Физика и техника полупроводников, 2007, том 41, вып. 4

Structural peculiarities of 4*H*-SiC irradiated by Bi ions

© E.V. Kalinina[¶], V.A. Skuratov, A.A. Sitnikova, E.V. Kolesnikova, A.S.Tregubova, M.P. Scheglov*

Ioffe Physicotechnical Institute, Russian Academy of Sciences,
194021 St. Petersburg, Russia
* Joint Institute for Nuclear Research,
141980 Dubna, Russia

(Получена 12 сентября 2006 г. Принята к печати 3 октября 2006 г.)

X-ray diffraction, photoluminescence, micro-cathodoluminescence, scanning and transmission electron spectroscopy were used to study the 710 MeV Bi ion irradiation effect in fluence range of $1.4 \cdot 10^9 - 5 \cdot 10^{13}\,\text{cm}^{-2}$ on the structural and optical characteristics of pure high-resistivity *n*-type 4*H*-SiC epitaxial layers grown by chemical vapor deposition. It was established that the distribution of structural damages along the ion trajectory follows the computed profile of radiation defects formed in elastic collisions. The high density ionization effect on the material characteristics has not been found under the irradiation conditions used. Optical methods revealed a wide spectrum of radiation-induced defects, with some of them contributing to the recombination process. The damaged 4*H*-SiC crystal lattice party recovers after annealing at the temperature of 500°C.

PACS: 61.82.Fk, 71.55.Ht, 78.60.Hk, 78.66.Li, 81.65.-b

1. Introduction

Silicon carbide is one of the most radiation-resistant semiconductors and is attractive for the use in harsh environments, including strong radiation, high temperature and chamical activity. SiC finds application in space electronics, various nuclear-power setups, in control of dissionable materials, and as perspective material for inert matrix fuel host. Moreover, long-time radiation control detectors are required to make physical experiments with intensive radiation, which are being planned for the next generation of accelerators such as Large Hadron Collider and its modification SLHC in European Organization for Nuclear Research (CERN). Considering possible wide use of such radiation-resistant equipment, it is necessary to study in detail the effect of various high-energy particles on structural, electrical and optical properties of silicon carbide.

The results of numerous experiments shown that electron, proton, and neutron irradiation leads to similar kind of radiation damage and change in the SiC structure (see, e.g, [1–4]). In contrast to such conventional radiation, the effect of high-energy heavy ions on SiC properties has not been studied in detail yet. At the same time the study of the mechanism of defect formation in SiC subjected to irradiation by heavy ions with mass and energy more then 80 and 100 MeV, respectively, is great interest for simulation of structural damage induced by fission fragments. Under the condition of high and superhigh ionization energy loss and the high rate of generation of radiation defects, there is possibility of point and extended radiation defects formation, as well as latent tracks.

The first studies of structural, optical and electrical properties of *n*- and *p*-6*H*-SiC crystals irradiated by high-energy heavy ions were carried out using Xe ions with the energy of 124 MeV [5,6] and 5.5 GeV [7,8]. It was concluded that xenon ions created radiation defects, which were similar to those induced by light particls. For example, formation of point defects, which due to their high mobility, especially under annealing, easily formed extended defects, such us divacancies and their complexes, was observed. These defects were produced via elastic scattering. Any specific lattice damage, which could be associated with electronic stopping, was not observed up to specific ionization loss level of Se = 21.9 keV/nm. Similar conclusion was done when *n*-6*H*-SiC crystals were irradiated by I ions with energy of 72 MeV [9] and by Kr ions with the energy of 246 MeV [10]. The absence of latent tracks at Se = 34 keV/nm was noted in the first works on irradiation of *n*-6*H*-SiC crystals by 710 MeV Bi ions, which shows high radiation resistance of SiC [11]. Further optical and electro-physical studies of defect formation in high-purity high-resistivity *n*-6*H*-SiC CVD epitaxial layers irradiated by Bi ions with 710 MeV energy in $10^9 - 5 \cdot 10^{10}\,\text{cm}^{-2}$ fluence range, made it possible to reveal the formation of a wide spectrum of radiation defects. Their parameters were similar to those of defects, which occurred in SiC subjected to irradiation by electrons, neutrons and light ions [12,13]. In addition, it was shown that heating of irradiated samples up to 500°C led to partial recovert of the characteristics of the device structures, which had degraded after irradiation by Bi ions [13].

The aim of this work is to study structural and luminescence characteristics of pure *n*-4*H*-SiC CVD epitaxial layers subjected to irradiation by high-energy Bi ions followed by post-irradiation thermal treatment. Such experiments allow for revealing the contribution of radiation defects to recombination processes, which take place in irradiated epitaxial layers and device structures based on them.

2. Experiment

The 26 μm thick 4*H*-SiC epitaxial layers with concentration of uncompensated donors $10^{15}\,\text{cm}^{-3}$ were grown CVD on commercial 4*H*-SiC wafers with

---

[¶] E-mail: evk@pop.ioffe.rssi.ru
Fax: +7(812)2976425

$N_\mathrm{d} - N_\mathrm{a} \approx 10^{19}\,\mathrm{cm}^{-3}$. Before the growth of the CVD layers, thin $(\sim 0.1\,\mu\mathrm{m})n^+$-4*H*-SiC layers with $N_\mathrm{d} - N_\mathrm{a} = 10^{19}\,\mathrm{cm}^{-3}$ were grown on the substrates using liquid-phase epitaxy (LPE). The substrates and the structures with epitaxial layers were irradiated along the *c* axis by 710 MeV Bi ions with fluence ranging from $1.4 \cdot 10^9$ up to $10^{13}\,\mathrm{cm}^{-2}$.

The thickness of the LPE and CVD epitaxial layers, as well as their structure before and after irradiation were determined on freshly cleaved adges of the samples in a scanning electron microscope (SEM) with the beam energy of 20 keV. Structural characteristics of the n^+-4*H*-SiC substrates and the epitaxial layers before and after irradiation were studied using X-ray topography (XRT) and X-ray diffractrometry (XRD). The topograms were taken using Cu$K\alpha1$ radiation in (1128) reflection, where the thickness of the layer, with formed reflection of structural defects, was $\sim 25\,\mu$m. Diffraction curves were recorded in double-crystal mode using Cu$K\alpha1$ irradiation for two symmetrical reflections (0004) and (0008), where estimated depth of reflected beam formation was $\sim 5\,\mu$m and $\sim 25\,\mu$m, respectively. Distribution of radiation-induced defects along the track of implanted Bi ions, as well as the structure and transformation of the defects during annealing, was studied with the use of transmission electron microscopy (TEM). To study the formation of radiation-induced defects at the depth of the CVD epitaxial layer in detail, step-by-step lapping down to the thickness of $\sim 5\,\mu$m was used. TEM measurements were carried out near the surface and at the depth of the CVD layer, as well as in area, which was close to the epitaxial layer/substrate interface. The acquired data were compared with the results of photo- and cathodoluminescence (PL, CL). PL (80 K) was excited by a He–Cd-laser (20 mW) at 325 nm with laser beam filtered by an UFC-1 filter. CL (300 K) measurements were carried along the depth of the CVD layer using angle lapping, with the exposition of 0.1 s and electron beam current and energy of 30 nA and 10 keV, respectively. The diameter of electron beam was $\sim 1\,\mu$m, so the generation region was estimated as 1 to $3\,\mu$m.

3. Results and discussion

The projected range of 710 MeV Bi ions in SiC, according to SRIM 2000 code calculation is $28.8\,\mu$m (see Fig. 1). Therefore, considering the fact that the thickness of the CVD epitaxial layer was $26\,\mu$m, we can assume that the data acquired during the study of the effect of ion irradiation represent to processes, which took place in the epitaxial layer.

According to the SEM data, the initial CVD epitaxial layers had a high degree of structural perfection, which was due to the presence of a thin buffer LPE layer that is well seen at the interface between the CVD layer and the substrate. The LPE layer hindered the penetration of defects from the substrate into the CVD layer [14]. After the irradiation by Bi ions with $5 \cdot 10^{10}\,\mathrm{cm}^{-2}$ fluence, the formation of a thin sub-surface damaged layer with the thickness $\leq 1\,\mu$m, as well as accumulation of radiation defects in the CVD layer, was observed. These defects were produced in the region with the thickness of $3{-}4\,\mu$m, which was close to the interface with the substrate (Fig. 1).

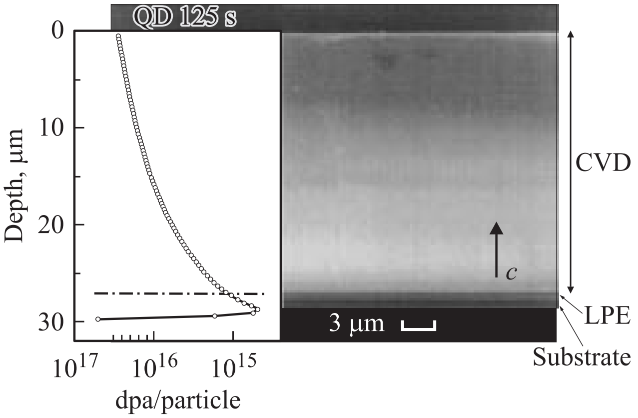

Figure 1. SEM image of the cross-section of the structure comprising *n*-4*H*-SiC CVD epitaxial layer, which was grown in *n*-4*H*-SiC substrate overgrown by a thin LPE epitaxial layer, and irradiated with Bi ions with the energy 710 MeV with $5 \cdot 10^{10}\,\mathrm{cm}^{-2}$ fluence. The insert shows the calculated profile of primary radiation defects in 4*H*-SiC. The edge of the CVD layer is marked with a dotted line.

High structural perfection of the initial epitaxial layers was also confirmed by the analysis of *X*-ray topograms. The presence of basal dislocations was found in highly doped n^+-4*H*-SiC substrates. These dislocations formed cellular structure, which was uniformly distributed across the whole area with dislocation density of $\sim 10^5\,\mathrm{cm}^{-2}$. In some parts of the substrates there were also pores of different size. After the growth of the CVD layers no changes in defect images on the topograms were found, which proved high structural quality of the epitaxial layers. The analysis of the topograms of the samples irradiated by Bi ions with fluence $\geq 10^{12}\,\mathrm{cm}^{-2}$ showed significant degradation of the structure of the CVD layer, which was obviously caused by the increase in the concentration of radiation defects whose density exceeded $10^6\,\mathrm{cm}^{-2}$. The structural perfection of the layer was decreasing with the Bi ion fluence increasing, which was confirmed by the XRD data. Fig. 2 presents XRD profiles of the initial sample with the CVD layer (curve *1*) and of the samples irradiated with fluence $10^{10}\,\mathrm{cm}^{-2}$ (curve *2*) and $10^{12}\,\mathrm{cm}^{-2}$ (curve *3*). The data, which were recorded in (0008) reflection, showed the broadening of rocking curves after the irradiation. The broadening increased with the ion fluence increasing. At the same time, the full linewidth at half-maximum (FWHM) of the rocking curves recorded in (0004) reflection before and after irradiation of these samples hardly differed regardless of the fluence used. It points to insignificant concentration of radiation-induced defects at the beginning of the ion track (at the penetration depth for (0004) reflection, which is $\leq 5\,\mu$m), and to a

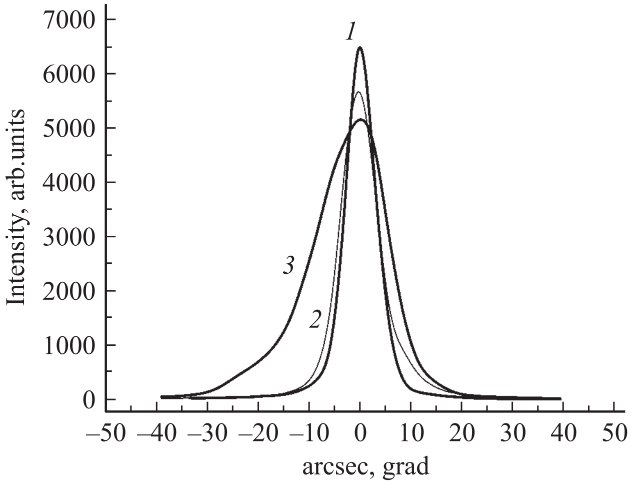

Figure 2. X-ray diffraction curves taken in (0008) reflection for initial 4*H*-SiC CVD epitaxial layer (curve *1*) and the layer irradiated with Bi ions (710 MeV) with fluences: $10^{10}\,\mathrm{cm}^{-2}$ (curver *2*) and $10^{12}\,\mathrm{cm}^{-2}$ (curve *3*).

sharp increase in defect concentration at the end of Bi ion track (at the penetration depth fo (0008) reflection, which is $\sim 25\,\mu$m). This finding agrees with the SEM data. The increase in the concentration of radiation defects in proportion to the fluence, which was established using various measurment methods, was observed after irradiation of SiC by electrons [15], protons [16], neutrons [17], and Xe ions [6] as well. Also, after irradiation of *n*-6*H*-SiC bulk crystals and epitaxial layers by low-energy H^+ ions, an area of high concentration of defect complexes such as vacancy clusters was revealed at the end of the ion trajectory [18,19].

Similar distribution of radiation–induced defects along Bi ion track in the CVD layers was also determined by the TEM studies. In the CVD epitaxial layer irradiated by Bi ions with $5 \cdot 10^{10}\,\mathrm{cm}^{-2}$ fluence, a thin ($\leq 1\,\mu$m) damaged layer was formed close to the surface. Then there was a clear picture of perfect lattice with atomic planes perpendicular to *c* direction, which could also be observed in the middle part of the ion range (Fig. 3, *a*). Accumulation of radiation defects was observed in the CVD layer at the end of Bi ion track at the 3–4 μm distance from the interface with the substrate (Fig. 3, *b*). There is seen a broad band of linear defects, which were decorated with clusters and grouped in the basal planes; formation of amorphous regions was not observed. The probability of the formation of defect clusters in SiC as a result of irradiation by heavy Xe ions was discussed in Ref. [6], and cluster formation at the end of light ion track was discovered using position annihilation spectroscopy after irradiation of *n*-6*H*-SiC CVD epitaxial layer by protons [18]. Annealing of the irradiated samples at the temperature 500°C led to a transformation of the epitaxial layer defect structure; some linear defects merged into continuous planes, whose image is similar to the contrast of a polytype insertion. A fragment of the annealed part of the CVD layer, located at the distance of $\sim 1\,\mu$m from the layer/substrate interface, is presented in Fig. 3, *c*. Possibly, it was this kind of transformation of radiation defects that led to the recovery of rectifying properties of ion-doped diode structures, which had degraded after irradiation with 710 MeV Bi ions [19].

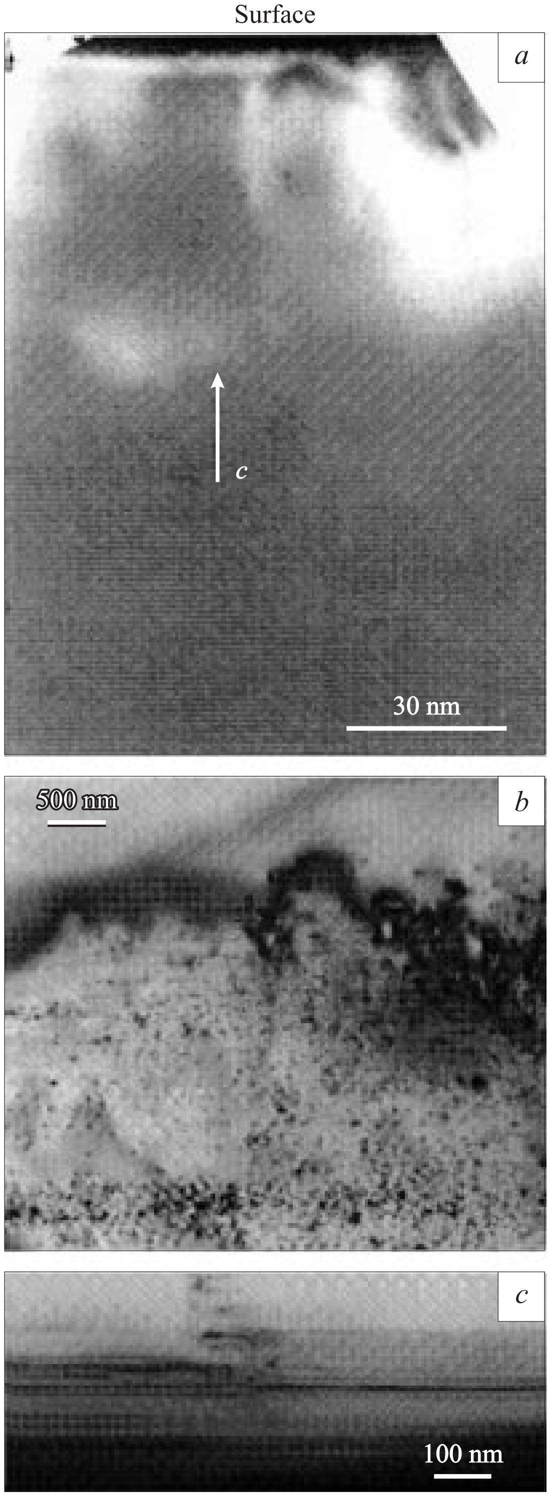

Figure 3. TEM image of the cross-section of *n*-4*H*-SiC CVD epitaxial layer irradiated with Bi ions (710 MeV, $5 \cdot 10^{10}\,\mathrm{cm}^{-2}$), which was taken near the surface of the layer (*a*) and at the end of Bi ion path before (*b*) and after (*c*) annealing at 500°C.

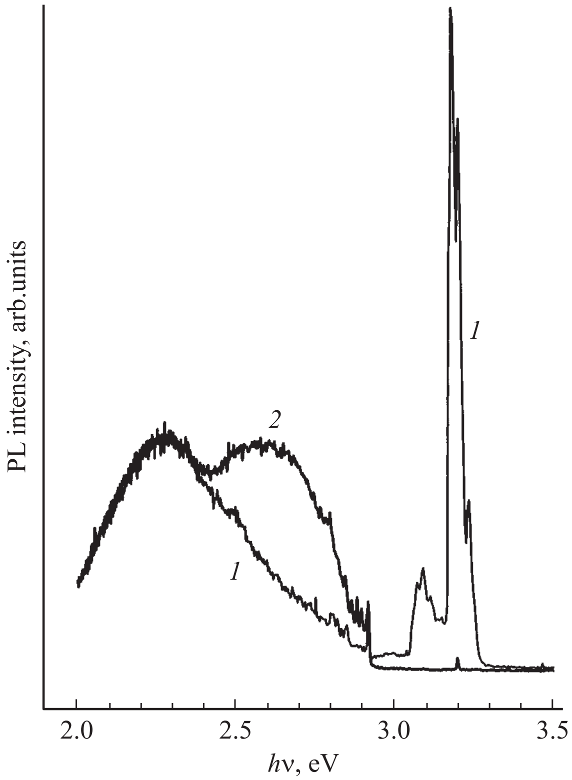

Figure 4. PL spectra (80 K) of *n*-4*H*-SiC CVD epitaxial layer, recorded before (*1*) and after (*2*) irradiation with Bi ions (710 MeV, $5 \cdot 10^{10}$ cm^{-2}).

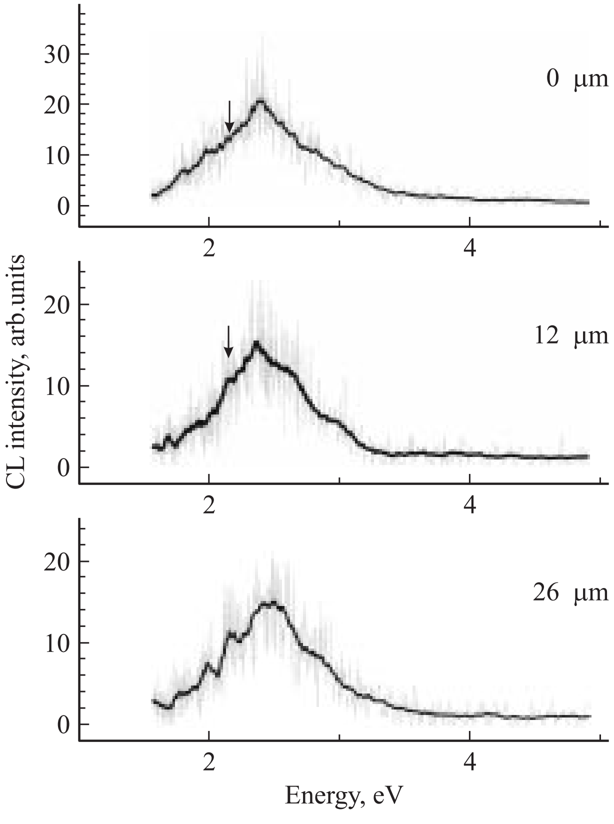

Figure 5. Micro-CL spectra (300 K) of *n*-4*H*-SiC CVD epitaxial layer, recorded before (*1*) and after (*2*) irradiation with Bi ions (710 MeV, $5 \cdot 10^{10}$ cm^{-2}).

PL and CL spectra of initial CVD epitaxial layers were very similar. Fig. 4 presents PL spectra of the initial sample (curve *1*) and of the sample irradiated by Bi ions with $5 \cdot 10^{10}$ cm^{-2} fluence (curve *2*). For the initial CVD layers, there was recorded an intensive luminescence band with the maximum at 3.169 eV, which was causes by recombination of a free excition in 4*H*-SiC [20]. The spectra also contained a wide „defect“ band with the maximum at 2.35 eV, which is typical for SiC and is caused by the presence of deep levels [21]. After the layer was irradiated by Bi ions, the free excition band disappeared, and along with the presence of the defect band, there appeared a wide energy spectrum centered at ~ 2.6 eV, a so-called D1 spectrum [22]. CL spectra, as recorded along the depth of the irradiated CVD layer on the angle lap, demonstrated the broadening of D1 spectra to the and of Bi ion track, as well as the gradual decrease of the signal intensity. This proves that irradiation introduces a wide set of defects with different energy levels, with some of them being centers of non-radiative recombination.

4. Conclusion

For the first time, experimental data on the distribution of radiation-induced defects along the high-energy Bi ion trajectory in pure CVD 4*H*-SiC epitaxial layers were acquired. The absence of amorphous phase over the ion range at the specific ionization energy losses of 34 keV/nm was confirmed. It is experimentally proven that radiation defects are partly annealed at the prospective working temperatute of SiC devices of 500°C, with leads to the recovery of electrical characteristics of the devices based on this semiconductor.

The authores are grateful to V.M. Busov for SEM measurements and to G.N. Violina for useful advice.

This work was partly supported by RFBR (grant N 05-02-08012).

References

[1] V.S. Vainer, V.S. Ilyin. Phys. Sol. St., **23**, 3659 (1981).
[2] T. Dalibor, G. Pensl, H. Matsunami, T. Kimoto, W.J. Choyke, A. Schoner, N. Nordel. Phys. Status. Solidi A, **162**, 199 (19997).
[3] S.G. Sridhara, D.G. Nizhner, R.P. Devaty, W.J. Choyke, T. Dalibor, G. Pensl, T. Kimoto. Mater. Sci. Forum, **264**–**268**, 493 (1998).
[4] D.V. Davydov, A.A. Lebedev, V.V. Kozlovski, N.S. Savkina, A.M. Strel'chuk. Physica B, **308**–**310**, 641 (2001).
[5] A.I. Girka, A.Yu. Didik, A.D. Mokrushin, E.N. Mokhov, S.V. Svirida, A.V. Shishkin, V.G. Shmarovoz. Techn. Phys. Lett., **15**, 24 (1989).
[6] A.I. Girka, A.D. Mokrushin, E.N. Mokhov, V.M. Osadchiev, S.V. Scirida, A.V. Shishkin. JETP, **97**, 578 (1990).
[7] M. Levalois, I. Lhermitte-Sebire, P. Marie, E. Paumier, J. Vicens. Nucl. Instr. Meth. B, **107**, 239 (1996).

[8] I. Lhermitte-Sebire, J.L. Chermant, M. Levalois, E. Paumier, J. Vicens. Phil. Mag. A, **69**, 237 (1994).
[9] D.V. Kratic, M.D. Vlajic, R.A. Verrall. Key Engin. Mater., **122–124**, 387 (1996).
[10] L. Liszkay, K. Havancsak, M.-F. Barthe, P. Desgardin, L. Henry, Zs. Kajcsos, G. Battistig, E. Szilagyi, V.A. Skuratov. Mater. Sci. Forum, **363**, 123 (2001).
[11] S.J. Zinkle, J.W. Jones, V.A. Skuratov. MRS Symp. Proc., **650**, R 3.19.1 (2001).
[12] E. Kalinina, G. Kholujanov, G. Onushkin, D. Davydov, A. Strel'chuk, A. Zubrilov, A. Hallén, A. Konstantinov, V. Skuratov, J. Staňo. Mater. Sci. Forum, **433–436**, 467 (2003).
[13] E.V. Kalinina, G.F. Kholuyanov, G.A. Onushkin, D.V. Davydov, A.M. Strel'chuk, A.O. Konstantinov, A. Hallén, A.Yu. Nikiforov, V.A. Skuratov, K. Havancsak. Semiconductors, **38**, 1187 (2004).
[14] E. Kalinina, G. Kholujanov, V. Solov'ev, A. Strel'chuk, A. Zubrilov, V. Kossov, R. Yafaev, A.P. Kovaeski, A. Hallén, A. Konstantinov, S. Karlsson, C. Adås, S. Rendakova, V. Dmitriev. Appl. Phys. Lett., **77**, 3051 (2000).
[15] M. Gong, S. Fung, C.D. Beling, Z. You. J. Appl. Phys., **85**, 7604 (1999).
[16] L. Storasta, F.H.C. Carisson, S.G. Shidhara, A. Åberg, J.P. Bergman, A. Hallén, E. Janzén. Mater. Sci. Forum, **353–356**, 431 (2001).
[17] S.B. Orlinski, J. Schmidt, E.N. Mokhov, P.G. Baranov. Phys. Rev. B, **67**, 125 207 (2003).
[18] D.T. Britton, M.-F. Barthe, C. Corbel, A. Hempel, L. Henry, P. Desgardin, W. Bauer-Kugelmann, G. Kögel, P. Sperr, W. Triftshüser. Appl. Phys. Lett., **78**, 1234 (2001).
[19] E. Kalinina, A. Strel'chuk, A. Lebedev, N. Strokan, A. Ivanov, G. Kholuyanov. Accepted for publication for Proceedings of ICSCRM2005 (Pittsburg, USA, Sept. 18–23, 2005).
[20] M. Ikeda, H. Matsunami. Phys. Status Solidi A, **58**, 657 (1980).
[21] Yu.A. Vodakov, G.A. Lomakina, E.N. Mokhov, M.G. Ramm, V.I. Sokolov. Semiconductores, **20**, 2151 (1986).
[22] L. Patrick, W.J. Choyke. Phys. Rev. B, **5**, 3253 (1972).

Редактор Т.А. Полянская