

Research Article

Spectral Dependence of Optical Absorption of 4H-SiC Doped with Boron and Aluminum

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Optical absorption of *p-n*-4H-SiC structures doped with boron and aluminum by low-temperature diffusion was studied for the first time. Diffusion of impurities was performed from aluminum-silicate and boron-silicate films (sources) fabricated by various methods. In the spectral dependences of optical absorption at room temperature, bands associated with transitions from impurity levels, as well as absorption bands associated with defects of the vacancy nature, were observed. The level of absorption in the samples was used to estimate concentration of defects. It was shown that the use of sources of impurity atoms created by using boron and aluminum chlorides allows one to reduce the concentration of vacancy defects.

1. Introduction

Among wide-gap semiconductor materials (GaP, ZnS, ZnSe, ZnTe, CdS, and SiC), silicon carbide is a unique material due to high thermal conductivity and mechanical, chemical, and radiation hardness. Based on silicon carbide, power electronics elements, nuclear radiation detectors, and UV LEDs for special applications are made [1, 2]. In this regard, there is a significant interest drawn by researchers and technologists to this material.

Impurities of boron and aluminum are used to form *p*-regions in structures based on 4H-SiC by means of ion implantation or thermal diffusion. Diffusion of these impurities in the silicon carbide is based on rather complex mechanism taking place at temperatures above 2000°C. Impurities move both through carbon and silicon sublattices of the crystal. Moreover, solubility and diffusion coefficient of impurities in different sublattices differ greatly.

For example, in the silicon sublattice, the boron solubility ($\sim 6-9 \times 10^{19} \text{ cm}^{-3}$) is almost an order of magnitude higher than that in the carbon sublattice ($1-10 \times 10^{18} \text{ cm}^{-3}$) [3]. Differences in diffusion coefficients lead to formation of the so-called “tails” in the impurity distribution depthwise, which significantly reduces quality of the *p-n* junctions fabricated by means of thermal diffusion. Tails reduce the

breakdown voltage, and traps associated with nitrogen (which are formed at high diffusion temperatures) increase the switching time of the diodes [4].

The ion implantation method allows one to achieve impurity concentration to be close to the maximal solubility. However, in the case of silicon carbide, annealing of defects requires temperatures up to 1800–2000°C. At such high temperatures, one can observe redistribution of impurities depthwise, formation of defects on the surface, and so on. That is why instead of thermal diffusion and ion implantation methods [5, 6], the method of epitaxial growth of a silicon carbide layer can be only used to manufacture high-voltage *p-n* junctions, since the epitaxial film does not contain growth defects such as micropipes.

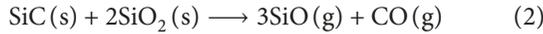
We have developed a new low-temperature method for shallow impurities diffusion in silicon carbide at temperatures of 1150–1300°C. The method is described in details in publications [7–11] and patented in Uzbekistan and the USA [12, 13]. A significant decrease in temperature is due to the fact that diffusion occurs in the flow of carbon and silicon vacancies. Below we describe briefly the mechanism of formation of V_C and V_{Si} vacancies.

In [14], it is described that, at temperatures 1100–1400°C, SiC exhibits two types of oxidation behavior, “active” and

“passive,” depending upon the ambient oxygen potential. At high oxygen pressures, “passive” oxidation occurs wherein a protective film of $\text{SiO}_2(\text{s})$ is formed on the surface by the reaction:



At low oxygen potentials, severe “active” oxidation occurs due to the formation of gaseous products according to the following reactions:



Active oxidation of SiC occurs only at oxygen pressures lower than $\sim 3 \cdot 10^{-4}$ atm at 1400°C .

As seen from (2) and (3), surface oxidation of silicon carbide in this condition leads to production flow of both as carbon and silicon vacancies from the surface into the bulk of the crystal (may be mostly of carbon vacancies). Obviously, the vacancy concentration in this case can be much higher as compared with the introduction of vacancies by irradiation.

Advantages of low-temperature diffusion are as follows: shallow impurity concentration of up to 10^{20} cm^{-3} (unreachable for conventional thermal diffusion and ion implantation technique), and fast switching time of < 10 ns of p - i - n SiC diodes fabricated by this method (> 20 ns for diodes fabricated by conventional technology) [10, 11].

However, the technology of manufacturing of such p - i - n SiC diodes needs to be improved. In particular, it is necessary to improve the technology of creating a source of impurity atoms on the surface of the crystal for conducting low-temperature diffusion.

The source of impurity atoms for diffusion is a borosilicate or almosilicate layer, which is formed on the surface of the sample before diffusion. The source-layer is formed at 600°C by different methods (synthesis from a boric acid layer, synthesis from aluminum chloride layer, and by oxidation of aluminum metal layer deposited by thermal evaporation in vacuum).

As the diffusion occurs in the flow of defects, different defects with deep levels [15] as well as clusters of impurity atoms are formed in the sample [16]. It is clear that the concentration of defects depends on the technology of manufacturing aluminum and borosilicate films.

In this article, the optical absorption spectral dependence data was used to estimate the concentration of defects in crystals and to improve the technology for p - n junctions manufacturing by the low-temperature diffusion method.

2. Experimental

In this paper, we used single-crystal samples of silicon carbide $4H$ - n -SiC grown by means of the physical vapor transport (PVT) method (Cree Research, Inc, USA) with a relatively low concentration of growth defects: N_d dislocations 10^4 cm^{-2} and N_m micropipes ~ 10 – 10^2 cm^{-2} , thickness ~ 300 – $600 \mu\text{m}$, surface $\sim 0.25 \text{ cm}^2$, specific resistance ~ 3.6 – $20 \Omega \cdot \text{cm}$, and nitrogen impurity concentration $N_d - N_a \sim (0.5$ – $1.0) \times 10^{17} \text{ cm}^{-3}$.

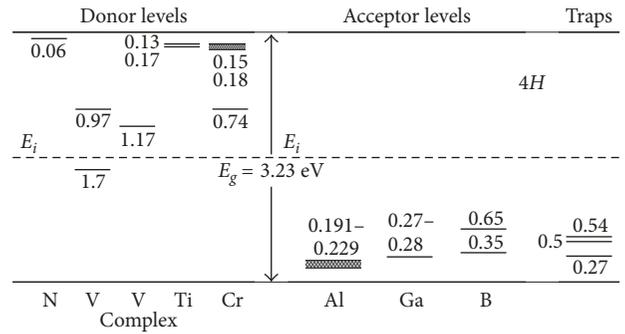


FIGURE 1: Levels of impurities and defects in $4H$ -SiC [20–22].

Prior to low-temperature diffusion, the samples were etched in KOH (potassium hydroxide)–water solution upon ultraviolet (UV) stimulation [17].

The source of boron impurity atoms was borosilicate film which was formed as follows: alcoholic solution of boric acid or boric anhydride was applied to the surface of silicon carbide, which then was dried and annealed at 650°C in air.

The source of aluminum impurity atoms for diffusion was formed in two ways: (1) aluminum film thermally sputtered onto the surface of the sample that was oxidized at 650°C in vacuum and (2) formation from aluminum chloride sputtered on the surface of the silicon carbide at 600 – 700°C .

Low-temperature diffusion was conducted in the air for 30 min at temperatures ranging between 1150°C and 1300°C .

As a result of the silicon carbide surface oxidation at 1150 – 1300°C , a flow of carbon and silicon vacancies was formed on the surface of the crystal [18, 19]. This flow interacting with the impurity atoms significantly increased their diffusion coefficient and solubility. As a result of the diffusion, a layer containing aluminum and silicon oxides was formed on the surface of the samples. This layer was removed by hydrofluoric acid to reveal the p -region of the sample.

According to electrophysical measurements, the impurity concentration reached 10^{20} – 10^{21} cm^{-3} in a thin near-surface layer [18]. According to luminescence data [15], the sample contained defects of the vacancy nature doped during diffusion.

To measure the spectral characteristics of the structures, dual-beam spectrophotometer (SPECORD 210 (Germany)) was used. This spectrophotometer had a wave band from 190 to 1100 nm. The Spectrum BXII Fourier spectrometer with spectral range from 7800 to 350 cm^{-1} was used for measurements in the IR spectral region.

3. Results and Discussion

The levels of impurities and defects in silicon carbide are studied in details. Based on the literature data [20–22], levels of the background nitrogen impurity, the acceptor levels of boron and aluminum, and the vacancy levels and traps in $4H$ silicon carbide are presented in Figure 1. It is assumed that the 2 acceptor levels with different energies correspond to different impurity positions (in the carbon and silicon

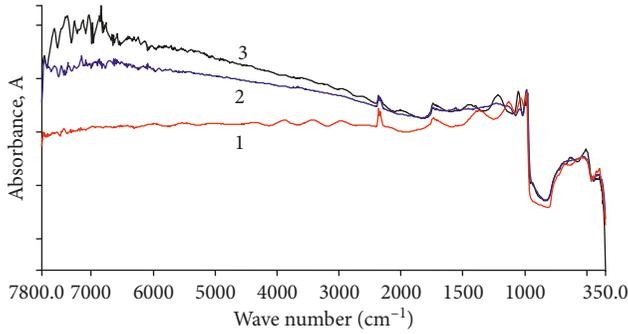


FIGURE 2: Spectral dependence of optical absorption in the IR region: 1, initial 4H-SiC crystal; 2, spectrum taken with Al-doped side; 3, spectrum taken from the reverse side of the crystal.

sublattices). However, it is still not finally established which level corresponds to which sublattice.

It should be noted that there are also experimental data on carbon vacancy levels obtained by photocapacitance measurements. The vacancy of carbon has a band containing up to 5 levels with ionization energy from $E_C - 1.80$ to $E_C - 0.74$ eV for various charge vacancy states [23].

The optical absorption coefficient α can be determined by using the following known expression:

$$I = I_0(1 - R) \exp(-\alpha d) \quad (4)$$

$$\text{or } \alpha = -\frac{1}{d} \ln \frac{I}{I_0(1 - R)},$$

where I is intensity of light that passes through the sample, I_0 is initial light intensity, R is coefficient of reflection, and d is thickness of sample. The reflection coefficient depends both on the optical properties of the material and on the state of the sample's surface. In case of a mirror surface and normal incidence of rays, the reflection coefficient is related to the refractive index of the material n determined by the Fresnel formula [24]:

$$R = \frac{(1 - n)^2}{(1 + n)^2} \quad (5)$$

For long-wave radiation, the refractive index does not practically change, although in a region close to its own absorption the refractive index can change its value. According to the data of [25], in the wavelength region up to 440 nm (band-band transitions and above), the refractive index of silicon carbide varies nonmonotonically in the range of 2.4–3.4. However, in the region of absorption by defects (from the levels within the band gap), n varies insignificantly from 3.4 to 3.2. Respectively, according to (5), the reflection coefficient also varies insignificantly within 0.27–0.29.

As it is known, the Fourier spectrometer allows taking absorption spectra of very thin layers on the crystal surface [26]. We measured absorption spectra of both doped thin layer and undoped reverse side of the sample. Such spectra of doped and undoped layers of the same sample make it possible to increase confidence of the conclusions. Figure 2 shows the optical absorption spectral dependence in the IR region.

As one can see from Figure 2, a wide structureless band observed in the absorption spectrum at 2500 cm^{-1} or more after diffusion evidences of the presence of relatively closely located defect levels in the crystal with different transition energies.

In this part of the spectrum, transitions from the valence band to boron levels (with energies of 0.35 and 0.65 eV) can be also found. Let us also consider the IR absorption spectrum of the initial crystal. The region up to 2000 cm^{-1} relates to absorption by lattice vibrations. According to [27], phonon energy TA, LA, TO, and LO are 0.045, 0.067, 0.0955, and 0.1055 eV, respectively. Moreover, in samples treated with hydrofluoric acid, a surface phonon is observed at 950 cm^{-1} (energy 0.116 eV) [28].

Thus, in the region up to 1000 cm^{-1} , single-phonon absorption peaks are observed. Peaks appeared after diffusion in the defect flow at ~ 1100 , ~ 1300 , ~ 1400 , $\sim 1750 \text{ cm}^{-1}$, and $2340\text{--}2360 \text{ cm}^{-1}$ according to [27] refer to (2LA or TO + TA), (TO + LA), (LO + LA), 2LO, and 3TO multiphonon absorption.

Figure 3 shows the optical absorption spectral dependence measured at room temperature for the p - n -4H-SiC structures doped with boron. As one can see from the diagram, transitions from the valence band to the conduction band (beginning at 3.23 eV), transitions of electrons through acceptor levels of boron to the conduction band (from 2.6 to 2.9 eV), and transitions from the valence band to boron levels (from 0.35 to 0.65 eV) should be observed.

In addition, the sample has defects of vacancy nature after the low-temperature diffusion process. According to the diagram, carbon vacancies also allow absorption bands from 0.74 eV to 2.6 eV. Contribution of each absorption band is determined by concentration of impurities and defects, cross sections for capture of current carriers, and so on.

In Figure 3, a sharp increase in the absorption at 2.7–2.8 eV is observed in the absorption spectrum of the sample doped with boron, which is associated with transitions from the boron levels to the conduction band. A sharp yield to saturation indirectly confirms our data obtained by electrophysical measurements on a significant boron concentration up to 10^{20} cm^{-3} [18]. Absorption in the region of 1.5–2.6 eV is associated with transitions to vacancy-type defects. However, as one can see in the previous figure, at lower energies the structureless broad band tail continuation can be observed. Thus, in general, the absorption spectrum corresponds to the diagram.

Figure 4 shows the optical absorption spectrum of p - n -4H-SiC structures doped with aluminum (from a source created using aluminum chloride) measured at room temperature and a diagram of optical absorption transitions.

As it can be seen from Figure 4, the absorption spectrum is similar to the previous case. Absorption bands from acceptor levels of aluminum to the conduction band of 2.9–3.0 eV are observed. A wide absorption band at energies below 2.8 eV is associated with vacancy defects in the crystal. Similarly to those observed in Figure 3, one can see a small step at 1.7 eV as well. However, the level of absorption on the defects is significantly, to 3 times, lower, which indicates a reduced concentration of defects.

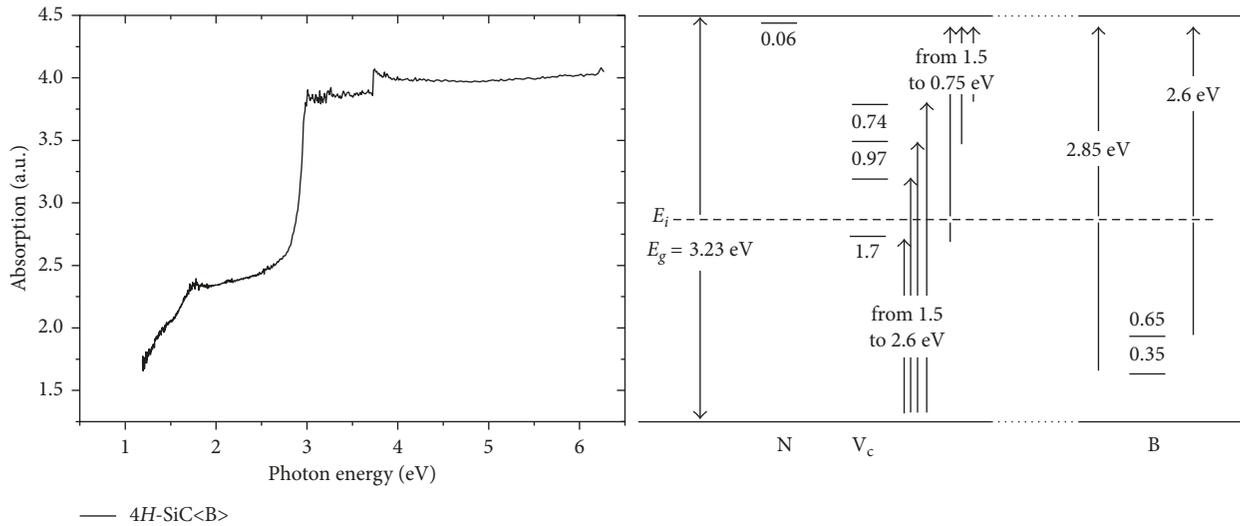


FIGURE 3: Spectrum of optical absorption of p - n - $4H$ -SiC structures doped with boron (measured at room temperature) and the diagram of optical absorption transitions.

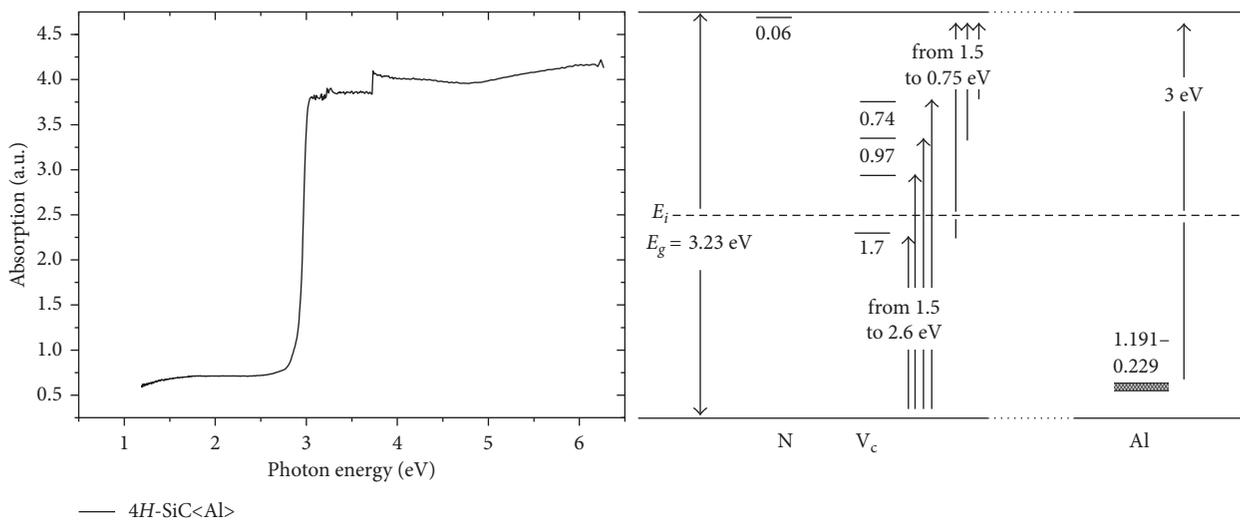


FIGURE 4: The optical absorption spectrum of p - n - $4H$ -SiC structures doped with aluminum (from a source created by using aluminum chloride) measured at room temperature and a diagram of optical absorption transitions.

Figure 5 shows the absorption spectrum of the sample doped with aluminum (from a source created from a thin aluminum film sputtered in vacuum).

As it can be seen from Figure 5, along with the absorption band at 3.0 eV (transitions to the conduction band from aluminum levels), an additional absorption band with the energy of 2.5–2.6 eV is observed. A high level of absorption indicates a high concentration of defects. As it can be seen from Figures 4 and 5, relative contribution of absorption to the defects is higher when the impurity source is created from a thin film of aluminum sputtered in vacuum. Consequently, in this case, additional defects of the vacancy nature are formed in the crystal during diffusion.

In all samples (doped with both boron and aluminum), an increase in absorption of up to 1.7 eV (the carbon vacancy

level in silicon carbide is around 1.7 eV), then a step, which extends to 2.5 eV, and then again the growth of absorption on the defects are observed. In view of the complexity of the optical absorption processes in the presence of many types of defects, it is difficult to identify which defects are responsible for peaks.

We can note, however, that 1.7 eV is close to the transition energy of an electron from the valence band to the vacancy level of carbon, and 2.3 and 2.5 eV are close to the energies of the transition of electrons from the valence band to other levels of the same carbon vacancy.

Further, with an increase in the quantum energy up to the energy of transition from the levels of boron or aluminum impurities to the conduction band, a sharp increase in absorption is observed, confirming the data on the high impurity concentration.

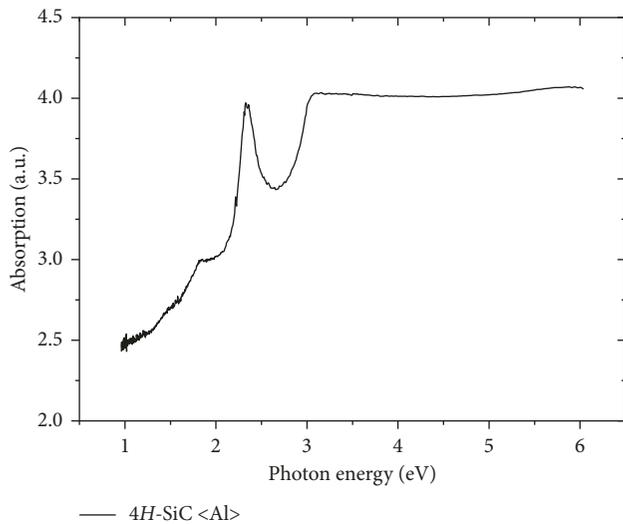


FIGURE 5: Spectrum of optical absorption of p - n - $4H$ -SiC structures doped with aluminum (from a source created from a thin aluminum film sputtered in vacuum).

4. Conclusions

Optical absorption of p - n - $4H$ -SiC structures doped with boron and aluminum by low-temperature diffusion was studied for the first time. Diffusion of impurities was performed from aluminum-silicate and boron-silicate films (sources) fabricated by various methods.

In the spectral dependences of optical absorption at room temperature, bands associated with transitions from impurity levels as well as absorption bands associated with defects of the vacancy nature were observed.

The level of absorption in the samples was used to estimate the concentration of defects. It was shown that the use of sources of impurity atoms created by using boron and aluminum chlorides allows one to reduce the concentration of vacancy defects.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References

- [1] T. V. Blank and Y. A. Gol'dberg, "Semiconductor photoelectric converters for the ultraviolet region of the spectrum," *Semiconductors*, vol. 37, no. 9, pp. 999–1030, 2003.
- [2] K. Nakayama, R. Ishii, K. Asano, T. Miyazawa, M. Ito, and H. Tsuchida, "Component technologies for ultra-high-voltage $4H$ -SiC pin diode," *Materials Science Forum*, vol. 679–680, pp. 535–538, 2011.
- [3] Y. Gao, S. I. Soloviev, and T. S. Sudarshan, "Selective doping of $4H$ -SiC by codiffusion of aluminum and boron," *Applied Physics Letters*, vol. 83, no. 5, pp. 905–907, 2003.
- [4] N. I. Kuznetsov and J. A. Edmond, "Effect of deep levels on current excitation in $6H$ -SiC diodes," *Semiconductors*, vol. 31, no. 10, pp. 1049–1052, 1997.
- [5] S. Tamura, K. Fujihira, T. Kimoto, and H. Matsunami, "High-purity and thick $4H$ - and $6H$ -SiC(0001) epitaxial growth by cold-wall chemical vapor deposition and high-voltage pin diodes," *Japanese Journal of Applied Physics*, vol. 40, no. 4, pp. L319–L322, 2001.
- [6] H. Tsuchida, I. Kamata, T. Miyanagi et al., "Growth of thick $4H$ -SiC(0001) epilayers and reduction of basal plane dislocations," *Japanese Journal of Applied Physics*, vol. 44, no. 24–27, p. L806, 2005.
- [7] C. C. Tin, S. Mendis, K. Chew et al., "Oxide film assisted dopant diffusion in silicon carbide," *Thin Solid Films*, vol. 518, no. 4, pp. 118–120, 2010.
- [8] S. Mendis, C. C. Tin, I. G. Atabaev, and B. G. Atabaev, "The method of solid state impurity diffusion and doping in $4H$ -SiC," *International Journal of Fundamental Physical Sciences*, vol. 3, no. 4, pp. 75–78, 2013.
- [9] C. C. Tin, S. Mendis, M. T. Tin, T. I. Smith, and J. R. Williams, "A new approach in impurity doping of $4H$ -SiC using silicidation," *Journal of Applied Physics*, vol. 114, no. 24, p. 244502, 2013.
- [10] I. G. Atabaev, Kh. N. Juraev, and V. A. Pak, "Fast switching $4H$ -SiC pin structures fabricated by low temperature diffusion of Al," *Advances in Condensed Matter Physics*, vol. 2017, Article ID 7820676, 8 pages, 2017.
- [11] I. G. Atabaev and Kh. N. Juraev, "Research of p-i-n junctions based on $4H$ -SiC fabricated by low-temperature diffusion of boron," *Advances in Materials Science and Engineering*, vol. 2018, Article ID 8797031, 10 pages, 2018.
- [12] I. G. Atabaev, T. M. Saliev, and E. N. Bakhranov, "Method of diffusion of boron in silicon carbide," UZ Patent, IAP 02792, 2006.
- [13] C. C. Tin, A. V. Adedeji, I. G. Atabayev et al., "Low temperature impurity doping of silicon carbide," US Patent 7999268 B2, 2011.
- [14] S. C. Singhal, "Oxidation kinetics of hot-pressed silicon carbide," *Journal of Material Science*, vol. 11, no. 7, pp. 1246–1253, 1976.
- [15] I. G. Atabaev, C. C. Tin, B. G. Atabaev et al., "Diffusion and electroluminescence studies of low temperature diffusion of boron in $3C$ -SiC," *Materials Science Forum*, vol. 600–603, pp. 457–460, 2009.
- [16] I. G. Atabaev, T. M. Saliev, B. G. Atabaev, and R. Jabbarganov, "Negative secondary ion mass spectra under Cs⁺ ion bombardment of the p -SiC-B- surface," *Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques*, vol. 5, no. 4, pp. 796–800, 2011.
- [17] I. G. Atabaev, C. C. Tin, B. G. Atabaev, S. L. Lutpullaev, and Kh. N. Juraev, "The method of etching silicon carbide," Patent UZ, No IAP 05087, 2015.
- [18] I. G. Atabaev, T. M. Saliev, E. N. Bakhranov et al., "Nonequilibrium diffusion of boron in SiC at low temperatures," *Materials Sciences and Applications*, vol. 1, no. 2, pp. 53–58, 2010.
- [19] I. G. Atabaev, T. M. Saliev, D. Saidov et al., "Influence of defects on low temperature diffusion of boron in SiC," *Materials Sciences and Applications*, vol. 2, no. 9, pp. 1205–1211, 2011.
- [20] A. A. Lebedev, "Deep level centers in silicon carbide: a review," *Semiconductors*, vol. 33, no. 2, pp. 107–130, 1999.
- [21] "The diagram of main impurities in $4H$ -SiC," 2017, <http://www.ioffe.ru/SVA/NSM/Semicond/SiC/impurities.html>.
- [22] S. R. Smith, A. O. Ewvaraye, W. C. Mitchel, and M. A. Capano, "Shallow acceptor levels in $4H$ - and $6H$ -SiC," *Journal of Electronic Materials*, vol. 28, no. 3, pp. 190–195, 1999.

- [23] N. T. Son, X. T. Trinh, L. S. Løvlie et al., “Negative-U system of carbon vacancy in 4H-SiC,” *Physics Review Letters*, vol. 109, no. 18, p. 187603, 2012.
- [24] L. A. Kosyachenko, A. V. Pivovarov, and V. M. Sklyarchuk, “Prebreakdown electroluminescence spectra of silicon carbide in various polytypes,” *Journal of Applied Spectroscopy*, vol. 36, no. 2, pp. 178–183, 1982.
- [25] J. I. Larruquert, A. P. Pérez-Marín, S. García-Cortés, L. Rodríguez-de Marcos, J. A. Aznárez, and J. A. Méndez, “Self-consistent optical constants of SiC thin films,” *Journal of the Optical Society of America A*, vol. 28, no. 11, pp. 2340–2345, 2011.
- [26] J. S. Gaffney, N. A. Marley, and D. E. Jones, *Fourier Transform Infrared (FTIR) Spectroscopy*, John Wiley & Sons, Hoboken, NY, USA, 2003.
- [27] L. Patrick and W. J. Choyke, “Lattice absorption bands in SiC,” *Physical Review*, vol. 123, no. 3, pp. 813–815, 1961.
- [28] H. Nienhaus, T. U. Kampen, and W. Mönch, “Phonons in 3C-, 4H-, and 6H-SiC,” *Surface Science*, vol. 324, no. 1, pp. L328–L332, 1995.

