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Influence of boron doping on the photosensitivity of cubic silicon carbide

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Abstract. Photoelectric properties have been studied for 3C-SiC single crystals obtained by thermal decomposition of methyl trichlorosilane with addition of boron in the process of growing or using diffusion into intentionally undoped crystals. Boron-doped samples demonstrate the band of photosensitivity within the range 1.3…2.0 eV with the peak near 1.7 eV. Doping of 3C-SiC single crystals with B impurity leads to appearance of an efficient recombination center with the thermal activation energy 0.27 ± 0.02 eV inside the band gap and to widening the spectral sensitivity of the material over the impurity long-wave range. Availability of boron results in changing the temperature dependence of photoconductivity from the decay characteristic to the activation one. It will allow expanding the operation range of devices based on 3C-SiC⟨B⟩ up to 500 °C and above it. In addition, the lux-ampere characteristics becomes linear, *i.e.*, more convenient from the metrological viewpoint. Depending on the type of doping of 3C-SiC⟨B⟩ samples, pronounced variations of line positions in photoluminescence spectra in near-infrared range are revealed.

Keywords: cubic silicon carbide, boron doping, photoconductivity, photoluminescence.

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1. Introduction

Cubic and hexagonal polytypes of silicon carbide are considered as a promising material for high-power, high-frequency and high-temperature electronics due to their wide bandgaps, large thermal conductivities, high mobility of carriers and breakdown electric fields [1]. With respect to other polytypes, cubic silicon carbide 3C-SiC is more stable at lower temperature, and it can be grown below the melting temperature of Si (1414 °C), which permits its epitaxial growth on Si substrates. Recent progress in growth of 3C-SiC epitaxial films [2] has opened widespread possibilities for production of high-quality devices and sensors. Application of SiC devices for harsh environment operation necessitates detailed knowledge of impurities, intrinsic and irradiation damage defects and their thermal stability. This paper is devoted to studying the photoconductivity (PC) of boron-doped 3C-SiC single crystals within the temperature range 100…500 K.

The particular feature of 3C-SiC single crystals is their sectorial structure, which is related with difference in the velocities of crystal faces growth: the faces {111}, {211}, {100} as well as {*hhl*} of the crystallographic belt ⟨110⟩ develop the most fast [3]. In the process of doping, there takes place selective adsorption of impurities by different faces, which causes differences in their physical-and-chemical properties. For instance, the boron impurity most efficiently penetrates into the faces {111} and {211}, while that of nitrogen – into the faces {*hhl*}. The role of boron, as one of the most important acceptor impurities in SiC, in recombination processes is mainly studied in electrical, luminescent and absorption investigations aimed at hexagonal 4H and 6H as well as cubic polytypes [4–8]. At the same time, characteristics of non-radiative recombination channels defining photoelectric properties of 3C-SiC⟨B⟩ are not practically investigated up to date, and it limits their application as various sensors. It is noteworthy that polycrystalline

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3C-SiC with the boron impurity was offered as a material for temperature sensors in the high-temperature range as well as sensors for gas flows [9].

It was earlier shown [10, 11] that in *n*-type 3C-SiC crystals the recombination process of non-equilibrium charge carriers is controlled by two types of centers of non-radiative recombination (*r*- and *s*-centers) as well as by centers of trapping for major carriers. The *r*-centers define thermal decay of photocurrent with the activation energy of 0.2 eV and capture cross-section for electrons by them $C_{er} = 5 \cdot 10^{-18}$ cm^2, while the latter value for the *s*-centers is $C_{es} = 10^{-16}$ cm^2. The trapping cross-sections for holes by these centers are sharply different $C_{pr} >> C_{ps}$, and, due to it, the *r*-centers in *n*-type 3C-SiC are the centers of photosensitivity [11]. It was ascertained [12] that the increase in nitrogen concentration results in enhancing the quantum yield for exciton luminescence and in decreasing the lifetime of electrons. In this case, the highest efficiency of photoluminescence is observed in the {*hhl*} growth pyramids with high concentration of uncompensated donors, while the highest photosensitivity – in the {111} growth pyramids.

As known, the boron impurity in SiC can create both shallow and deep levels [4, 5]. The shallow B-level observed in measurements of deep-level transient spectroscopy (DLTS), Hall effect [4, 5, 13] and electron paramagnetic resonance (EPR) [14] is related to the acceptor centers possessing the activation energy $E_v + (0.3\ldots0.4)$ eV. The deep B-level pronounced in photoluminescence (PL) and DLTS [4], in absorption [5] and EPR [15] is characterized by creation of a deeper acceptor level. Estimations of the ionization energy for the deep B-level lead to the following values: 0.73 to 1.0 eV, when the boron impurity concentration changes from $3.5 \cdot 10^{16}$ up to $1 \cdot 10^{18}$ cm^{-3} [7]. The relationship between concentrations of shallow and deep acceptor B-centers depends on technology of material doping. It is believed that the yellow in 6H-SiC [4] and infrared in 3C-SiC [7] PL bands are related with these deep B-centers. With account of results obtained using EPR and electron-nuclear double resonance (ENDOR), it was drawn the conclusion that boron atoms corresponding to shallow levels substitute silicon atoms in SiC lattice and create B_{Si}-centers [14, 16]. In regard to deep B-levels, they are ascribed to the boron – carbon vacancy ($B_{Si} + V_c$) complex in accord with the results of ENDOR measurements [17].

The study of PL on undoped epitaxial 3C-SiC films implanted with boron ions found that their spectra, except for typical lines inherent to defects, contain a wide band with the maximum close to 1.6 eV related with boron centers [8]. The estimate of energy for optical ionization of acceptors gives the value 0.7 eV above the valence band top E_v, which is in good accordance with the results of [7]. The obtained films were offered as photodetectors, but their photoconductive properties remained uncertain.

The aim of this work is to study the influence of the boron acceptor impurity on stationary and relaxation characteristics inherent to the photosensitivity of 3C-SiC.

2. Materials and methods

Studied in this work are photoelectric properties of 3C-SiC single crystals obtained by thermal decomposition of methyl trichlorosilane with addition of boron in the process of growing or using diffusion into intentionally undoped plate-like crystals, separated from which were growth pyramids of the faces {111} and {211}. Before boron diffusion, the crystals were grinded from the side of small face A {111} down to the thickness 100 µm to reach more uniform distribution of boron. Then the crystals were degreased in CCl_4, etched in $HF+HNO_3$ and washed out in distilled water. In the diffusion process, as a source of doping impurity we used amorphous boron placed on the chamber heater. Diffusion was performed at the temperatures 1700…1800 °C for 20…30 hours in the helium atmosphere. After diffusion, the surface layer of several micrometers was removed. Then, the type of conduction was determined using measurements of thermal e.m.f. or Hall effect. As a result of embedding boron, conduction of the samples was considerably lowered and became of *p*-type. For some samples, we performed measurements of EPR and PL spectra. The availability of boron impurity has been proved by detecting the EPR spectrum of shallow boron in all the samples studied.

In this work, we studied stationary characteristics of photoconductivity: the temperature ones within the range 100…500 K, spectral, lux-ampere as well as those of photo-response relaxation.

3. Results

Adduced in Fig. 1 are the spectral characteristics of photocurrent measured at the temperature T = 90 K on specially undoped 3C-SiC sample with $N_d - N_a = 10^{16}$ cm^2 (curve *1*), on the sample of the same set as that where diffusion of the boron impurity was performed (curve *2*), and on the sample doped with boron in the process of growing (curve *3*). It is seen from this figure that the spectrum of undoped sample within the impurity range has a weak structure that can be related with availability of background impurities in these crystals [4, 11]. The sample doped in the process of growing demonstrates the band of photosensitivity within the range 1.3…2.0 eV with the peak near 1.7 eV. The sample doped by diffusion, as compared with the undoped one, also has the considerable photosensitivity within all the impurity range with a weak peak in the same region and approximately the same long-wave boundary for photoconduction.

Essential qualitative changes are observed in the temperature dependence of the concentration of non-equilibrium charge carriers $\Delta n \sim I/\mu$ (Fig. 2), where I is the photocurrent, µ – mobility of charge carriers. In the initial sample of *n*-type (curve *1*), within the range of high temperatures $T \geq 170$ K one can observe the photocurrent decay with the activation energy close to 0.2 eV. High-temperature boron diffusion or boron

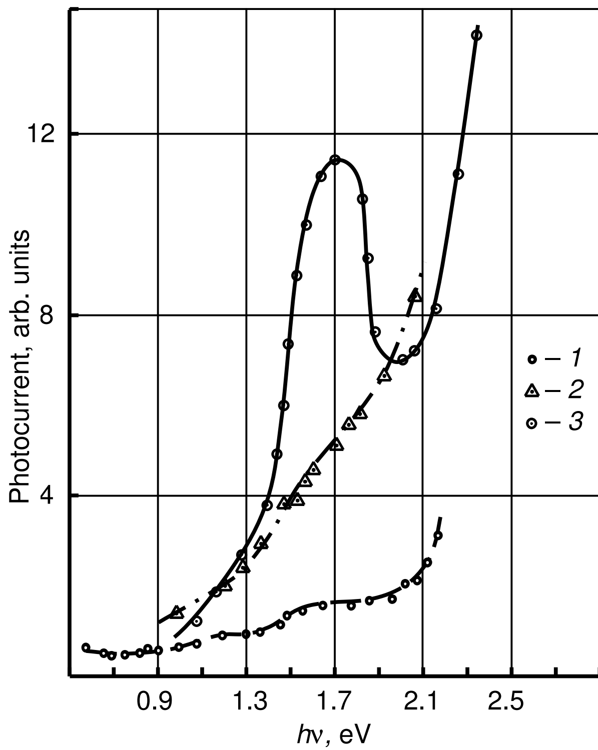

Fig. 1. Spectral dependences of the photocurrent for monocrystalline 3CSiC samples at $T = 90$ K: *1* – undoped, *2* – diffusion-doped, *3* – doped during growth.

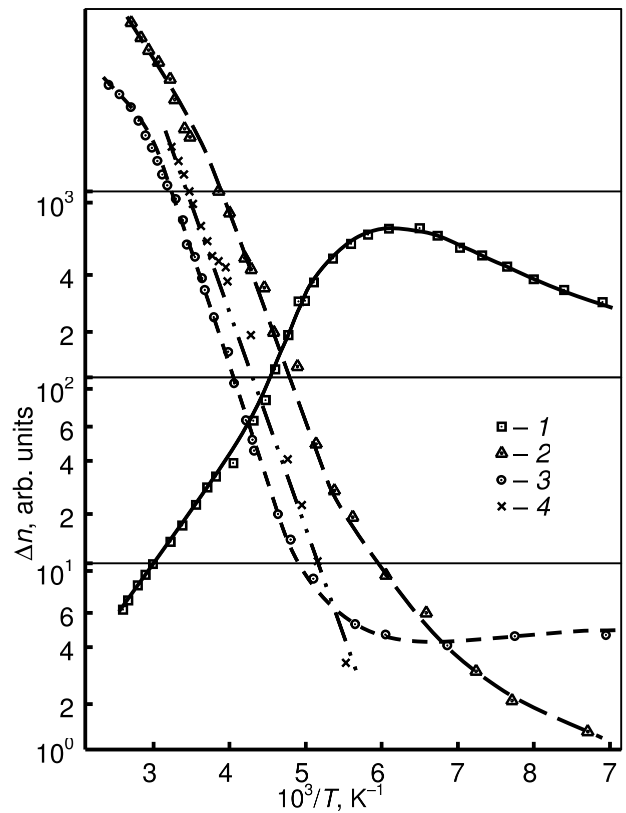

Fig. 2. Temperature dependences of the concentration inherent to non-equilibrium charge carriers, Δn: *1* – for undoped, *2* – diffusion-doped, and *3* – crystal doped during growth, *4* – dependence of the concentration of equilibrium charge carriers on temperature of a sample doped during growth.

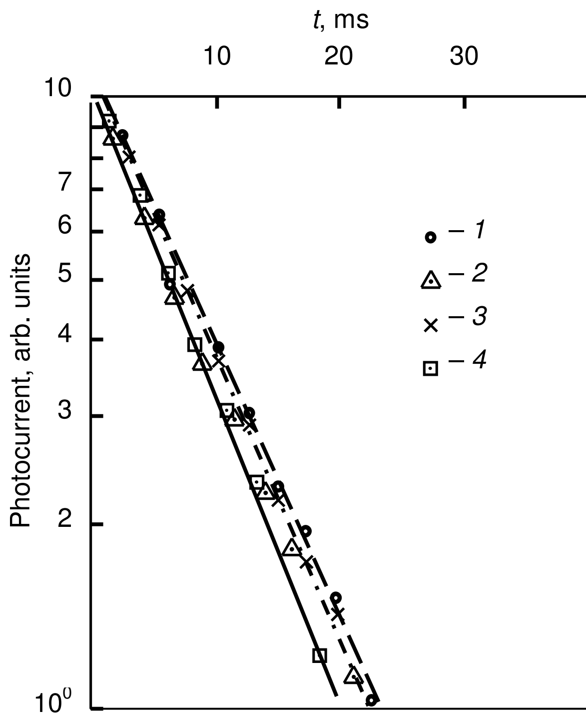

Fig. 3. Photocurrent relaxation under additional illumination Φ_{ill} within the range of intrinsic absorption (filter C3C-3): *1* – without illumination, $\Phi_{ill} = 0$, *2* – $\Phi_{ill}/\Phi_0 = 5$, 3 – $\Phi_{ill}/\Phi_0 = 8$. Φ_0 – amplitude of pulsed excitation within the intrinsic band. *4* – illumination within the impurity absorption band Φ_{ill} (filter KC-2), $\Phi_{ill}/\Phi_0 = 1$.

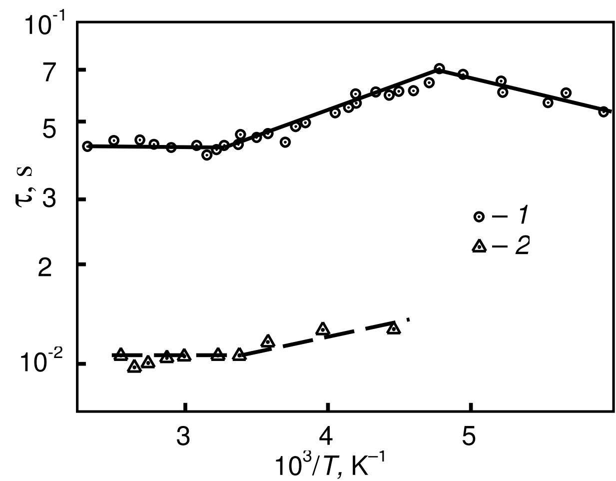

Fig. 4. Temperature dependences of the time constant of the photocurrent decay for the samples doped in the process of growing (*1*), diffusion (*2*).

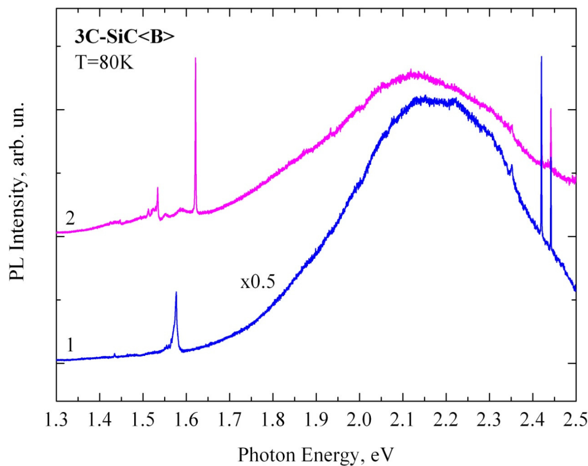

Fig. 5. PL spectra of 3C-SiC⟨B⟩ samples at 80 K doped with N and B during crystal growth (*1*) and by B diffusion (*2*). Narrow peaks in the range of 2.41–2.45 eV belong to Raman spectrum.

doping in the process of growing change the character of this temperature dependence (Fig. 2, curves *2* and *3*), namely: the photocurrent increases with temperature, and this dependence becomes exponential in a wide temperature range.

The relaxation curves of photocurrent for the samples doped during the process of growing or by diffusion are symmetrical relatively their rise and drop, therefore, they can be approximated with the only exponent having the time constant $\tau = 0.01\ldots0.05$ s (Fig. 3). In this case, τ very weakly changes with temperature in the range studied (Fig. 4) both for doped during growth (curve *1*) and diffusion (curve *2*) samples. Besides, it does not depend on the intensity of additional illumination Φ_{ill} with intrinsic or impurity light in regard to the main pulsed illumination Φ_0 (Fig. 3).

Lux-ampere characteristics of the studied samples, which were measured in the range of intrinsic absorption at room temperature, indicate that introduction of boron during growth or diffusion results in increasing the exponent in the expression $I \sim \Phi_0^{\alpha}$ from $\alpha = 0.3$ inherent to the initial undoped sample up to $\alpha = 0.8\ldots1.0$ for the samples doped by diffusion or during their growth.

4. Discussion

As it follows from experimental data, doping of the 3C-SiC crystals with the boron acceptor impurity by using both above methods leads to the increase in the material resistivity, changes in the shape of PC spectrum, in the character of photocurrent temperature dependence, its kinetics, as well as changes in the exponent of lux-ampere characteristics. PC measurements reveal a new band with the long-wave edge near 1.3 eV and the maximum close to 1.7 eV (Fig. 1), which is in accord with the data of absorption measurements [8]. As compared with the initial samples, the ones doped by diffusion show an enhanced photosensitivity inside a wider range up to the fundamental edge of material (curve *2*). As it follows from this figure, PC spectra of the doped samples differ: in the case of diffusion doping, the impurity band is considerably wider, which can be caused by creation of impurity-defect complexes in the process of B introduction [18]. It is also noteworthy that the samples doped by diffusion demonstrate the emission band related with B impurity in 6H polytype [19], which is not observed in the samples doped during their growth [18].

As it follows from Fig. 2 (curve *2*), temperature activation of samples doped by diffusion is related with the center possessing the energy of thermal ionization 0.27 ± 0.02 eV. Its appearance is caused by boron introduction, since the samples doped in the process of growing (curve *3*) have approximately the same slope. Taking into account that the temperature dependence of carrier dark concentration after boron doping has approximately the same look (curve *4*), one can assume that this center of acceptor type defines also PC spectral characteristics of 3C-SiC doped with boron. Like to the centers in CdS [20], it is fully or partly radiationless. Activation of the photocurrent in 3C-SiC of *p*-type can be explained by the decrease in filling recombination centers with holes, when temperature is increased, as well as with increasing the stationary lifetime of holes in the temperature range $T \geq 150$ K.

It follows from Fig. 3 that relaxation of photocurrent is defined by one exponent with the time constant weakly depending on temperature in a wide range (Fig. 4) and on additional illumination with light from the fundamental edge or from the impurity absorption range as well. This fact along with the linear lux-ampere characteristic means that photoconductivity in the B-doped samples in our experimental conditions has monopolar character, and the process of non-equilibrium carriers recombination is controlled by the only efficient deep center. To identify it, we need some additional investigations.

It has been found earlier for 6H-SiC that B-related PL band position and intensity vary in dependence on the type of doping [6]. Our verification with PL of 3C-SiC⟨B⟩ samples prepared by doping of crystals simultaneously with N and B during crystal growth as well as the samples prepared using B diffusion into unintentionally N-doped crystals reveals the same feature. Fig. 5 shows PL spectra of both samples at 80 K excited by the 488-nm line of an Ar^{+}-ion laser with an interferential filter. Both of these spectra display broad emission band centered at about 2.15 eV and sets of narrow peaks in near-infrared region. By contrast to H. Kuwabara *et al.* [7], who observed a broad band for nitrogen donor – boron acceptor pair recombination with zero-phonon line (ZPL) at 1.640 eV in crystals grown from the melt, the positions of ZPL equal to 1.621 and 1.577 eV for 3C-SiC⟨B⟩ samples doped from vapor and by diffusion, respectively. Pronounced variation of position and general view of PL spectra for 3C-SiC⟨B⟩ samples, depending on the type of doping, needs further investigations.

5. Conclusions

- Doping of 3C-SiC single crystals with the acceptor B impurity during growing or diffusion leads to appearance of the efficient recombination center with the thermal activation energy 0.27 ± 0.02 eV inside the material band gap and to widening the spectral sensitivity of this material over the impurity long-wave range.
- Doping with boron results in changing the temperature dependence of photoconductivity from the decay characteristic to the activation one. It will allow expanding the operation range of devices based on 3C-SiC⟨B⟩ up to 500 °C and above it.
- After embedding boron, the lux-ampere characteristic becomes linear, *i.e.*, more convenient from the metrological viewpoint.

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