 10^{-16}$	0.004
E2	0.30	$4.0 \cdot 10^{13}$	$2.0 \cdot 10^{-16}$	0.016
E3	0.38	$7.5 \cdot 10^{13}$	$1.7 \cdot 10^{-15}$	0.03
E4	0.45	$3.0 \cdot 10^{13}$	$2.0 \cdot 10^{-15}$	0.012
E5	0.52	$8.0 \cdot 10^{13}$	$5.0 \cdot 10^{-16}$	0.032
E6, before irradiation	0.62	$2.3 \cdot 10^{13}$	$1.0 \cdot 10^{-15}$	
E6	0.62	$5.5 \cdot 10^{13}$	$3.0 \cdot 10^{-15}$	0.022
E7	0.75	$4.0 \cdot 10^{13}$	$1.3 \cdot 10^{-14}$	0.016

Again, the effective production rate of deep levels in the irradiated *n*-SiC (4H) can serve as a rough measure of the production rate of Frenkel pairs separated into isolated components. The production rate of such Frenkel pairs estimated at $0.1\,\mathrm{cm}^{-1}$ is approximately 3% relative to the calculated production rate of all Frenkel pairs in SiC irradiated with 0.9 MeV electrons, being $\eta_{\mathrm{FP}} \sim 3\,\mathrm{cm}^{-1}$. Generally speaking, this value can be considered as a lower limit taking into account possible contributions of mutual annihilation and trapping of mobile intrinsic defects, similarly to the case of moderately doped *n*-Si (FZ). Interestingly, this fraction f_{FP} for *n*-SiC (4*H*) turned out to be only a half of that found for the electron-irradiated *n*-Si (FZ). As the energy of fast electrons is raised to 6 [17] and 8.2 MeV [29,30], the fraction f_{FP} of separated primary defects in *n*-SiC goes up to 25% [29,30]. Such an increase of f_{FP} in SiC under electron irradiation can be interpreted in a way similar to the irradiated *n*-Si (FZ); see above.

3.3. Proton Irradiation of *n*-Si (FZ)

Fig. 3 displays the temperature dependences of the charge carrier concentration, $n(1/T)$, for the *n*-Si (FZ) prior to and after irradiation with 15 MeV protons. The $n(1/T)$ curves feature saturation plateaus lowering with the increasing irradiation dose which makes it possible to determine the removal rate of charge carriers from the conduction band under proton irradiation. Under our conditions, the removal rates η_e were found to be 120 and $190\,\mathrm{cm}^{-1}$ for 15 and 8 MeV proton irradiation, respectively.

It should be noted that the removal rates of charge carriers η_e are also indicated in earlier radiation experiments on *n*-type silicon lightly irradiated with protons at doses $\Phi \ll 10^{13}\,\mathrm{cm}^{-2}$ [31]. However, changes in the concentration of shallow donor states due to defect interactions in irradiated materials were not investigated at that time. This was done in the present work making use of analysis of $n(1/T)$ curves for separate estimates of N_d and N_a in initial and proton-irradiated materials. Similar to the case of fast electron irradiation, it was found that the concentration of charge carriers in the proton-irradiated *n*-Si (FZ) drops in the course of proton irradiation due to two processes: (i) a decrease in the concentration of shallow donor states of phosphorus impurity atoms and (ii) an increase in the concentration of radiation-produced acceptors. Contrary to the case of fast electron irradiation of *n*-Si (FZ), the loss of shallow donor states turned out to be much larger than the increase in the acceptor concentration. For these processes at the beginning of irradiation with protons at $E_p = 15$ MeV, we found that the removal rate of shallow donor states was $\eta_{\mathrm{SD}} \approx -80\,\mathrm{cm}^{-1}$, whereas the production rate of compensating acceptors was $\eta_a \approx +40\,\mathrm{cm}^{-1}$. It can be seen that the removal rate of charge carriers $|\eta_e| = |\eta_{\mathrm{SD}}| + \eta_a \approx 120\,\mathrm{cm}^{-1}$ is the sum of two unequal terms. It means that the model of compensation of shallow donors by deep acceptor states due to E-centers and divacancies, adopted earlier in literature [32,33] must be replaced by another model with a modified reaction path leading to effective "deactivation" of shallow donors in proton-irradiated *n*-Si (FZ). It should be recalled that for the same material irradiated with fast electrons the model of E-center formation was shown to be absolutely adequate for describing the observed radiation degradation of electrical parameters; see above. It is thought that the observed difference of the defect formation in proton- vs electron-irradiated materials is associated with the probability of successive capture of vacancies by V group impurity atoms: in the case of fast electron irradiation mobile vacancies are produced uniformly in the bulk, whereas in the case of proton irradiation they are primarily produced in cascades. As a result of a non-uniform spatial distribution of vacancies in the latter case the formation of multi-vacancy complexes may be enhanced. We believe that the most probable

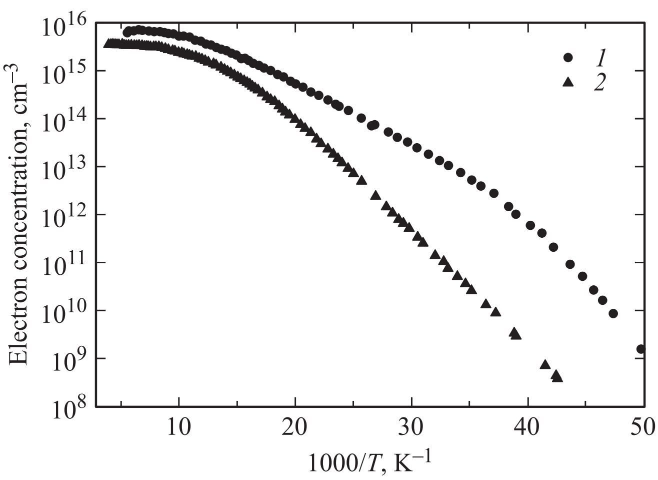

Figure 3. Temperature dependences of the charge carrier concentration in the *n*-Si:P (FZ) before (curve *1*) and after irradiation with 15 MeV protons (curves *2*). Dose Φ, cm^{-2}: *1* — 0, *2* — $4 \cdot 10^{13}$.

candidate in proton- irradiated n-Si (FZ) can be a complex containing a phosphorus atom tied to two vacancies $[PVV]$ or $[VPV]$. What is more, this complex should be a deep donor, not seen in the n-type material by our electrical measurements when the Fermi level is shifted from $E_c - 0.21$ eV to $E_c - 0.28$ eV due to proton irradiation. It should be noted that DLTS measurements revealed deep donor centers at $\sim E_c - 0.30$ eV in proton-irradiated n-Si [34]. Earlier it was believed that similar complexes may be formed in electron-irradiated n-Si, too [35].

3.4. Proton Irradiation of n-SiC $(4H)$

$C-V$ and DLTS measurements on proton-irradiated n-SiC $(4H)$ samples were similar to those carried out in the case of electron irradiation. The temperature in DLTS experiments did not exceed 560 K (Fig. 4), which was sufficient for detecting levels with depths down to 1.1 eV

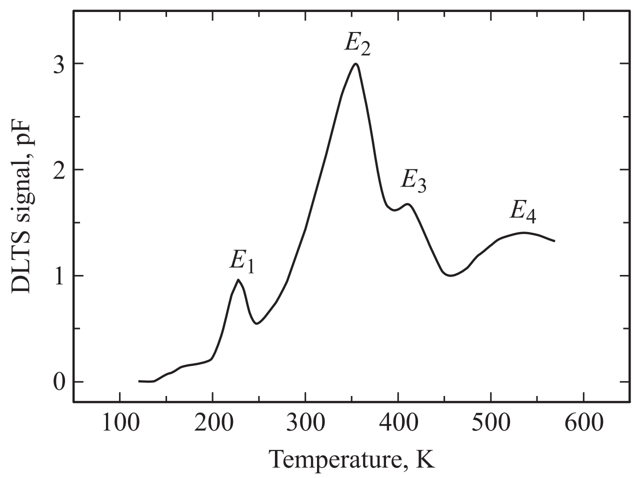

Figure 4. DLTS spectrum for the n-SiC $(4H)$ irradiated with 8 MeV protons at a dose Φ of $6 \cdot 10^{11}$ cm^{-2}.

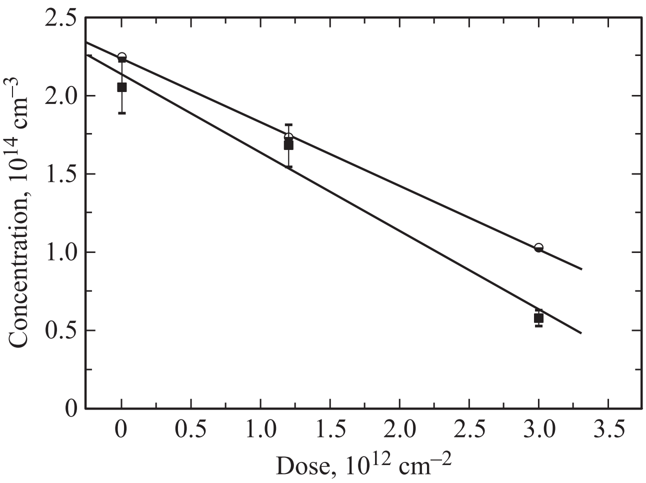

Figure 5. Dose dependences of the charge carrier concentration for the two n-SiC $(4H)$ samples subjected to irradiation with 15 MeV protons.

Table 3. Energy levels, electron capture cross-sections, and concentrations of deep centers in the n-SiC $(4H)$ samples after irradiation with 15 MeV protons at a dose of $6 \cdot 10^{11}$ cm^{-2}.

	E_e, eV	σ_n, cm^2	N, cm^{-3}
E1	0.39	$0.9 \cdot 10^{-16}$	$8 \cdot 10^{12}$
E2	0.62	$1.7 \cdot 10^{-15}$	$3.5 \cdot 10^{13}$
E3	0.72	$3 \cdot 10^{-15}$	$1.6 \cdot 10^{13}$
E4	1.08	$5.6 \cdot 10^{-13}$	$1.1 \cdot 10^{13}$

from the conduction band. The DLTS spectra of samples irradiated with 8 MeV and 15 MeV protons turned out to be identical. As an example, Table 3 lists some important parameters of dominant deep centers in the samples irradiated with 15 MeV protons. A comparison of deep defects in the proton- and electron-irradiated n-SiC $(4H)$ given in Tables 2 and 3 has revealed the presence of two similar radiation-produced centers at $E_c - 0.39$ eV and $E_c - 0.62$ eV, labeled $EH1$ and $Z1/Z2$ centers [29,30], respectively. Other deep centers are characteristic for one kind of irradiation only. From our capacitance-voltage measurements one can assess the charge carrier removal rates in n-SiC $(4H)$ $\eta_e \approx 110$ and 45 cm^{-1} at proton energies of 8 and 15 MeV, respectively (see Fig. 5). The fact that the removal rate becomes lower with the increasing proton energy is primarily due to a substantial decrease in the cross-section of primary defect production by more energetic protons. It was noted that lowering the measurement temperature to 77 K leads to a pronounced increase in η_e. This correlation with the data of [12] confirms that the main process responsible for the removal of charge carriers in proton-irradiated n-SiC $(4H)$ is the introduction of compensating acceptors [17,36], rather than „deactivation" of donor impurity atoms due to interactions with mobile intrinsic defects, like vacancies and self-interstitials [16,37].

To determine the general pattern of radiation defect formation in both semiconductors, we numerically simulated the scattering of 8 and 15 MeV protons by using the TRIM software [19]. By way of illustration, Table 4 gives the number of vacancies produced on each sublattice by the protons and recoil atoms, separately in primary and secondary collisions. In the latter case, silicon and carbon atoms can be dislodged from their lattice sites by recoil atoms of any nature (equally by Si and C). The last column allows one to calculate the total number of vacancies produced by one proton in SiC films 50 μ thick.

As is seen in this table, the total numbers of vacancies are 2.69 and 1.46 at proton energies of 8 and 15 MeV, respectively. It should be noted that the analysis is based on the statistics of twenty thousand protons incident onto the film. The data in Table 4 are in good agreement with Rutherford scattering laws.

To explain the observed difference of DLTS spectra obtained upon electron and proton irradiation of n-SiC $(4H)$, it is necessary to consider the amount of energy

Table 4. Number of vacancies produced per one proton in „thin“ SiC films 50 μm in thickness due to primary and secondary collisions

Proton energy, MeV	Sublattice	Vacancies produced due to primary collisions with a proton	Vacancies produced due to secondary collisions with recoil atoms	Total number of vacancies on the sublattice
8	Si	0.69	1.10	1.79
	C	0.18	0.72	0.90
15	Si	0.37	0.61	0.98
	C	0.09	0.39	0.48

Table 5. Total energy imparted by protons to silicon atoms in SiC films due to primary collisions. The cases of the imparted energies below and above 130 eV are distinguished

Proton energy	Low-energy range range, ≤ 130 eV	High-energy range, > 130 eV	Average energy in high-energy range per one Si atom
	Total energy transferred to the Si atoms		
8 MeV	15.97 keV in 320 events	67.24 keV in 80 events	0.84 keV
15 MeV	16.59 keV in 325 events	75.15 keV in 75 events	1.0 keV

imparted to recoil atoms. For this purpose we plotted some histograms of the energy received by silicon and carbon atoms in collisions with protons, based on our TRIM calculations. The majority of scattering events are associated with transfer of small portions of energy. Let us discuss the energy spectrum of recoil silicon atoms upon scattering of 15 MeV protons on the Si sublattice (see Fig. 6). Here one takes into account only collisions associated with the vacancy production when the energy transferred exceed the threshold energy for atomic displacement. The total number of collisions was 400, which, in our opinion, is sufficient for revealing the general pattern. The scale in Fig. 6 is limited to a recoil energy of 300 eV for covering the energy range typical for electron irradiation at 0.9 MeV. Actually, in the latter case their characteristic energies are $E_{\text{av}} = 51$ eV and $E_{\max} = 130$ eV (see Table 1). The events with large energy portions transferred, up to tens eV, fall outside the range in Fig. 6. Such events are discussed below.

Let us consider two energy ranges of recoil atoms, less than 130 eV and greater than 130 eV, by convention labeled a „low-energy“ and „high-energy“ range, respectively (see second and third columns in Table 5). Reasoning from Table 5 one can arrive to an important conclusion regarding the comparison of events in which MeV electrons and protons are scattered on Si atoms. For simplicity, let us assign an average energy of 1.0 keV to all the collisions in which an energy exceeding 130 eV is transferred to Si atoms. In doing so, the real histogram for 400 events of scattering is replaced by two components, the first one including 325 events when the average energy of knocked-on atoms is 51 eV and another one including 75 events when the average energy of knocked-on atoms is 1 keV; see the upper inset in Fig. 6. The first component appears to be similar in its effectiveness to MeV electrons, whereas the second component is characteristic for MeV protons only. Our calculations demonstrated that a Si atom at an energy of 1.0 keV creates 13.32 vacancies. These vacancies are produced in a microscopically small volume covered by a 1 keV recoil Si atom. As a rough estimate, this volume can be defined as R^3 where $R = 24$ Å, which is the stopping range of such atoms. The appearance of regions with high concentration of primary radiation defects in proton-irradiated material differs greatly from the situation under

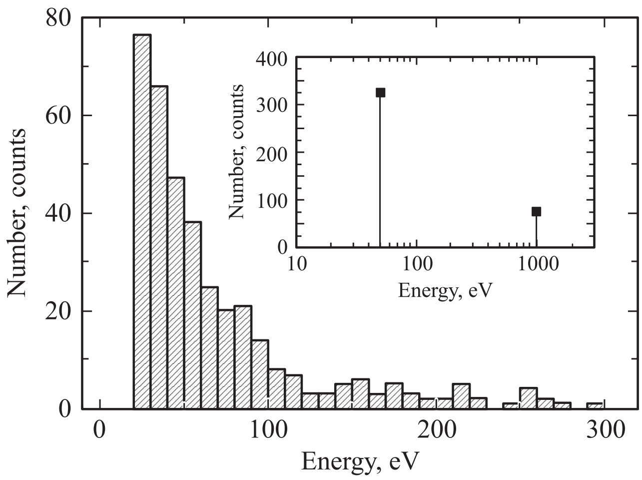

Figure 6. Low-energy part of the histogram of primary knocked-on Si atoms during irradiation of SiC with 15 MeV protons, obtained by calculations using the TRIM software [19]. By way of illustration, the upper inset shows an effective substitution for the real histogram of scattering of 15 MeV protons on the Si sublattice in SiC (see in text).

Table 6. Production rates of primary radiation defects (η_{FP}) and removal rates of charge carriers (η_e) in the n-Si (FZ) and n-SiC ($4H$) under irradiation with protons and fast electrons. The η_{FP} rates are calculated for the samples studied, with $d_{Si} = 400\,\mu$m and $d_{SiC} = 50\,\mu$m in thickness. The η_e rates are measured.

Irradiation		n-Si(FZ)	n-SiC ($4H$)
0.9 MeV electrons	η_{FP}, cm^{-1}	2.0	3.0
	η_e, cm^{-1}	0.23	0.1
8 MeV protons	η_{FP}, cm^{-1}	500	540
	η_e, cm^{-1}	190	110
15 MeV	η_{FP}, cm^{-1}	190	290
	η_e, cm^{-1}	120	45

fast electron irradiation when they are produced randomly in the bulk; see also above. Table 6 shows the calculated production rates of Frenkel pairs η_{FP} compared to the removal rates of charge carriers η_e experimentally measured in electron- and proton- irradiated n-Si (FZ) and n-SiC ($4H$).

As is seen in Table 6, the production rate of Frenkel pairs η_{FP} in n-SiC ($4H$) exceeds the similar rates in n-Si (FZ) under both proton and electron irradiation. Under proton irradiation, the values of η_{FP} for n-SiC ($4H$) and n-Si (FZ) are affected not only by the difference in the scattering cross-sections (e.g., 2400 barns for Si and 1400 barns for SiC at a proton energy of $E_p = 8$ MeV) but also by the numbers of secondary displacements of lattice atoms in recoil events. Our calculations demonstrated that the fractions of primary radiation defects produced on the Si and C sublattices due to direct interactions with protons at 8 MeV are only 40 and 20%, respectively, whereas the larger fractions, 60% and 80%, correspondingly, are related to cascades. The average energies imparted to silicon and carbon atoms in collisions with a 15 MeV proton are 228 and 147 eV, respectively; cf E_{th}, the relevant threshold energies for atomic displacement. It should be noted that in the case of electron irradiation at $E_e = 0.9$ MeV the average energies are lower by three to four times, 51 and 55 eV, correspondingly. Our calculations showed that upon irradiation of a $400\,\mu$m thick silicon sample, arbitrarily called a „thick“ sample, with 8 MeV protons the average calculated rate η_{FP} is 500 cm^{-1}. At the same time, upon irradiation of a $50\,\mu$m thick SiC sample, arbitrarily called a „thin“ sample, with protons at the same energy the calculated rates η_{FP} are 360 and 180 cm^{-1} on the silicon and carbon sublattices, respectively, giving the total rate $\eta_{FP} = 540$ cm^{-1}. As the proton energy is raised to 15 MeV, η_{FP} decreases with an inverse proportion to energy, down to 290 cm^{-1} for SiC.

Comparison of the calculated and experimental data in Table 6 indicates that the fraction of primary radiation defects revealing their presence in irradiated n-Si (FZ) and n-SiC ($4H$) via interactions with shallow donors and/or compensation of shallow donor states by radiation- induced deep acceptors is only several per cent relative to the total number of Frenkel pairs produced under both electron and proton irradiation. Besides, this fraction in irradiated n-Si (FZ) turned out to be considerably larger than that in irradiated n-SiC ($4H$). These results dispel some of the doubts expressed in studies devoted to ion implantation of helium and boron into SiC [37–39], where SiC was claimed to be less resistant to radiation damage than Si. It should also be noted that the degradation rate of another important parameter η_τ, based on the lifetime of minority charge carriers governed by the concentration of recombination centers of radiation origin, is considerably lower in irradiated n-SiC, as compared to irradiated n-Si[40].

4. Conclusions

A direct comparison of defect production in moderately doped n-Si (FZ) and n-SiC ($4H$) under fast electron and proton irradiation was performed in this work. It was determined that under irradiation with protons and fast electrons the removal rates of charge carriers η_e in n-SiC ($4H$) are approximately one half of those observed in irradiated n-Si (FZ). It has been established that the well-known model of E-center formation in electron-irradiated n-Si (FZ) appears to be inadequate for understanding the radiation defect formation in the same material subjected to proton irradiation. In the latter case, losses of shallow donor states due to interactions with intrinsic point defects turned out to be a decisive factor in the removal of charge carriers, whereas the formation of compensating acceptors of radiation origin plays a subsidiary role.

The observed difference between radiation defect formation under fast electron and proton irradiation should be attributed to a marked difference in vacancy production conditions. An analysis of histograms of the energy of recoil atoms under proton irradiation showed that, together with isolated Frenkel pairs, microscopic regions with high densities of primary defects (vacancies) make their appearance. As a result, multi-vacancy complexes can be formed in these regions. It is suggested that under these conditions the E-centers can trap additional vacancies, giving rise to the appearance of group-V atom — two vacancy complexes with deep donor states. This is in sharp contrast to the situation under fast electron irradiation, where primary defects are produced uniformly in the bulk and the formation of such defects has not been reported.

Comparing the removal rates of charge carriers and the production rate of primary defects for n-Si (FZ) and n-SiC ($4H$), it is possible to roughly estimate the fraction of separated Frenkel pairs whose isolated constituent defects, i.e. vacancies and self-interstitials, are taking part in interactions with shallow donor impurities and/or their usual compensation. Taking into consideration that the fractions of Frenkel pairs separated into isolated components under proton irradiation of the both semiconductor materials exceed greatly those observed under fast electron irradiation, high-energy protons can be used for the formation of local high- resistivity regions in Si- and SiC-based devices.

References

[1] G.D. Watkins. In: *Materials Science and Technology*, ed. by R.W. Cahn, P. Haasen, E.J. Kramer (WILEY–VCH Verlag GmbH & Co.KGaA, Weinheim, 2005) vol. 4/5, p. 105.
[2] В.С. Вавилов, Н.Ю. Исаев, Б.Н. Мукашев, А.В. Спицын. ФТП, **6** (6), 1041 (1972).
[3] L.C. Kimerling, P. Blood, W.M. Gibson. In: *Defects and Radiation Effects in Semiconductors*, 1978 edited by Conf. Ser. No 46 (The Institute of Physics, Bristol and London, 1979) p. 273.
[4] S. Makinen, H. Rajainmaki, S. Linderoth. Phys. Rev. B, **42**, 11 166 (1990).
[5] G. Davies, S. Hayama, L. Murin, R. Krause-Rehberg, V. Bondarenko, A. Sengupta, C. Davia, A. Karpenko. Phys. Rev. B, **73**, 165 202 (2006).
[6] J.B. Casady, R.W. Johnson, Sol. St. Electron, **39**, 1409 (1996).
[7] S. Nishino, J. Powell, N.A. Will, Appl.Phys.Lett., **42**, 460 (1983).
[8] G. Lindstrom, M. Moll, E. Fretwurst, Nucl. Instrum. Meth. A, **426**, 1 (1999).
[9] V. Kozlovski, V. Abrosimova. *Radiation Defect Engineering* (World Scientific, 2005).
[10] J.W. Steeds, F. Carosella, G.A. Evans, M.M. Ismail, L.R. Danks, W. Voegeli. Mater. Sci. Forum, **353**–**356**, 381 (2001).
[11] J.W. Steeds, G.A. Evans, S. Furkert, M.M. Ismail, L.R. Danks, W. Voegeli, F. Carosella. Diamond Relat. Mater.,**11**, 1923 (2002).
[12] J.W. Corbett, J.C. Bourgoin. In: *Point Defects in Solids*, vol. 2. Semiconductors and Molecular Crystals, ed.by J.H. Crawford, L.M. Slifkin (Plenum Press, London–N.Y., 1975) p. 84.
[13] E.L. Elkin, G.D. Watkins. Phys. Rev., **174**, 881 (1968).
[14] G.D. Watkins, J.W. Corbett. Phys. Rev., **134**, A1359 (1964).
[15] M. Huhtinen. Nucl. Instrum. Meth. A, **491**, 194 (2002).
[16] A.A. Lebedev, A.I. Veinger, V.V. Kozlovski, D.V. Davydov, N.S. Savkina, A.M. Strelchuk, J.Appl.Phys. **88**, 6265 (2000).
[17] M. Mikelsen, U. Grossner, J.H. Bleka, E.V. Monakhov, B.G. Svensson, R. Yakimova, A. Henry, E. Janzen, A.A. Lebedev, Mater. Sci. Forum **600**–**603**, 425 (2009).
[18] W.A. MacKinley, H. Feshbach, Phys.Rev., **74**, 1759 (1948).
[19] J.F. Ziegler, J.P. Biersack, U. Littmark. *The Stopping and Range of Ions in Solids* (Pergamon, N.Y., 1985).
[20] E. Holmstrom, A. Kuronen, K. Nordlund, Phys. Rev. B, **78**, 045 202 (2008).
[21] G.J. Dienes, G.H. Vineyard. *Radiation Effects in Solids* (Interscience Publishers, N.Y., 1957), p. 12.
[22] G.H. Kinchin, R.S. Pease. Rep.Progr. Phys., **18**, 1 (1955).
[23] J.W. Corbett, G.D. Watkins. Phys. Rev. **138**, A555 (1965).
[24] J.S. Blakemore, *Semiconductor Statistics* (Pergamon Press, N.Y., 1962).
[25] J.M. Poate, J.S. Williams. In: Ion Implantation and Beam Processing, ed. by J.S. Williams, J.M. Poate (Academic, Sydney, 1984) p. 13.
[26] B.G. Svensson, C. Jagadish, A. Hallen, J. Lalita, Phys.Rev.B, **55**, 10 498 (1977).
[27] L.L. Sivo, E.E. Klontz. Phys.Rev., **178**, 1264 (1969).
[28] V.V. Emtsev, P. Ehrhart, K.V. Emtsev, D.S. Poloskin, U. Dedek. Physica B, **376**–**377**, 173 (2006).
[29] A. Castaldini, A. Cavallini, L. Rigutti, F. Nava, Appl. Phys. Lett., **85**, 3780 (2004).
[30] A. Castaldini, A. Cavallini, L. Rigutti, F. Nava, S. Ferrero, F. Giorgis. J. Appl. Phys., **98**, 053 706 (2005).
[31] Yu.V. Bulgakov, T.I. Kolomenskaya. Sov. Phys. Semicond. (AIP), **1**, 422 (1967).
[32] H. Kauppinen, C. Corbel, K. Skog, K. Saarinen, T. Laine, P. Hautojarvi, P. Desgardin, E. Ntsoenzok. Phys.Rev. B, **55**, 9598 (1997).
[33] W. Wondrak, K. Bethge, D. Silber. J. Appl. Phys. **62**, 3464 (1987).
[34] L. Palmetshofer, J. Reisinger. J. Appl. Phys. **72**, 2167 (1992).
[35] T. Wada, K. Yasuda, S. Ikuta, M. Takeda, H. Masuda. J. Appl. Phys., **48**, 2145 (1977).
[36] H.J. von Bardeleben, J.L. Cantin, I. Vickridge, G. Battistig. Phys. Rev. B, **62**, 10 126 (2000).
[37] D. Aberg, A. Hallen, P. Pellegrino, B.G. Svensson. Appl. Surf. Sci., 184, 263 (2001).
[38] B.G. Svensson, A. Hallen, M.K. Linnarsson, A.Yu. Kuznetsov, M.S. Janson, D. Aberg, J. Osterman, P.O.A. Persson, L. Hultman, L. Storasta, F.H.C. Carlsson, J.P. Bergman, C. Jagadish, E. Morvan. Mater. Sci. Forum, **353**–**356**, 549 (2001).
[39] A. Hallen, A. Henry, P. Pellegrino, B.G. Svensson, D. Aberg. Mater. Sci. Eng. B, **61**–**62**, 378 (1999).
[1] A.L. Barry, B. Lehmann, D. Frish, D. Braunig. IEEE Trans. Nucl. Sci., **38**, 1111 (1991).

Редактор Т.А. Полянская