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Doping of SiC Crystals during Sublimation Growth and Diffusion

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Abstract

The preparation of SiC crystals doped with various impurities introduced during the process of sublimation growth and diffusion is described. The growth of SiC crystals was carried out by a sublimation-sandwich method, proposed by us in 1970. Crystals of the n- and p-type conductivity with maximum content of electrically active impurities (of the order of 10^{21} cm^{-3}) were obtained. The solubility values of more than 15 impurities were determined. Special tantalum containers with several temperature zones, allowing to introduce any impurity into SiC practically, are developed. The dependences of the impurities concentration on the temperature, growth rate and seed orientation are found. Diffusion of impurities of boron, aluminum, gallium, beryllium, lithium, nitrogen and phosphorus in silicon carbide polytypes was studied. Diffusion coefficients of these impurities in a wide temperature range are determined. It is shown that for a number of impurities diffusion cannot be described by standard distributions that are explained by the presence of several states of diffusing centers. Fast-diffusing states are atoms located in interstices, as well as centers, including the impurity atom and point defect. The extremely low diffusion mobility of lattice point atoms in the SiC lattice is noted.

Keywords: doping, impurity, diffusion, sublimation growth, polytypes

1. Introduction

Controlled doping of the semiconductors is a necessary condition for the creation of device structures on their basis. The main attention in the SiC doping is usually paid to impurities with shallow levels in the bandgap—N, Al and B [1, 2]. These impurities are characterized by high solubility in SiC that allows to receive low-resistance SiC layers [3]. Other impurities—elements of II, III, IV and V groups, transitional metals and rare-earth elements—are less often used for SiC doping, though they are of interest for fabrication of high-resistance and semi-insulating SiC layers and special types of light-emitting diodes. The impurities may effect on the polytype structure [4]. For example elements of IV group allow to grow the 4H-SiC crystals on the seeds of other polytypes. Finally, incorporation of impurities is necessary for identification of the nature of impurity centers, which is important for prospects assessment of creation of new semiconductor devices generation.

Doping of SiC crystals is carried out by various methods: during the growth process, by ion implantation and by thermal diffusion. A perspective way is also transmutation doping. It allows to receive SiC crystals uniformly doped with

impurities. In this review we will limit ourselves to the description of SiC doping during the sublimation growth and by thermal diffusion.

The doping of SiC is characterized by a number of specific features. Doping process is carried out at high temperatures (1700°C and higher); concentration of doped impurities considerably depends on various factors, such as growing surface conditions (crystallographic orientation, density of structural and morphological defects, and thickness of the growth steps [5]), stoichiometry deviation and structure of the polytypes [6, 7]. Incorporated impurities easily form precipitates [6] and durable, thermal stable associates with matrix atoms or native defects [8].

The goal of the present work is observation of the SiC doping by different impurities during the sublimation growth or the thermal diffusion. Impurities of II, III and IV groups of the periodic table, the transitional metals and rare-earth elements were incorporated into SiC crystals of various polytypes. The conducted investigations have allowed not only to define solubility of these elements in SiC but also to identify the impurity centers and to estimate their influence on semiconductor SiC properties. Some results of this work were presented previously [8–11].

2. SiC doping during sublimation growth

Impurity incorporation was carried out during physical vapor transport (PVT) growth. Usually SiC crystals or epitaxial layers were grown by sublimation sandwich method (between the source and the seed (no more than 0.2 from the linear size of the source)). It is important that at a small gap in the growth cell a self-contained system is realized. It provides quasi equilibrium conditions on the growing crystal surface [12]. The schematic diagram of SSM is shown in Figure 1. The feature of SSM is the existence of a narrow gap and the evaporated surfaces in the wide range of temperatures and pressures. As a result the temperature range of SiC crystal growth by SSM is very wide: from 1700 to 2700°C. Growth of high-quality crystals and epitaxial layers (EL) is possible in vacuum and in gas phase environment. SSM is successfully used for growth of SiC bulk crystals [13] and epitaxial layers [14] and also growth of GaN [15] and AlN [16] crystals.

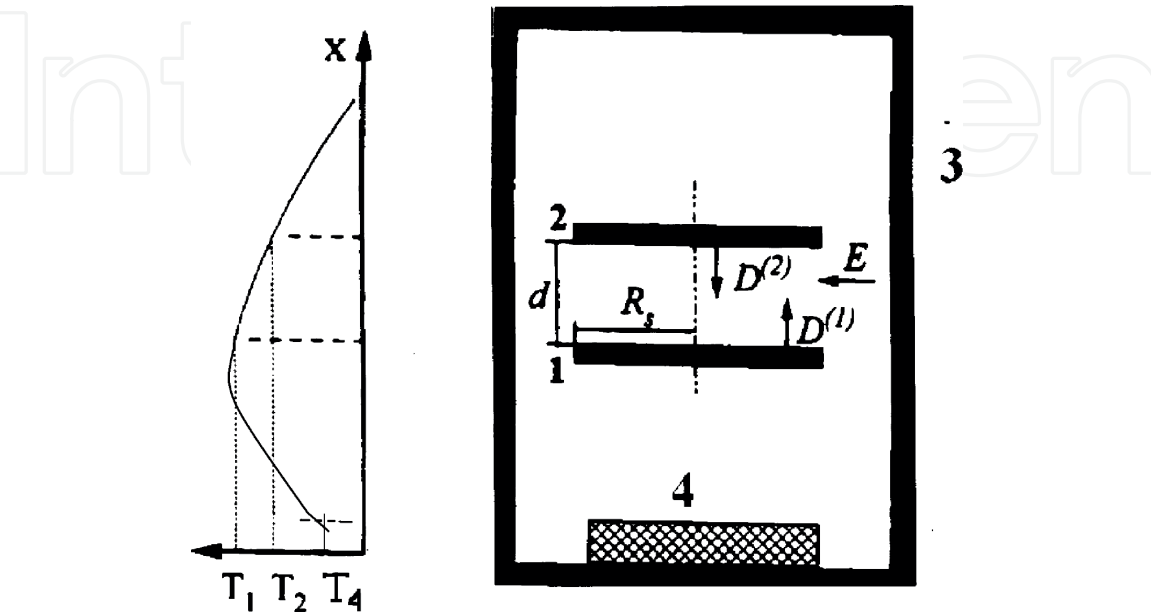


Figure 1. Schematic view of the sublimation sandwich system for growth of the doped SiC crystals. Source of SiC vapor (1); seed (2); container (3) and source of impurity (4). Temperature distribution is shown (left).

In this method high efficiency of impurity mass transfer is reached that is difficult to realize in other gas transport techniques, for example CVD [17]. For SSM the influence of impurities on the quality of the growing crystal is not so essential. Therefore, SSM is an effective method for growth of the high-doped SiC crystals with solubility limit of the impurities. The choice of impurity is almost unlimited.

The schematic diagram of the container used by doping is shown in **Figure 1**. By growth of doped crystals in a crucible there are no less than two temperature zones. The source of SiC vapors and the seed are placed into the hot zone. The impurity is located in the zone with lower temperature. The concentration of the entered impurity is defined by impurity source temperature. For growing of heavily doped crystals, it is preferable to use the impurity source, which is in an elementary state. The impurity can also be loaded directly in SiC source. Volatile impurities (for example, nitrogen) are entered through the gas phase.

Growth is usually carried out in graphite or tantalum containers. The use of a Ta container helps to reduce the content of background impurities, to reduce sharply the loss of the sublimated material and to provide growth of SiC crystals without graphitization of the source [18]. The last is very important for receiving high-quality SiC crystals with low dislocation and micropipe density. Unfortunately, Ta impurity creates a deep level in band gap [19].

For determination of impurity content in SiC crystals neutron-activation analysis [20, 21] secondary ion mass-spectroscopy (SIMS) and different electro-physical methods (van der Pauw, surface local breakdown [22], and C-V measurements) were used.

2.1 Solubility limit of the impurities in SiC crystals

Solubility limit of more than 20 impurities incorporated during PVT growth by SSM is presented in **Table 1**. Besides, we studied doping of SiC crystals with Fe, Ni, and Er impurities and found that its solubility in SiC was at the level of 10^{17} cm^{-3} . Neutron-activation analysis (NAA) [20] was used for determination of the impurities concentration in uniformly doped parts of crystals.

As shown in **Table 1** there is very limited set of impurities with high solubility in SiC. These are, first of all, acceptors (Al, B, Be, and Ga), donors (N and P) and Ge. For the majority of impurities the maximum level of SiC doping is reached at extremely high temperatures ($T_g > 2400^\circ\text{C}$) and for [0001]Si growth direction.

Element	Concentration cm^{-3}	Element	Concentration cm^{-3}	Element	Concentration cm^{-3}
Li	1.2×10^{18}	Cr	3.0×10^{17}	In	9.2×10^{16}
Be	8.0×10^{20}	Mn	3.0×10^{17}	Sn	10×10^{16}
B	2.5×10^{20}	Cu	1.2×10^{17}	Sb	8.0×10^{15}
N	8.0×10^{20}	Ga	1.8×10^{19}	Ho	6.0×10^{16}
Al	2.0×10^{21}	Ge	3.0×10^{20}	Ta	2.4×10^{17}
P	2.8×10^{18}	As	5.0×10^{16}	W	2.5×10^{17}
Sc	3.2×10^{17}	Y	2.0×10^{16}	Au	4.9×10^{16}
Ti	3.3×10^{17}	Mo	3.5×10^{17}		

Table 1.
Solubility limit of impurities in SiC crystals doped during sublimation growth [23].

2.2 Dependence of doping of impurities on crystallographic orientation

It was determined that SiC doping level strongly depends on crystallographic orientation of the substrate. Higher concentration of impurities of the III-a group (In, Al, Ga) and also transitional elements is observed by growth in the direction of [0001]Si, in comparison with the direction [0001]C [24–26] (**Figure 2**).

On the contrary the concentration of V-group impurities (N, P, As and Sb) is higher by growth on the [0001]C surface [23, 26, 27]. At low growth temperatures the effect of orientation anisotropy of SiC doping is very considerable. For example the concentration of acceptor Al and Ga impurities grown on polar {0001} sides at the temperature 1800°C differs 5–10 times [24, 25]. The dependence of impurity concentration on substrate orientation noted above also remains by inversion of the sample conductivity type.

The obtained data are explained by the absence of equilibrium vapor-crystal at the typical growth conditions. It is known [27] that the condition of equilibrium vapor-crystal is the inequality: $V_g < D_i/h$ (V_g —growth rate, D_i —impurity diffusion coefficient, h —thickness of the growing layer).

We have obtained that for impurities N, P, Ga and Al [9] at practically realized temperatures and growth rates this condition is not satisfied and doping anisotropy is a consequence of various adsorptive properties of polar {0001} sides.

It is known that chemical bonds in the surface layer are rehybridized in such a way that individual properties of the element located on the surface become essential [28]. This feature results in differences in the character of surface sides, which consist of only silicon or carbon atoms. With the increase of temperature the

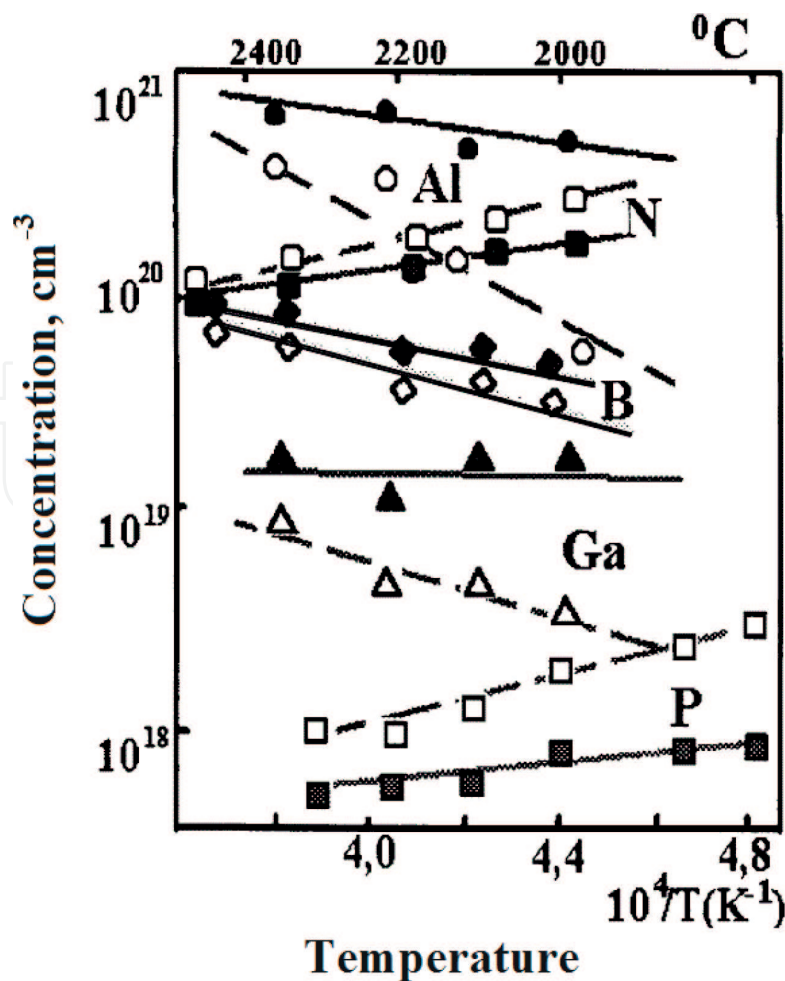


Figure 2. Dependence of the concentrations of N, B, Ga, Al, and P in SiC on the growth temperature. Orientation of the growing SiC: [0001]Si, solid lines; [0001]C, dashed lines.

anisotropy of polar sides doping decreases. A similar effect is got by introduction of silicon vapors [29, 30] or impurities, such as tantalum, promoting enrichment of the surface layer by the silicon into the growth cell [31].

The influence of substrate orientation also becomes apparent at small angles of its misorientation in relation to singular {0001} planes [32]. For example nitrogen concentration in epilayers grown on on-axis (0001)C face is 1.7–2 times higher than on off-axis one. This results from the fact that increase of the growth steps density in the second case leads to a raised desorption of impurity atoms. Such strong dependence of the doping impurity concentration on the misorientation angle leads to nonuniform doping of the grown crystal and emergence of morphological imperfections on the growing surface [32]. Impurities incorporation also depends on growth layer thickness due to step bunching process [33].

As a rule, with temperature increases, the concentration of impurities is enhanced (**Figure 2**). However, for V-group elements nitrogen and phosphorus the opposite effect was observed, i.e., the doping level went down with the temperature (**Figure 2**). The abnormal temperature dependence for nitrogen and phosphorus is explained by the fact that capture of these impurities is limited by the process of desorption in which probability increases with temperature rise [34].

Thus, for receiving SiC samples heavily doped by acceptor impurities high temperatures of growth are preferable (2400–2500°C) and low-resistance layers of n-type conductivity with extremely high content concentration of nitrogen or phosphorus can be grown at the moderate temperatures (1800–1900°C).

In all cases the dependence of $C_i(T)$ can be described by Arrhenius's equation: $C_i = A \exp(-\Delta H/RT)$, where ΔH is dissolution enthalpy. If the doping impurities are entered in the process of crystal growth, values A and ΔH strongly depend on crystallographic orientation of the substrate. For IIIa-group impurities the values A and ΔH are significantly higher for growth in the direction of [0001]C than in the direction of [0001]Si [35].

2.3 Influence of partial pressure of the impurity

Dependence of impurities concentration of Al, B, Ga and N on partial pressure is presented in **Figure 3**. Conditions of saturation achievement differ strongly for each impurity. It is seen (**Figure 3**) that in case of B and Al impurities the solubility limit is now realized by rather low partial pressure of impurity (about 10^0 – 10^2 Pa) [23]. Solubility limit of Ga impurity is observed at pressures 10^2 – 10^3 Pa [36]. But the saturation of N concentration even at extremely high pressures of molecular nitrogen is not observed [37].

The dependence $N_d \sim P_i^{1/2}$ is realized in very wide range of pressures (10^0 – 10^5 Pa) (where N_d —concentration of donors, P_i —partial pressure of nitrogen). It is a consequence of the Henry's law implementation and assumes existence of equilibrium like $N_2 \leftrightarrow 2N$. At the same time the density of adsorption centers on the surface is much higher than impurity concentration in chemisorbate because of very small life time of nitrogen molecules on the growth surface [37].

2.4 Dependence of the doping level on the growth rate

Growth rate in some cases also influences concentration of the entered impurity. We observed the diminishing of N impurity concentration at high growth rates (**Figure 4**).

In these experiments the impurity source was combined with the SiC source and located inside the growth cell [30, 31]. The influence of the growth rate on the level of doping by nitrogen has been quantitatively explained within the model according to which the capture of impurity is limited by kinetics of adsorption [31].

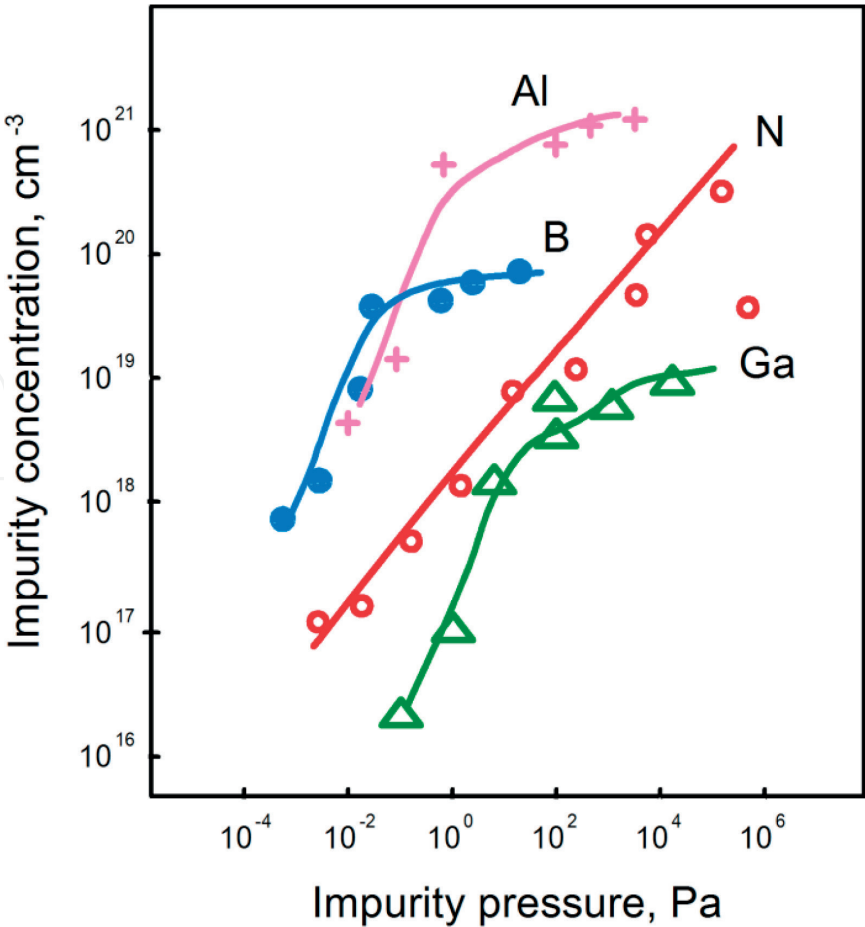


Figure 3.
Dependence of the impurity concentration in the growing SiC on the dopant partial pressure inside the growth cell for the cases of doping by N, B, Al and Ga. $T = 2000^{\circ}\text{C}$. Doping with N is performed on (0001)C surface; with B, Al and Ga on [0001]Si surface.

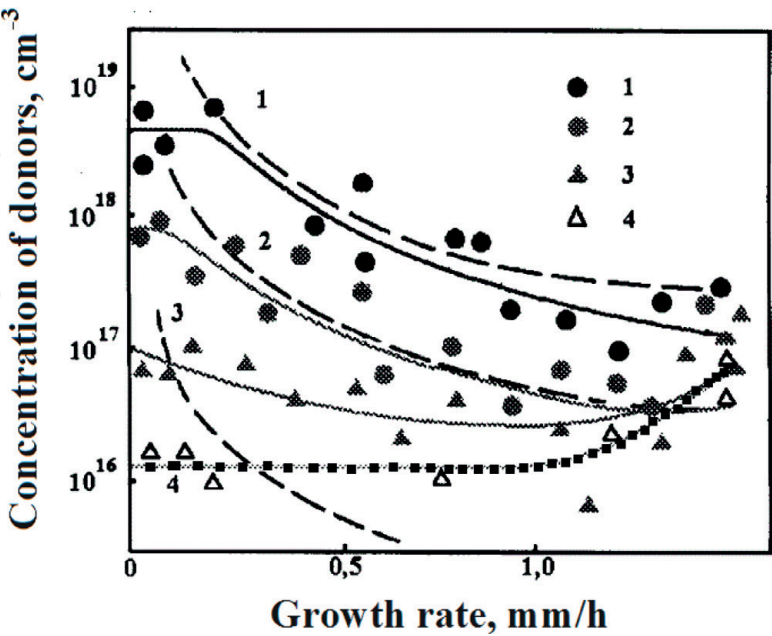


Figure 4.
Dependence of the donor concentration (N) in SiC epitaxial layer on growth rate. Concentration of nitrogen in the source: (1) 2×10^{19} , (2) 3×10^{18} , (3) 3×10^{17} and (4) 7×10^{16} cm⁻³. The growth temperature is 1850°C. Dashed lines are theoretical results.

However, good correlation data calculation with the experiment was observed only when the heavily doped nitrogen SiC source was used [31]. At low concentration of nitrogen in the source ($<10^{18} \text{ cm}^{-3}$) the concentration of donors in the grown crystal either poorly depended on the deposition rate or even increased with its increase. The obtained result has been explained by the fact that by growth of SiC there could take place not only capture of impurity (nitrogen) atoms but also nonequilibrium native defects of donor type. Their concentration increased with the increase of the deposition rate. Native defects in SiC crystals grown at high rates were found also by other researchers.

On the contrary increase of growth rate leads to higher Ga impurity incorporation [35]. At low growth rates ($V_g < 10 \text{ } \mu\text{m/h}$) the concentration of Ga in SiC did not exceed $(3-5) \times 10^{17} \text{ cm}^{-3}$. The increase of growth rate up to $0.2-0.5 \text{ mm/h}$ leads to increase of impurity concentration up to 10^{19} cm^{-3} . This dependence can be explained within the conception of nonequilibrium capture of impurity [27].

2.5 Influence of stoichiometry deviation on the doping level

As it is stated, the concentration of Al, Ga and N impurities in the grown SiC layers significantly depends on the ratio Si: C in the vapor phase [32]. By introduction of silicon vapors into the growth zone the doping level of Al and Ga impurities considerably decreases. Especially, sharp decrease of concentration of these impurities (almost in order of magnitude) is observed by growth in the direction of [0001] Si [32]. As a result it appears impossible to receive low-resistance layers of p-type conductivity in the SiC-Si system. By surplus of silicon the concentration of nitrogen in the grown SiC layers also decreases [29]. A similar dependence of impurity concentration on surplus of Si is revealed for growth of SiC layers by the method of gas transport deposition [38]. Obviously, the reduction of impurity capture efficiency by growth in the SiC-Si system is a consequence of the competing adsorption of silicon [32]. Therefore, density of sorption centers on the growing surface decreases.

Besides, it was found that introduction of silicon vapors to the growth zone leads to sharp reduction of orientation anisotropy of doping SiC layers by N, Al and Ga impurities [26, 32]. It facilitates receiving of bulk SiC crystals with more uniform impurity distribution.

We note that a similar effect of the influence of stoichiometry deviation, known as site-competition epitaxy, is described in the works of [38]. By growth of SiC crystals by CVD method the authors found that high tension of Si vapors promotes decrease of the acceptor doping level. On the contrary, at excess of carbon, the concentration of nitrogen decreases, especially by growth in the direction of [0001] Si. The concentration of electrically active impurity depends on Si/C ratio in the gas phase (CVD). High concentration of C prevents introduction of nitrogen atoms but only on the Si side (decrease by 4–5 times). It has allowed to receive crystals with $(\text{Nd-Na}) = 10^{14} \text{ cm}^{-3}$ [38]. For acceptor impurities excess of Si lowers their concentration.

2.6 Coefficients of impurity capture

Within the bounds of classic approach for quantity description of doping process coefficient K_t of impurity transfer from source to substrate is usually used. But K_t depends on impurity contents in the source, on geometrical sizes of the source and the substrate and on the distance between them.

The value defining probability of the impurity capture by a single collision with growing surface is the coefficient of elementary impurity capture (K_i). It is easier to

Impurity	K_i , [0001]Si	K_i , [0001]C	Ref.
N	5.0×10^{-2}	1.2×10^{-1}	[35]
B	4×10^{-2}	2×10^{-2}	[35]
Al	8×10^{-3}	4.5×10^{-4}	[35]
P	2×10^{-4}	5×10^{-3}	[40]
Ga	1.5×10^{-3}	4.5×10^{-5}	[35]

Table 2.
Impurity unit capture coefficients (K_i) for sublimation SiC growth at the temperature 1850°C and growth directions [0001]C and [0001]Si.

define K_i value by transfer of impurity from the source to the substrate in the conditions of vacuum [34, 39]. For this purpose SiC bulk crystals with a certain content of doping impurity are usually used as a source.

By means of this technique we have calculated the unit impurity capture coefficients (K_i) for the most important electrically active impurities—nitrogen, boron, aluminum, gallium, phosphorus—depending on the growth temperature, substrate orientation and impurity concentration [35, 40].

Some results of this research are shown in **Table 2**.

It is clear that during sublimation growth the most effectively captured impurities are nitrogen and boron. Unit capture coefficients of other impurities are much less.

The main reasons of low coefficients of impurity capture during sublimation growth are high probability of desorption of impurity atoms and their interaction with matrix atoms with formation of precipitates.

At high concentration of impurity essential decrease of K_i value is observed (**Figure 5**) [23, 37, 40]. In case of nitrogen and phosphorus this effect can be explained by the fact that with impurity concentration increase in the adsorbing layer, probability of its desorption in the form N or P molecules increases. Reduction of K_i boron and aluminum is possibly caused by limitation of centers of effective sorption or is a consequence of these impurities' precipitates formation.

2.7 Macrosegregation of impurities

In this work essential attention was paid to study the behavior of impurities entered into crystal. It has become clear that in heavily doped SiC layers, a considerable part of impurity is in inactive state and poorly influences material properties [41]. It has been found that the main reason for it is the formation of precipitates enriched by the doping impurities. Macrosegregation of impurities

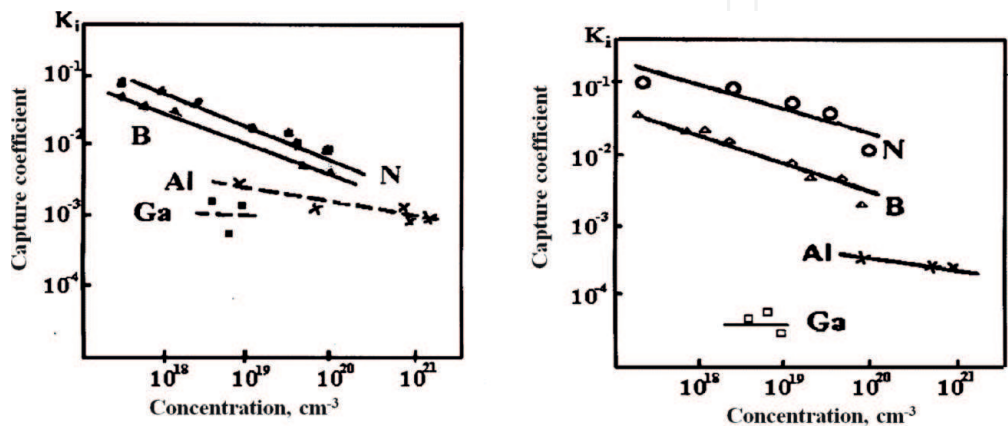


Figure 5.
Dependence of unit capture coefficients of impurities on the source impurity concentration. Growth directions: [0001]Si (left) and [0001]C (right).

caused by formation of precipitates leads to sharp deterioration of material and device structures on its basis. Therefore, we have paid much attention to this question.

In this work we have studied the reasons of precipitates formation. For this purpose we have investigated characteristic features of impurity macrosegregation in SiC layers grown from vapor phase depending on temperature, growth rate, substrate orientation and vapor phase structure [42–44]. The behavior of various impurities including Al, B, Ga, Ta and W in SiC crystal doped by growth and diffusion has been studied. Definition of impurity concentration and the nature of distribution were carried out by the combined method of neutron activation analysis including tool and autoradiographic options.

It was shown [34] that the precipitates enriched by impurities are usually observed in the SiC layers doped with Al, B, W, Ta and other impurities. As a result total concentration of these impurities in the doped layers can exceed on 2–3 orders of magnitude of the value of solubility limit typical for homogeneous solid solution. X-ray analysis shows that precipitates in SiC are usually carbides of the doping impurities.

Precipitates were observed in SiC crystals with low impurity content. For example precipitates enriched by boron impurity were discovered in SiC crystals, in which concentration of boron in homogeneous solid solution was near 10^{16} cm^{-3} , i.e., four orders of magnitude lower than solubility limit [23].

Impurity rich precipitates are concentrated on the crystal surface mainly near dislocations, pores, macrosteps, interpolytype boundaries and other structural and morphological defects (**Figure 6**) [36]. As a rule, higher impurity content caused by existence of precipitates was observed in SiC layers grown on (0001)C face. But concentration of the same impurities in homogeneous solid solution, on the contrary, is higher for layers grown on (0001)Si face. According to the results of autoradiographic investigations it is caused by larger sizes of the inclusions which are formed by growth on (0001)C faces [43].

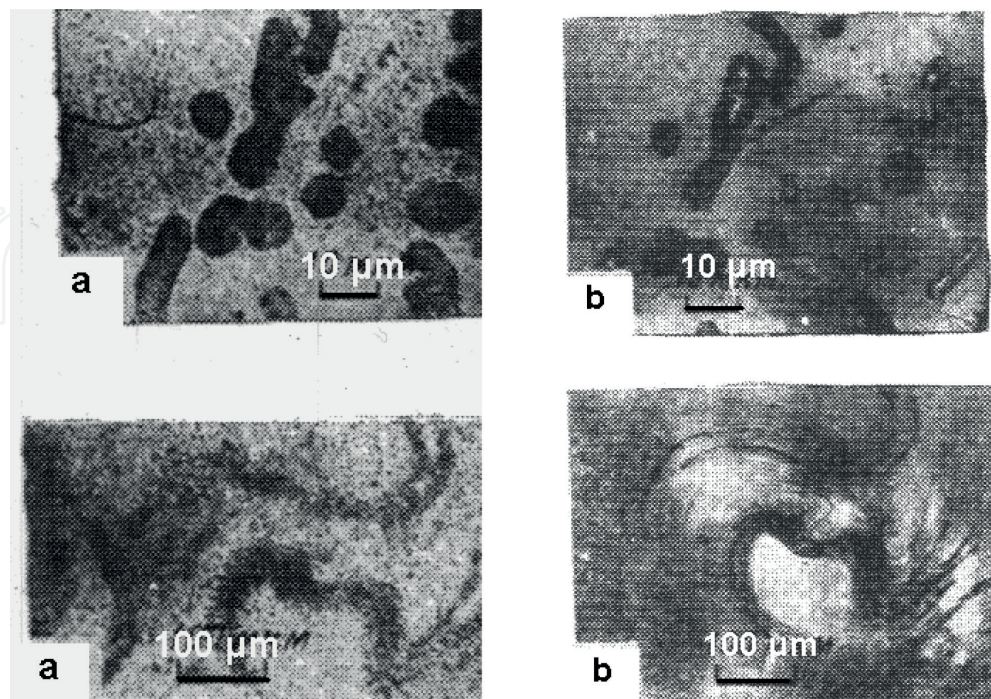


Figure 6. Alpha-particle autoradiogram of 6H SiC sample after diffusion of boron from vapor phase (magnitude X40). It can be seen that second phase inclusions enriched boron are concentrated mainly at points of dislocations emergence and macrostep boundaries (a). Optical microscopy of the same parts of the surface is shown (b) [42].

At high growth rates the probability of precipitates enriched by impurities formation increases, which leads to worse crystal quality [43]. It is interesting that high density of precipitates leads to the decrease of impurity concentration in homogeneous solid solution. It was explained by the fact that precipitates could be getters for impurity atoms.

Features of macrosegregation on polar {0001} faces are explained by various surface energies of these sides. Lower surface energy of the C-face promotes formation of three-dimensional germs on it. Taking into account that formation of precipitates reduces desorption of impurity atoms, it becomes clear why total concentration of impurity is higher in the layers grown on the C-face than on the Si-face.

3. Doping of SiC during thermal diffusion

Diffusion of impurities is one of the main ways of device structures formation in semiconductors. Investigation of diffusion in solid states gives rich information on the nature of native defects, mechanisms of defect formation and migration and interactions of native defects with impurity atoms at high temperatures.

We have studied diffusion of impurities B, Al, Ga, Be, Li, N, P and O. Diffusion of impurities was carried out from vapor phase, and impurity vapor pressure was set by the source temperature. The investigated samples were located in the hot zone. In the colder zone a diffusant was placed. It was usually in an elementary state.

For measurement of diffusive distribution we applied the whole set of methods including special nuclear and physical techniques, which allowed to study the concentrational distribution of impurity both in intrinsic SiC and in heavily doped SiC samples. If these methods could not be used, the diffusive profile was defined with the help of standard semiconductor techniques, such as Hall method, C-V measurements and p-n junction method.

3.1 Diffusion of lithium

Diffusion of Li was carried out from vapor phase at the temperatures 1250–2200°C [45]. The method of track autoradiography [45], based on registration by a solid-state track detector the Li (n, α) H nuclear reaction products, was applied for direct definition of Li concentration in the diffusive layer by radiation of samples with a flow of thermal neutrons.

The results of study of Li diffusion in SiC are presented in [45]. They demonstrate that diffusive distribution of Li in SiC can be described by standard erfc function. The dependence of diffusion coefficient (D_{Li}) on the doping level and the conductivity type of the studied samples was not revealed. The temperature dependence D_{Li} on the temperature is shown in **Figure 10**. High diffusive mobility of Li atoms in combination with rather low activation energy ($\Delta E = 1.7 \text{ eV}$) leads to claim that Li in SiC, as well as in Si and Ge, diffuses by interstitial mechanism.

Diffusion of Li and hydrogen in SiC was also studied in works [47, 48]. Impurities were entered into the crystal by ionic implantation. It was shown that these impurities diffuse with rather high rate along interstates, and diffusion parameters rather well correlate with the data of the work [45].

3.2 Diffusion of beryllium

Diffusion of Be in SiC was carried out at the temperatures 1700–2250°C [49]. The p-n junction method was used for diffusion profile discover. It was supposed

that Be impurity near p-n junction is completely ionized. At temperatures of diffusion above 1900°C the concentration profile had two clearly marked regions. Each of them could be described by one coefficient of diffusion.

Diffusion of Be in p-SiC <A1> was studied at temperatures 1300–2000°C by the methods of layer-by-layer measurement of conductivity and Hall effect [50]. After diffusion of Be the reduction of value (Na-Nd), concentration of holes and their mobility were observed. Since the mobility of free holes falls and conductivity value along the impurity zone grows after diffusion of Be, it is possible to assume that the value (Na-Nd) decreases due to compensation of acceptors by the incorporated donor impurity (in this case, Be). It helped to define the diffusive profile of Be in p-SiC.

Parameters of diffusion of Be and Li in p-SiC were rather similar. Therefore, we made a conclusion that diffusion of Be, as well as Li, in heavily doped p-SiC is carried out by an interstitial mechanism. This assumption is supported by results of the analysis of donor-acceptor interaction [51], according to which donor Be has a charge +2. A small size of Be²⁺ ion (0.31Å) also promotes interstitial diffusion of Be. Apparently, in n-type SiC, the mechanism of diffusion is more complicated. And in this case, interstitial Be also quickly diffuses. But in p-type SiC quickly diffusing interstitial atoms are captured by traps (obviously, vacancies), which leads to diffusion slowing down. We believe that another diffusive-active state is the associate of Be atom with a vacancy. Such associates are found by electron paramagnetic resonance method in Be-doped SiC crystals [52]. Diffusion of Be in SiC from ion-implanted layer was studied in [53]. The results of this work correlate well with our data.

3.3 Diffusion of boron in SiC

Boron is the most important acceptor impurity and the activator of luminescence in SiC. Its introduction by diffusion is widely used for creation of various semiconductor devices. For better understanding of B diffusion mechanism, we carried out the research of B diffusion in pure and doped SiC at a wide variation of experimental conditions. The influence of temperature, structure of the vapor phase, boundary conditions and the initial condition of impurity on diffusion were specially studied.

In the majority of experiments diffusion was carried out from vapor phase in the temperature range 1500–2600°C. The diffusive profile of boron atoms was defined by the method of track autoradiography based on registration of α -particles according to nuclear reaction: $B^{10}(n, \alpha) Li^7$ [41]. The use of boron isotope B^{10} as diffusant allowed to increase sensitivity of the method up to $5 \times 10^{15} \text{ cm}^{-3}$ with an accuracy $\pm 15\%$. Distribution of boron acceptors was found additionally by Hall measurements at 77–1100 K temperature range, capacitive and p-n junction methods [54, 55]. The results of the diffusive profile measurements received by different methods [41, 54–56] rather well correlated with each other, except heavily doped near-surface layer, where concentration of boron atoms could exceed concentration of acceptors by 1.5–2.0 times [41].

As a rule concentration distributions of boron had a step two-branch profile and could not be described by one coefficient of diffusion (**Figure 4**) [55]. It has been stated that the character of diffusion distribution and rate of diffusion strongly depend on the value of surface concentration (C_s) [55]. For low $C_s < 1 \times 10^{18} \text{ cm}^{-3}$ the diffusive profile could be described by one coefficient of diffusion. At increase of C_s the rate of boron diffusion in the volume region of distribution increased and the concentration profile took a step form. Besides, at high temperatures ($> 2100^\circ\text{C}$)

on the “tail” of the volume branch at $C_v < 5-10 \times 10^{17} \text{ cm}^{-3}$ a region with an abrupt inclination of the diffusive profile occurred. More detailed research of concentration distribution has allowed to find a minimum on the border of near-surface and volume regions [25]. For finding a charging condition of diffusion centers and identification of the impurity migration mechanism we carried out the diffusion study in SiC highly doped by donor and acceptor impurities.

3.3.1 Diffusion of boron in highly doped SiC crystals

We have studied diffusion of boron isotope B^{10} in SiC of n- and p-type conductivity doped with Al and N. Diffusion distribution B in SiC highly doped with nitrogen are presented in **Figure 7a**. The obtained results definitely show that nitrogen impurity leads to slowing down the rate of boron diffusion [57, 58]. This effect was especially considerable at high concentrations of nitrogen and low temperatures of diffusion, when the coefficient of boron diffusion decreased almost to an order of magnitude. It could not be explained only by the donor-acceptor interaction, as it took place, in particular, in intrinsic material when concentration of impurity is lower than n_i . Therefore, the main reason for slowing diffusion down may be the formation of complexes according to reaction: $B_{Si} + N_c \rightarrow (BN)$. This interaction is promoted by high BN binding energy, and the fact that these impurities replace different units in the SiC lattice.

On **Figure 7b** concentration profile of Boron in SiC doped with Al impurity is shown. Concentration of impurities in the SiC samples was changed from 10^{17} to 10^{21} cm^{-3} [57]. According to the obtained results (**Figure 7b**) by increase of acceptor concentration the rate of boron diffusion in SiC considerably increases. In case of low surface concentration $C_s < 1 \times 10^{18} \text{ cm}^{-3}$, when distribution in n-type, as well as in p-type, is described by one coefficient of diffusion, this dependence is well described by one coefficient of diffusion. It looks like: $D = D_i (p/n_i)$, where D and D_i —coefficients of boron diffusion in p-type and intrinsic SiC, correspondingly; p —concentration of free holes; and n_i —concentration of own carriers. The energy activation of diffusion in heavily doped SiC is 3.4 eV, that is 2.2 eV lower than in pure SiC. Thus, within the frames of vacancy model, it is possible to make a conclusion that diffusion of boron is carried out with participation of the vacancies with a charge +1.

3.3.2 Diffusion of impurities in SiC polytypes

Our research of diffusion of impurities in SiC crystals of various polytypes (3C, 4H, 6H, 8H, 15R, 21R and 27R) has revealed dependence of the diffusion rate

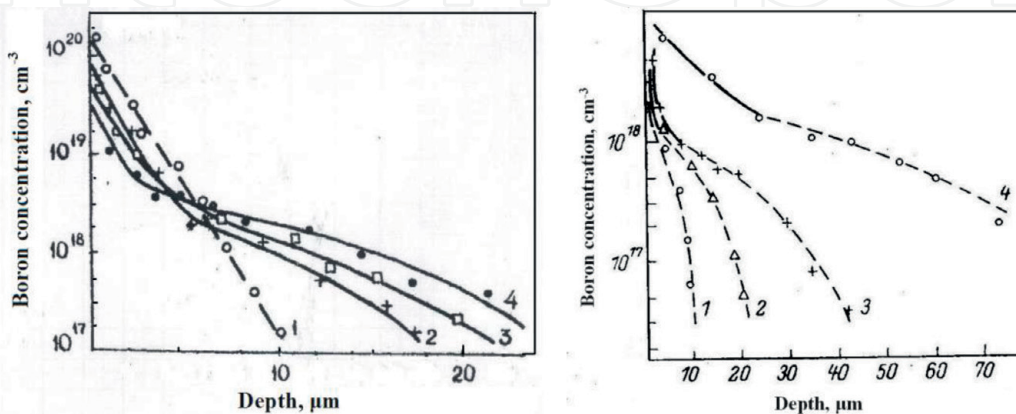


Figure 7. Diffusion distribution of Boron in SiC crystals doped with impurities N (a) and Al (b). Impurity concentrations (cm^{-3}): N— 1.1×10^{20} (1); 2.5×10^{19} (2); 1.5×10^{19} (3); 2×10^{17} (4). Al— 4×10^{17} (1); 2×10^{18} (2); 6×10^{19} (3); 10^{20} (4).

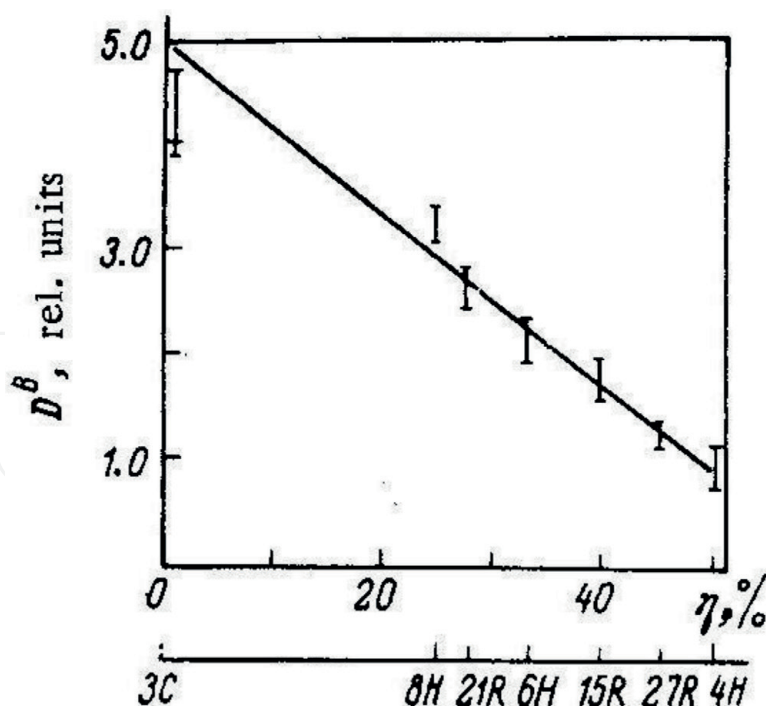


Figure 8.
 Dependence of boron diffusion coefficient in SiC on polytype hexagonality percent.

on the SiC polytype (**Figure 7**) [59]. The results for boron diffusion are presented in **Figure 8**. They show the existence of a correlation between the value of diffusion coefficient and the degree of polytype hexagonality. The highest rate of diffusion is observed in cubic SiC. On the contrary, the lowest one is revealed in the most hexagonal 4H SiC polytype. Such dependence is caused by the increasing concentration of carbon vacancies in more cubic polytypes [4].

3.3.3 Constant-concentration diffusion of boron

For clarification of abnormal nature of diffusive distribution at high concentrations of boron, we have used a technique of constant-concentration diffusion [60]. There is practically no gradient of concentration of diffusing impurity in this case. For this purpose we studied diffusion of isotope B^{10} in SiC crystal preliminary highly doped with isotope B^{11} at the level of $(5-6) \times 10^{19} \text{ cm}^{-3}$.

According to the obtained data concentration distribution at constant-concentration diffusion of boron, unlike chemical diffusion, has a standard form (**Figure 9**).

By analysis it is necessary to consider that boron is an acceptor impurity in SiC and consequently, with increase in its concentration, provided that $C_B > n_i$, the coefficient of diffusion of boron should increase. However, the coefficient of constant-concentration diffusion of B was even lower than that of chemical diffusion in intrinsic SiC. The difference in diffusion mobility of boron becomes especially considerable if we compare the diffusion distributions of constant-concentration diffusion and boron distribution in p-type SiC doped with Al (**Figure 9**). The results of the experiment show that at identical concentration of acceptor impurity, the diffusion coefficient in p-SiC (Al) is nearly three orders of magnitude higher than in p-SiC (B).

The obtained results can be explained consistently, having assumed that boron at concentration higher than 10^{18} cm^{-3} creates traps for diffusive-active state of boron. Existence of these traps, apparently, is responsible for occurrence of abrupt near-surface region of the diffusive profile at usual chemical diffusion. It is natural to assume that such traps are boron atoms located in units of the lattice and form

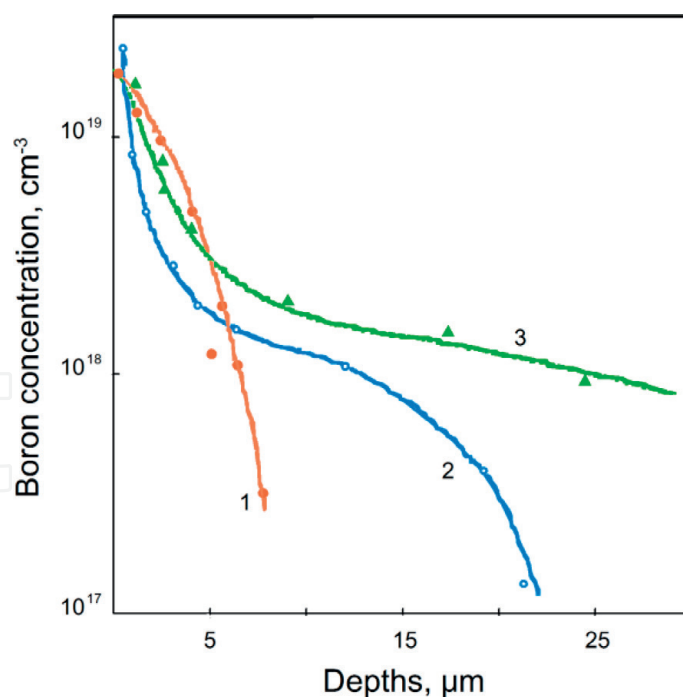


Figure 9.

Diffusion distributions of the isotope ^{10}B in SiC: 1—constant-concentration diffusion in SiC layer (^{11}B) with boron concentration (^{11}B) $5 \times 10^{19} \text{ cm}^{-3}$; 2, 3—chemical diffusion in samples with different impurity concentration Al (cm^{-3}): 2×10^{16} (2); 5×10^{19} (3).

the inactive associates or clusters including several atoms of boron with mobile boron center. This assumption is proved by high binding energy of boron atoms as well as experimentally observed formation of second phase clusters enriched by boron impurity during diffusion annealing [42].

3.3.4 Boron diffusion from solid phase

Comparative study of boron diffusion from vapor and solid phase revealed essential dependence of boron diffusion parameters on the initial state of impurity [9, 61]. In our experiments in case of diffusion from solid phase, the source of impurity was usually located in preliminary grown epitaxial SiC layer doped by boron. In both cases surface concentration of boron was practically the same.

At short periods of annealing there were no observed considerable differences in the character of distribution and the rate of boron migration by diffusion from vapor and solid phase. However, with increase of the annealing period in case of solid phase diffusion, there was a distinct tendency of diffusion slowing down. A similar effect was observed in experiments on study redistribution of impurity by secondary annealing of diffusive samples.

It was found out that the rate of boron diffusion from solid phase strongly depends on growth conditions of doped epitaxial SiC layer, serving as a source of diffusing impurity. The increase of growth temperature of this layer by maintaining the constant concentration of boron in it leads to decrease of the diffusion rate. For example by diffusion of boron from SiC (B) layer grown at 2550°C , the coefficient of boron diffusion was 10^3 – 10^4 times lower than by diffusion from vapor.

Comparison of concentration profiles of diffusive samples before and after secondary annealing has shown that boron transition to crystal volume generally comes from heavily doped layer ($C_B > 10^{19} \text{ cm}^{-3}$), where a considerable part of boron impurity was in electrically inactive state.

The obtained results demonstrate that there are several boron centers in SiC with various diffusive mobility and relaxation time of processes connected with change of impurity centers state. This time is rather long than time of diffusive annealing. If the impurity center is situated in diffusion-active state (for example, is found in interstitial position or forms a mobile associate with a vacancy or interstitial atom), then the rate of diffusion will be raised. On the contrary if the impurity atoms are located in the lattice points and probability of forming of mobile centers is very low, then impurities diffusion rate sharply decreases. Obviously, the creation of the mobile centers of impurities by ion implantation can explain high diffusion rate of implanted atoms in comparison with vapor phase diffusion. The same reason explains acceleration of diffusion at oxidation and silicidation of the surface [62].

3.3.5 Mechanism of boron diffusion

The mechanism of boron diffusion is difficult to explain in the frames of interstitial model. Actually, the activation energy of boron diffusion is considerably high. Unlike Be we do not observe noticeable compensation of acceptor centers during boron diffusion in p-type SiC. It is difficult to explain the whole set of experimental data within a simple vacancy model. Within such mechanism it is difficult to understand the reason of the complicated character of diffusion distribution of boron; dependence of the diffusion coefficient on the surface concentration band; and the features of boron diffusion from solid phase. It is also necessary to take into account that boron in SiC mainly replaces silicon, and a simple mechanism of its diffusion along carbon vacancies is seemed improbable. Besides, the activation energy of boron diffusion in heavily doped p-SiC is much less than calculated [57].

Obviously, it should be assumed that a rapidly diffusing component is complex (B-Vc), in which concentration is limited by a flow of carbon vacancies injected from the heavily doped surface layer [24]. It is possible, provided that the concentration of generated vacancies is higher than equilibrium, defined, for example, by Shottky constant. It is important that the defect states injected in the crystal volume are significantly nonequilibrium. Such assumption is confirmed by strong dependence of boron diffusion coefficient on surface conditions and also by experimental evidence of nonstationarity of diffusion process from solid phase [61]. By increasing the density of dislocations which are vacancy traps the coefficient of boron diffusion decreases [63].

With increase of diffusion temperature one should expect relative reduction of contribution of this mechanism, both due to increase of concentration of thermal vacancies and probability of disintegration of rapidly diffusing associates. Model of boron diffusion was presented [64].

Another mechanism of boron diffusion in SiC was proposed in refs. [65, 66]. The authors offered that boron diffusion was realized by kick out mechanism, in which silicon interstitials play main role. Excess Si interstitials are created by ion implantation or by high boron impurity concentration [65].

3.4 Diffusion of aluminum and gallium

Aluminum and gallium are the shallowest acceptors in SiC. Therefore, interest to diffusion as a method of obtaining diode structures of various devices on the basis of SiC, such as power diodes, has been shown for a long time. Meanwhile, studying of these impurities diffusion meets great difficulties, mainly, because of their low diffusion mobility.

Our investigation of Al and Ga impurities diffusion was carried out from vapor phase in the range of temperatures of 1800–2400°C [67]. Metal Al or Ga was used as source of impurity. Diffusion distribution was studied by van der Pauw method. P-n

junction method was also used. Then, the results [67] were supported by SIMS. The obtained results prove a rather complex mechanism of Al diffusion. Concentration distribution of Al has very abrupt near-surface region and a smoother volume region. The latter can be described by erfc function. The boundary concentration for the volume branch was $1 \times 10^{18} \text{ cm}^{-3}$. It is not less than three orders lower than true surface concentration of Al.

For studying Al diffusion in a near-surface layer the Hall method [68] was used, and the measurements were taken by consecutive removal of layers 0.2–0.3 microns thick. As a result the diffusion coefficient for the near-surface branch has been defined as $5.6 \times 10^{14} \text{ cm}^2/\text{s}$ at 2200°C . This value considerably exceeds the diffusion coefficient of Al found by the method of p-n junction in a sample with concentration of donors (nitrogen) $N_d = 10^{19} \text{ cm}^{-3}/\text{s}$.

The diffusion of Al from solid phase was also studied. The source of impurity was previously grown epitaxial SiC layer doped by Al. For study distribution of Al during diffusion annealing, the capacitive method was used. According to the obtained data the rate of Al migration from the epitaxial SiC(Al) layer was abnormally low (**Figure 7**). The diffusion coefficient for solid state diffusion was 10^3 – 10^4 times lower than by diffusion from vapor phase, and the activation energy (ΔE) was near 11 eV. Let us note for comparison that by diffusion from vapor, the activation energy of diffusion was $\Delta E = 6.1 \text{ eV}$. These results correlate with data of van Opdorp [69], which show that diffusion coefficient from solid phase was 10^4 times lower than in case of vapor phase diffusion.

It is possible to conclude that diffusion of Al from vapor phase is carried out by migration of metastable (Al-Vc) complexes or deep Al centers. However, in the SiC(Al) crystals grown at high temperature, most of Al atoms, obviously, are situated in silicon units, and the concentration of rapidly diffusing (Al-V) associates is very low. In this case diffusion is possible only along silicon vacancies and demands considerable power expenses.

Diffusion profiles of Ga have no sharp near-surface region [24]. However, surface concentration of Ga ($C_s = (3\text{--}5) \times 10^{17} \text{ cm}^{-3}$) is much lower (30–50 times) than its contents in the epitaxial SiC layers grown under the same conditions. In general parameters of Ga and Al diffusion are close, which indicates identity of their diffusion mechanisms.

3.5 Diffusion of phosphorus

Phosphorus (P) is a donor impurity in silicon carbide. For estimation of diffusive mobility of P in SiC we used samples containing P entered by the method of transmutation doping on charged high-energy particles [70]. Change of the concentration profile of phosphorus in the sample by its high-temperature annealing was investigated. The results received by this technique reflect more adequately the process of solid-phase diffusion; as in this case the impurity centers are not entered through the phase boundary, and diffusion is carried out only due to thermal activation of atoms located in regular positions in the crystal volume. Thus, the probability of participation of impurity conditions generated on the surface in diffusive stream is minimized. The obtained data characterize diffusion in own semiconductor according to the inequality: $C_p \ll n_i$; (where C_p is concentration of the transmuted phosphorus; n_i —concentration of intrinsic charge carriers). By transmutation doping radiation defects are also entered. However, they are generally annealed at $T < 2000^\circ\text{C}$, and their influence on the rate of impurity migration at higher temperatures can be neglected. 6H-SiC samples grown by the Lely method, mainly n-type of conductivity, doped by nitrogen were used. The concentration of noncompensated donors was $(N_d - N_a) = (2\text{--}4) \times 10^{18} \text{ cm}^{-3}$. In the number of experiments the samples of p-SiC heavily doped by aluminum ($C_{Al} \ll 5 \times 10^{20} \text{ cm}^{-3}$) were also used.

For transmutation introduction of P SiC samples were irradiated by α -particles with the energy of 16 and 20 MeV at the current density $j = 0.1 \text{ mA/cm}^2$. For receiving sharper concentration profile of phosphorus, radiation was carried out at oblique incidence of the beam at the angle of $6\text{--}30^\circ$. Transmutation doping was carried out due to a nuclear reaction $^{29}\text{Si}(\alpha, p)^{32}\text{P}$. After that radiation samples were annealed in closed graphite containers in the atmosphere of argon at the temperature of $2000\text{--}2600^\circ\text{C}$. For evaporation reduction samples were located in an isothermal zone surrounded from all sides by fine SiC powder. The time of annealing varied from 30 min to 10 h, the thickness of the evaporated SiC layer in the course of annealing did not exceed 2–3 microns. The concentration profile of phosphorus was defined by measurement of residual β -activity of samples at consecutive removal of surface layers by the method of chemical etching in KOH alkali solution. The thickness of the removed layers was 1 micron. The profile of radioactive phosphorus was at the same time analyzed in a control sample that was not exposed to diffusive annealing. According to the received results, noticeable changes of the concentration profile were revealed only at temperatures of annealing above 2400°C . The diffusion coefficient was defined in the assumption that Fick's law was realized. For this purpose one-dimensional diffusion in a half-space with impenetrable border was considered.

The temperature dependence of P diffusion coefficient is given in **Figure 10**. Very high value of activation energy of phosphorus diffusion $\Delta E^{\text{P}} = 11.2 \text{ eV}$ attracts attention. It is higher than in case of self-diffusion of silicon ($\Delta E^{\text{Si}} = 8.18 \text{ eV}$) and carbon ($\Delta E^{\text{C}} = -8.2 \text{ eV}$) in SiC [46]. Note that in the studied temperature range, D^{P} is closer to the self-diffusion coefficient of silicon. At the same time the coefficient of self-diffusion of carbon is 2–3 orders higher. Therefore, it is possible to assume that migration of phosphorus is carried out along carbon vacancies. However,

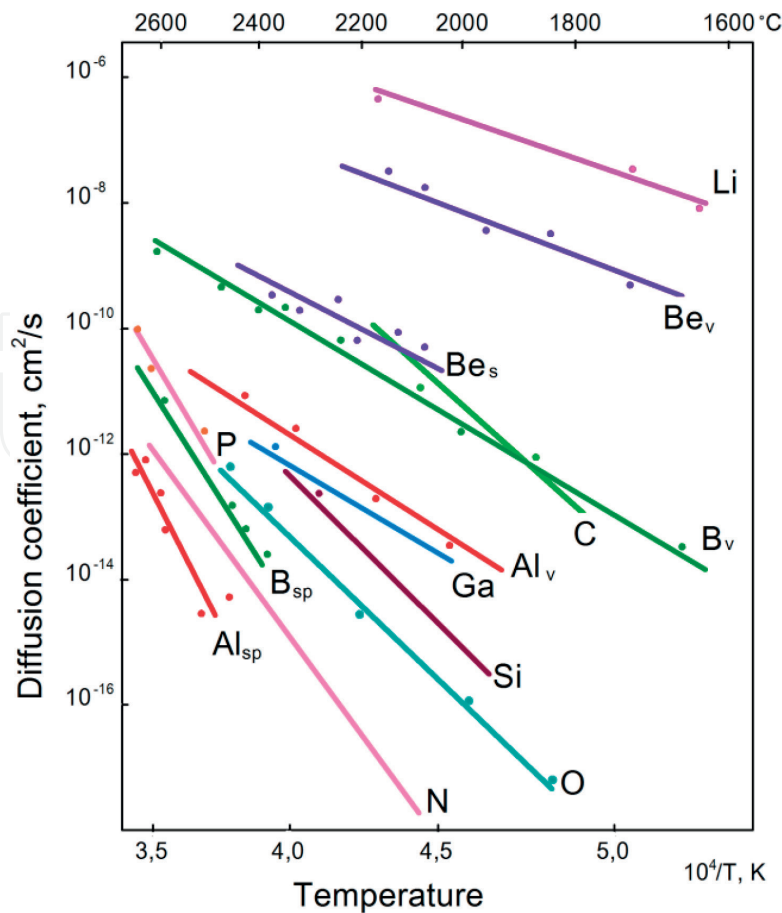


Figure 10. Dependence of diffusion coefficients of impurities in SiC from vapor phase (Li, Be_v, Be_s, B_v, Al_v, Ga and N) and from SiC solid phase (P, B_s, Al_{sv}). B_v, Al_v, Be_v—volume branch. Be_s—surface branch. Data on self-diffusion (C, Si) are taken from [46].

N	Impurity	$D_0, \text{cm}^2/\text{c}$	$\Delta E, \text{eV}$	References
1	Nitrogen	$4.6\text{--}8.7 \times 10^4$	7.6–9.35	[71]
2	Phosphorous	1.3×10^{10}	11.6	[70]
3	Boron	3.2	5.1	[14]
4	Aluminum	8.0	6.1	[5]
5	Gallium	0.17	5.5	[19]
6	Beryllium	0.3	3.1	[3]
	Quick diffusion	32	5.2	
	Slow diffusion			
7	Lithium	1.2×10^{-3}	1.7	[66]

Table 3.
Parameters of impurity diffusion in SiC from vapor phase.

within the frames of such model, it is difficult to understand the reason of higher rate of phosphorus migration in highly doped p-SiC.

It is known that silicon vacancies in SiC are charged negatively; therefore, their concentration has to decrease with the increase of concentration of acceptor impurity, leading to reduction of phosphorus mobility. A reverse effect rather proving the mechanism of phosphorus diffusion with participation of carbon vacancies was experimentally observed. In this regard we will note that activation energy of phosphorus diffusion (ΔE) does not greatly differ from earlier defined ΔE value for nitrogen diffusion [71]. Nitrogen replaces carbon in SiC lattice and, obviously, migrates along carbon vacancies.

3.6 Diffusion of nitrogen and oxygen in SiC

Nitrogen and oxygen are donor impurities in SiC. Diffusion of nitrogen was carried out in p-type SiC samples doped by Al [11]. The temperature of diffusion varied from 1900 to 2500°C. Diffusion depth was found by Hall and p-n junction methods. Molecular nitrogen was used as diffusant. The temperature dependence of nitrogen diffusion coefficient is presented in **Figure 10**. It supports the early data of Kroko and Milnes [71].

The sources of oxygen impurity were CO₂ or SiO₂. Diffusion depth is found by measurement of thickness of the luminescence layer [72]. Higher oxygen diffusion can be explained by forming mobile complexes of impurity atoms with native defects. Unfortunately, the lack of reliable methods of identification of oxygen in SiC complicates the analysis of its diffusion mechanism.

The data of impurity diffusion in SiC are presented in **Table 3** and in **Figure 10**.

Let us note that solid state diffusion of B and Al impurities is characterized by slower rate than self-diffusion [46]. We consider that self-diffusion coefficients are actually lower than provided in the quoted works. Authors of the work [73] come to the same conclusion.

4. Conclusion

We have studied the processes of SiC doping by sublimation growth that allowed to receive the crystals and epitaxial SiC layers doped by various impurities and to define the condition of a number of impurity centers, including B [74, 75], Be [76], P [77], Sc [78], Mo [79], Er [80], Fe and Ni [81].

It is shown that the mechanism of SiC doping can be described within kinetic approach. High binding energy and, as a result, low concentration of equilibrium point defects cause low rate of solid-phase diffusion of the majority of impurity atoms. Noticeable diffusion at atom replacement from their regular positions occurs in SiC at the temperatures above 1800°C. Low diffusive mobility of the majority of impurity atoms leads to the fact that at actual growth rates, the external phase–crystal balance is not realized. It makes impossible consideration of the doping process within thermodynamic concepts. Doping of SiC by growth has a kinetic nature and reflects the external phase–crystal surface balance. Therefore, the content of impurities strongly depends on orientation of the growing surface. The instability of growth process leads to nonuniform doping. Uniform doping can be achieved by growth on a nonsingular surface. Small areas of octahedral and tetrahedral emptiness limit solubility of impurities with large atoms sizes.

By analysis of the doping processes it is necessary to consider high reactionary ability of native point defects, leading to formation of nonequilibrium stable associates with participation of both own defects and impurity atoms. These associates or clusters keep stability up to high temperatures. Formation of clusters is promoted by high mobility of own point defects. Interaction of impurity and matrix atoms promotes formation of precipitates. Such process can actively proceed on the surface of growing crystal that is facilitated by high surface diffusion. The interaction of impurity atoms with own defects leads to creation of a number of impurity states.

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