On some specific features of the silicon carbide heteropolytype epitaxy

S. Yu. Davydov¹, A. A. Lebedev¹,², L. V. Shakhov¹, P. V. Bulat²

¹ Ioffe Physical Technical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia
² St. Petersburg National Research University of Information Technologies, Mechanics and Optics, St. Petersburg, 197101 Russia

ABSTRACT

Specific features of the SiC layer formation having the polytype differs from the SiC substrate polytype are considered within the scope of simple models. The effect of nonstoichiometry, impurities, C and Si faces on the heteropolytype epitaxy are considered. By means of Harrison’s bond orbital model it is shown that the adsorption energy for the C face is greater than for the Si face. On the bases of the earlier proposed D-model and vacancy model it is proposed that impurities which enforce the possibility of interpolytype transition decrease the time of processes and the transition layer widths. For the interpretation of the transition layer periodic structure consisted of initial and final polytypes, the model of specific spinodal decomposition is proposed.

Keywords: silicon carbide; heteropolytype epitaxy; impurities; models

1. Introduction

One of the most impressive features of silicon carbide is that it can form a great number of structures: at present, more than 200 different crystalline modifications (polytypes) of SiC are known. However, there still is no commonly accepted theory that can explain the existence of such row of polytypes and determine conditions for their mutual transformations. Only in two SiC polytypes the positions of all atoms are equivalent: they are cubic 3C polytype and hexagonal 2H polytype⁴⁻⁵. In all other cases, atoms may occupy sites of both types with the different numbers of atoms in hexagonal \((N\text{hex})\) and cubic \((N\text{cube})\) positions. Therefore, it is convenient to characterize polytypes by their hexagonality \(D\), which is defined as \(D = N\text{hex} / (N\text{hex} + N\text{cube})\). It was shown in [3-5] that the concentrations of carbon \((N\text{C})\) and silicon \((N\text{Si})\) vacancies in SiC polytypes strongly differ. With decreasing of the polytype hexagonality, i.e., on passing from 2H to 3C, the concentration \(N\text{C} / (N\text{Si})\) increases (decreases) by approximately a factor of 3 (4). It is noteworthy that this refers to the nonstoichiometric vacancies, but the Schottky and Frenkel defects (see, e.g.⁶).

It was also demonstrated in [3-5] that, in the processes of a heteropolytype epitaxy (HPE), impurities in the growth zone strongly affect the formation of a SiC polytype. So, for the 6H-SiC substrate doping by N, P, H, and Ba impurities stimulates the growth of 3C or other polytypes with hexagonality smaller than that of 6H. On the other hand, doping by Sc, Tb, Sn, Pb, Ge, Al, and B impurities favors formation of 4H or other polytypes with hexagonality larger than that of 6H. It was also noted that the crystallographic orientation of a substrate affects the impurity composition of a layer grown on this substrate. A higher content of Group-III impurities and transition metals was observed in the case of growth on the surface of the Si face. By contrast, the concentration of a Group-V impurity is higher in the case of growth on the surface of the C face.

It was found in the studies of 3C/6H-SiC heterostructure they that the transition layer is constituted by alternating stripes of 3C and 6H polytypes. These specific features of the transition region have also been observed by other authors (see references in [⁷]), but were not analyzed in detail.

All these specific features of the SiC polytypes HPE have no commonly accepted theoretical substantiations. In the present study, we suggest rather simple models making it possible to assess the specific features of how silicon carbide...
polytypes are formed.

2. On the comparative role of C and Si faces

Let us evaluate the adsorption properties of the C and Si faces of silicon carbide. We assume that surface atoms have dangling sp<sup>3</sup> orbitals whose energy \( \varepsilon_h = (\varepsilon_s + 3\varepsilon_p)/4 \), where \( \varepsilon_s(p) \) is the energy of the \( |s\rangle \) (|p\rangle)-state of C and Si atoms. Using the Mann's tables of atomic energy terms\(^{[8,9]}\), we obtain \( \varepsilon_h(C) = -13.15 \) eV and \( \varepsilon_h(Si) = -9.39 \) eV, where energy is reckoned from the vacuum level. These sp<sup>3</sup> orbitals contain one electron each.

In accordance with Harrison's bond orbital model\(^{[8,9]}\), the energy of the \( \sigma \) bond between sp<sup>3</sup> orbital and \( |a\rangle \) state of an atom being adsorbed is given by

\[
E_b = -2\sqrt{V_2^2 + V_3^2} \left( 1 - \frac{2}{3} \alpha_c^2 \right).
\]

Here the covalent energy \( V_2 = \eta h^2 / md^2 \), where m is free electron mass, d is the interatomic bond length taken to be equal to the sum of the atomic radii of carbon and the adsorbed atom, and \( \eta \) is a numerical multiplier determined by the types of the states involved in the bonding\(^{[8,9]}\); the polar energy \( V_3 = (\varepsilon_h - \varepsilon_a)/2 \), where \( \varepsilon_a \) is the energy of the \( |a\rangle \) state of the adsorbed atom; the bond covalency is \( \alpha_c = V_2 / \sqrt{V_2^2 + V_3^2} \). It is assumed here that the adsorption bond is formed by two electrons. If the state \( |a\rangle \) is an \( |s\rangle \) state, then

\[
\eta = \eta_{sp^3/s} = (\eta_{ss\sigma} - \sqrt{3}\eta_{sp\sigma}) / 2,
\]

in the case of a \( |p\rangle \) state

\[
\eta = \eta_{sp^3/p} = -(\eta_{sp\sigma} + \sqrt{3}\eta_{pp\sigma}) / 2,
\]

where \( \eta_{ss\sigma} = -1.32 \), \( \eta_{sp\sigma} = 1.42 \), and \( \eta_{pp\sigma} = 2.22 \). Then, \( \eta_{sp^3/s} = -1.89 \) and \( \eta_{sp^3/p} = -2.63 \).

The input data and the results of calculations for atoms adsorbed on C and Si faces of SiC are listed in Table 1. The energies for all adsorbates except hydrogen are assumed to be \( \varepsilon_a = \varepsilon_p \) and are taken from\(^{[8]}\). For the atomic hydrogen, we assumed \( \varepsilon_a = -I \), where \( I \) is the ionization energy. The atomic radii \( r_a \) are reported in\(^{[10]}\). It follows from Table 1 that, in all the cases under consideration, the bonding energy \( |E_d| \) for the C face exceeds that for the Si face. This is accounted for by the fact that the interatomic bond length d is smaller in the first case, compared with the second, since \( r_a(C) < r_a(Si) \). Consequently, it follows, with consideration for the predominantly covalent nature of the bonding \(|V_2| > |V_3|\), that the C face has a higher adsorption energy.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>C</th>
<th>Si</th>
<th>B</th>
<th>Al</th>
<th>N</th>
<th>P</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>- ( \varepsilon_a )</td>
<td>11.07</td>
<td>7.59</td>
<td>8.43</td>
<td>5.71</td>
<td>13.84</td>
<td>9.54</td>
<td>12.60</td>
</tr>
<tr>
<td>( r_a )</td>
<td>0.77</td>
<td>1.18</td>
<td>0.97</td>
<td>1.43</td>
<td>0.71</td>
<td>1.30</td>
<td>0.53</td>
</tr>
<tr>
<td>( -V_2 )</td>
<td>8.45</td>
<td>5.27</td>
<td>6.62</td>
<td>4.14</td>
<td>9.15</td>
<td>4.68</td>
<td>8.52</td>
</tr>
<tr>
<td>C face</td>
<td>1.04</td>
<td>2.82</td>
<td>2.36</td>
<td>3.72</td>
<td>-0.69</td>
<td>1.81</td>
<td>0.28</td>
</tr>
<tr>
<td>( \alpha_c )</td>
<td>0.99</td>
<td>0.88</td>
<td>0.94</td>
<td>0.74</td>
<td>1.00</td>
<td>0.93</td>
<td>1.00</td>
</tr>
<tr>
<td>C face</td>
<td>5.85</td>
<td>5.75</td>
<td>5.74</td>
<td>7.03</td>
<td>6.19</td>
<td>4.21</td>
<td>5.69</td>
</tr>
<tr>
<td>$-V_2$, Si face</td>
<td>5.27</td>
<td>3.60</td>
<td>4.34</td>
<td>2.94</td>
<td>5.61</td>
<td>3.26</td>
<td>4.925</td>
</tr>
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<td>------------------</td>
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<td>------</td>
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<td>------</td>
</tr>
<tr>
<td>$-V_3$, Si face</td>
<td>-0.84</td>
<td>0.90</td>
<td>0.48</td>
<td>1.84</td>
<td>-2.23</td>
<td>-0.08</td>
<td>-1.61</td>
</tr>
<tr>
<td>$\alpha_c$, Si face</td>
<td>0.99</td>
<td>0.97</td>
<td>0.99</td>
<td>0.85</td>
<td>0.93</td>
<td>1.00</td>
<td>0.95</td>
</tr>
<tr>
<td>$-E_b$, Si face</td>
<td>3.73</td>
<td>2.76</td>
<td>2.98</td>
<td>3.61</td>
<td>5.12</td>
<td>2.18</td>
<td>4.12</td>
</tr>
</tbody>
</table>

**Table 1.** Input data and calculation results for atoms adsorbed on the C and Si faces of silicon carbide (all the energy-related parameters are given in eV, and $r_a$, in Å).

In principle, similar estimates can also be made for adsorbed molecules. However, we encounter certain complications in this case. First, molecules can undergo dissociation at the growth temperatures (~2000°C). If this is not the case, a question arises about the configuration of the adsorption complex. For example, CO molecules are bound to the surface of metals [e.g., Ru (001), Pt (111)] via a carbon atom, with the C–O bond being directed perpendicularly to the metal surface[11]. If we assume that the same pattern also occurs in the adsorption on silicon carbide, take that

$$e_a = -I$$

(where the ionization potential of CO is 14.01 eV[10]), and consider that the $\langle p \rangle$-state of carbon is involved in the adsorption bonding, we obtain

$$V_2 = -8.45 \text{ eV, } V_3 = 0.43 \text{ eV, } \alpha_c \approx 1 \text{, and } E_b = -5.67 \text{ eV for the adsorption on the C face; and } V_2 = -5.27 \text{ eV, } V_3 = 2.31 \text{ eV, } \alpha_c = 0.92 \text{, and } E_b = -5.07 \text{ eV for that on the Si face. }$$

In the case of adsorption of molecular nitrogen on W (110), the axis of the N$_2$ molecule is perpendicular to the surface [11]. Carrying the same configuration over to the case of adsorption on silicon carbide, taking that

$$e_a = -I = -15.58 \text{ eV[10], and assuming that the } \langle p \rangle \text{ -state of nitrogen is involved in the adsorption bonding, we obtain } V_2 = -9.15 \text{ eV, } V_3 = 1.22 \text{ eV, } \alpha_c = 0.99 \text{, and } E_b = -6.37 \text{ eV for the adsorption on the C face, and } V_2 = -5.61 \text{ eV, } V_3 = 3.10 \text{ eV, } \alpha_c = 0.88 \text{, and } E_b = -6.26 \text{ eV for that on the Si face. Thus, in these two cases, the C face adsorbs better than the Si face, although the differences between the values of $E_b$ are substantially smaller than those in the case of the atomic adsorption. However, in adsorption of NH$_3$ on Ru (001), the bonding occurs via a nitrogen atom and the symmetry axis of the molecule is parallel to the normal to the ruthenium surface[11]. In the case of adsorption on Si(100)-(2×1), the NH$_3$ molecule dissociates, with hydrogen atoms passing to the dangling sp$^3$ orbitals of silicon and passivating its surface. Hence follows that an automatic transfer of the structure of an adsorbed complex from a metallic to a SiC substrate may lead to errors.}

Thus, we demonstrated that the adsorption energy for the C face of silicon carbide exceeds that of the Si face. Because the fly-off (desorption) probability of an adsorbed species is $P_{des} \propto \exp\left(\frac{E_d}{k_BT}\right)$, it is clear that the C face of silicon carbide will contain a larger amount of impurities adsorbed from the ambient space, compared with the Si face. Because various impurities may favor, or hinder formation of a required polytype[1-5], it is necessary to choose the appropriate face of the substrate. It should be noted that the presence of an impurity in the growth zone is associated not only with the energies of adsorption on the C or Si face, but also with the accommodation coefficients K. These coefficients are determined by the probability that a particle impacting the surface remains there and transfers its kinetic energy to the substrate, rather than being rebound from the surface. For example, for N and P atoms, the coefficient K at a temperature of 1850°C for the C face exceeds that for the Si face, with the situation for B and Al atoms being the opposite. Thus, it is equally necessary to take into account both $P_{des}$ and K.

3. Influence of impurities

3.1 Hexagonality approach

Let us consider the HPE by the scheme used in [12], with the transition from the initial polytype to the final polytype characterized by the change in hexagonality D. In what follows, we address this description scheme as the D-model.

Assume that due to the HPE polytype 2 with hexagonality $D_2$ is formed on the polytype 1 with hexagonality $D_1$. These two polytypes are separated by the transition layer with thickness $L_T$. If the growth rate of this layer is G, then
the time of its formation \( t_T = L_T / G \). We write the equation describing the 1 \( \rightarrow \) 2 transition as

\[
\frac{dD}{dt} = \pm \frac{D}{\tau_{12}},
\]

(2)

where \( \tau_{12} \) is the transition time constant, the upper sign in the right-hand part of equation (2) corresponds to the case \( D_2 > D_1 \), and the lower sign, to \( D_2 < D_1 \), with \( D_1 \neq 0 \). According to \([12]\), the thickness of the transition layer is given by

\[
L_T^{12} = \pm G \tau_{12} \ln(D_2 / D_1).
\]

(3)

It is easy to show \([9]\), that for \( D_1 = 0 \) equation (2) becomes

\[
\frac{dD}{dt} = \frac{D + 1}{\tau_{12}}
\]

(4)

and expression (3) is transformed to

\[
L_T^{12} = G \tau_{12} \ln(1 + D_2).
\]

(5)

Because the only parameter of the D-model is the transition time constant \( \tau_{12} \), it may be assumed that it is this parameter that is affected by an impurity. If an impurity favors a higher yield of some definite polytype, it can be assumed that the corresponding time constant decreases as compared with the impurity-free case. For the case in which given impurity favors the 1 \( \rightarrow \) 2 transition, we rewrite the differential equation (2) in the form

\[
\frac{dD}{dt} = \pm \frac{D}{\tau_{12}^i} \pm \frac{D}{\tau_{12}^j},
\]

(6)

and for the opposite case in which the impurity hinders this transition, we have

\[
\frac{dD}{dt} = \pm \frac{D}{\tau_{12}^i} \mp \frac{D}{\tau_{12}^j},
\]

(7)

where \( \tau_{12}^i \) is the time constant, which describes the effect of the impurity (it is assumed that \( \tau_{12}^i > \tau_{12} \)). Then the resulting time constant of the process, \( \tilde{\tau}_{12} \), is given by

\[
\tilde{\tau}_{12} = \frac{\tau_{12}^i \tau_{12}^j}{\tau_{12}^i \pm \tau_{12}^j},
\]

(8)

where the upper sign refers to an impurity promoting the 1 \( \rightarrow \) 2 transition, and the lower sign, to that hindering this transition. As a result, according to (3) and (5), the width of the transition layer decreases for the impurity favoring this transition and increases otherwise. It is noteworthy that the change in the width of the transition layer allows an experimental verification.

### 3.2 Vacancy model

Let us now consider the vacancy model of the HPE process \([13,14]\), based on the fact that each silicon carbide polytype is uniquely characterized by the concentrations of carbon \( \left( N_C \right) \) and silicon vacancies \( \left( N_{Si} \right) \). In this case, the HPE process is a transition from the concentrations \( N_{1C} \) and \( N_{1Si} \) characterizing the substrate (polytype 1) to the concentrations \( N_{2C} \) and \( N_{2Si} \) characterizing the layer being formed (polytype 2). As shown in \([13]\), the time variation of the vacancy concentrations is described by the expressions

\[
N_C(t) = N_{1C} \exp(\mp t / \tau_C), \quad N_{Si}(t) = N_{1Si} \exp(\pm t / \tau_{Si}),
\]

(9)

where \( \tau_C \) and \( \tau_{Si} \) are the lifetimes of carbon and silicon vacancies in the transition layer, with the upper signs
related to the HPE process with \( D_2 > D_1 \), and the lower signs, to the opposite situation. Here, we assume that the changes in the concentrations of carbon and silicon vacancies are independent. A more general situation is considered in Appendix.

We reckon the coordinate \( z \) along the external normal to the substrate surface. The thickness of the layer formed during time \( t \) is \( z = Gt \). Then, expressions (9) can be rewritten as

\[
N_C(z) = N_{1C} \exp(\tau z / G \tau_C), \quad N_{Si}(z) = N_{1Si} \exp(\pm z / G \tau_{Si}).
\]  

(10)

On the assumption that the concentrations \( N_{2C} \) and \( N_{2Si} \) are reached at the same time \( t_T \), we obtain for the \( 1 \rightarrow 2 \) transition the following ratio

\[
\eta_{12} = \frac{\tau_{Si} / \tau_C}{\ln(N_{1C} / N_{2C}) / \ln(N_{2Si} / N_{1Si})}.
\]  

(11)

Fig. 1 shows how the ratio \( \eta = \eta_{12} \) dependence on the hexagonality \( D \) (\( D = D_2 \)) of the polytype grown on substrates with \( D_1 < D_2 \) (Fig. 1a) and \( D_1 > D_2 \) (Fig. 1b). It follows from Fig. 1a that, for all substrates except 3C, the function \( \eta(D) \) monotonically increase with increasing \( D \). For the 3C-substrate, the dependence \( \eta(D) \) has a minimum at \( D = 0.4 \) (15R). It follows from Fig. 1b that, in the \( 3C \rightarrow 8H \) transition, the ratio \( \eta \) decreases for all substrates (except 4H), and then increases with increasing \( D \).

For the transitions \( 27R \rightarrow 4H \) and \( 8H \rightarrow 3C \) not shown in Fig. 1, we have, respectively, \( \eta = 1.60 \) and 0.8615).

Let us take into account that, with increasing \( D \), \( N_C \) decreases and \( N_{Si} \) increases. Then, it can be easily shown that, for the case \( D_1 < D_2 \) (Fig. 1a), the condition \( \eta > 1 \) reduces to the inequality \( N_{1C} N_{1Si} > N_{2C} N_{2Si} \) \( (N_{1C} N_{1Si} < N_{2C} N_{2Si}) \). If, however, \( D_1 > D_2 \) (Fig. 1b), then

\[
N_{1C} N_{1Si} < N_{2C} N_{2Si} \quad (N_{1C} N_{1Si} > N_{2C} N_{2Si}).
\]

Fig. 2a shows how the product \( N_C N_{Si} \) depends on the hexagonality \( D \). The product \( N_C N_{Si} \) reaches its maximum value for the polytypes 15R and 27R, and the minimum value, for 3C. Thus, if the 15R and 27R polytypes are substrates, we have \( \eta > 1 \) for the \( 1 \rightarrow 2 \) transitions satisfying the condition \( D_1 < D_2 \), and \( \eta < 1 \) for those corresponding to the inequality \( D_1 > D_2 \). If the 3C polytype serves as a substrate \( (D_1 = 0) \), we obtain \( \eta < 1 \) for all the transitions.

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Figure 1. Ratio of the Si and C vacancy lifetimes, $\eta = \tau_{Si}/\tau_{C}$, vs. the degree of hexagonality $D$ ($D = D_1$) of the polytype grown on substrates with $D_1 < D_2$ (a) and $D_1 > D_2$ (b). It is reasonable to assume that, as in the case of the D-model, impurities that favor growth of poly type 2 make
times $\tau_{C}$ and $\tau_{Si}$ shorter. It can be shown that now the lifetimes of carbon and silicon vacancies are given by

$$\tau_{C,\text{Si}} = \frac{\tau_{C,\text{Si}}^{*} \tau_{C,\text{Si}}}{\tau_{C,\text{Si}}^{*} \pm \tau_{C,\text{Si}}}.$$  \hfill (12)

Here $\tau_{C,\text{Si}}^{*}$ is the impurity-induced characteristic times, the upper sign corresponds to impurities accelerating the transition, and the lower sign, to those hindering the process. Substituting (12) into (13), we get

$$\frac{L_{T}^{2}}{\tau_{G}} = G \tau_{C} \ln \frac{N_{1c}}{N_{2c}}, \quad M_{Si} = AG \tau_{Si} \frac{N_{1s} \ln(1 - \exp(-L_{T} / G \tau_{Si}))}{N_{1c} \ln(1 - \exp(-L_{T} / G \tau_{C}))},$$

which can be verified experimentally.

4. Spinodal decomposition model

In [7,12], the presence of stripes of various polytypes in the intermediate layer of heterostructures formed on silicon carbide polytypes was attributed to the spinodal decomposition. Usually, theory of spinodal decomposition considers the transition from a specially homogeneous state to a periodic structure [13]. In our case, the initial (assumed to be unstable) state is characterized by a monotonic function of the coordinate $z$. Therefore, it was necessary to make some simplified assumptions. So, in terms of the vacancy model only the linearized variation of the concentration of carbon vacancies was taken into account in [7,12]. In [13], the D-model was formulated, in which the spinodal decomposition was considered for close values of $D_{1}$ and $D_{2}$, which made it possible to introduce the notion of the average homogeneous state. Here, we use the vacancy model with account of vacancies variations in both Si and C sublattices free of any linearization.

Let the area of a growing layer be $A$. Using (9), we can demonstrate that the numbers of carbon and silicon vacancies accumulated in the transition layer are given, respectively, by

$$M_{C} = AG \tau_{C} N_{1c} \left[ \exp \left( \frac{L_{T}}{G \tau_{C}} \right) - 1 \right], \quad M_{Si} = AG \tau_{Si} N_{1s} \left[ 1 - \exp \left( - \frac{L_{T}}{G \tau_{Si}} \right) \right].$$  \hfill (13)

Because $L_{T} / G \tau_{C} = \ln \frac{N_{2c}}{N_{1c}}$ and $L_{T} / G \tau_{Si} = \ln \frac{N_{1s}}{N_{2s}}$, we have

$$M_{C} = AL_{T} \rho_{C}, \quad \rho_{C} = \frac{N_{2c} - N_{1c}}{\ln \frac{N_{2c}}{N_{1c}}},$$

$$M_{Si} = AL_{T} \rho_{Si}, \quad \rho_{Si} = \frac{N_{1s} - N_{2s}}{\ln \frac{N_{1s}}{N_{2s}}}. \hspace{1cm} (14)$$

Let $n_{i}$ stripes of the polytype ($i = 1, 2$) with lengths $l_{i}$ and vacancy concentrations $N_{iC}, N_{iSi}$ appear in the transition layer. Then

$$\zeta_{1} N_{C} + \zeta_{2} N_{Si} = \rho, \quad \zeta_{1} + \zeta_{2} = 1,$$

where $\zeta_{i} = n_{i} l_{i} / L_{T}, \quad N_{i} = N_{iC} + N_{iSi}$ and $\rho = \rho_{C} + \rho_{Si}$. We have

$$\zeta_{1} = \frac{N_{2} - \rho}{N_{2} - N_{1}}, \quad \zeta_{2} = \frac{\rho - N_{1}}{N_{2} - N_{1}}. \hspace{1cm} (15)$$

Tables 2 and 3 list the values of $\zeta_{1}$ for the $1 \rightarrow 2$ transitions that lead to an increase and decrease in the hexagonality. In the first case ($D_{2} > D_{1}$), a decrease in $\zeta_{1}$ and the corresponding increase in $\zeta_{2} = 1 - \zeta_{1}$ are observed with increasing $D_{2}$. In the second case ($D_{2} < D_{1}$), the values of $\zeta_{1}$ increase and those of $\zeta_{2}$ become smaller with decreasing $D_{2}$. Thus, the values of $\zeta_{2}$ also increase with increasing $D_{2}$. It is noteworthy that the values of $\zeta_{1}$ and $\zeta_{2}$ correspond to the fractions of the transition layer, occupied by the poly types of the substrate (poly type 1) and the film (poly type 2). Assuming, for example, that the numbers of stripes of poly types 1
and 2 in the transition layer are the same, \( n = n_1 = n_2 \), we obtain the corresponding widths \( l_i = \zeta_i (L_T / n) \). If we consider that these stripes have the same width, \( l = l_1 = l_2 \), the corresponding number of stripes is \( n_i = \zeta_i (L_T / l) \). These results are quite verifiable experimentally.

<table>
<thead>
<tr>
<th>Final → 8H → Starting 6H</th>
<th>15R</th>
<th>27R</th>
<th>4H</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C</td>
<td>0.5</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>8H</td>
<td>-</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>6H</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
</tr>
<tr>
<td>15R</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>27R</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 2. Values of \( \tilde{\zeta} \) for transitions from the initial polytype with a smaller hexagonality to final polytypes with a larger hexagonality.

<table>
<thead>
<tr>
<th>Final → 27R → Starting 15R</th>
<th>6H</th>
<th>8H</th>
<th>3C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4H</td>
<td>0.6</td>
<td>0.6</td>
<td>0.7</td>
</tr>
<tr>
<td>27R</td>
<td>-</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>15R</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
</tr>
<tr>
<td>6H</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
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<tr>
<td>8H</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 3. Values of \( \tilde{\zeta} \) for transitions from the initial polytype with a larger hexagonality to final polytypes with a smaller hexagonality.

Fig. 2b shows \( N_C / N_{Si} \) ratio dependence on \( D \). It is apparent that, at large \( N_C / N_{Si} \), i.e., at small \( D \), it can be taken that \( N_i \approx N_{iC} \) and \( \rho \approx \rho_C \). If, in addition, the values of \( D_1 \) and \( D_2 \) are not too different, it is acceptable to replace the real function \( N_C (z) \) with a linear one. Just these approaches were made in \(^{[7,12]}\). All these simplifications have been made due to the lack of an energy-related hierarchy of silicon carbide polytypes. However, it is quite reasonable to assume that the transition layer in which the concentration of vacancies does not correspond to any one of the known polytypes is unstable.
Figure 2. Product $N_{C} N_{Si}$ (a) and the ratio $N_{C} / N_{Si}$ (b) vs. the degree of hexagonality $D$. 
5. Concluding remarks

Thus, we made an attempt to provide a simple theoretical description for the available experimental data on the influence exerted by the C and Si faces, nonstoichiometry, and impurities on the HPE of silicon carbide. The adsorption energy estimations demonstrate that the C face of SiC has a higher adsorption energy than the Si face. On the assumption that the impurities affect the characteristic times of the HPE process, their influence on the transition layers width is clarified. To explain the presence of stripes of various polytypes, we presented the spinodal decomposition model taking into account changes in the vacancy concentrations in both sublattices of SiC. In all cases, we aspired to achieve the maximal simplicity of description and a common approach to the phenomena under study. Unfortunately, the lack of quantitative information related to the issues under discussion hinders theoretical studies.

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Appendix

Let us take into account that in any \( 1 \leftrightarrow 2 \) transition between polytypes 1 and 2, an increase in the concentration of carbon vacancies, \( N_C \), is accompanied by a decrease in \( N_{Si} \) \[13\]. It can be concluded that a decrease (increase) in the vacancy concentration in one sublattice leads to generation (absorption) of vacancies in the other sublattice. Then we can write

\[
\frac{dN_C}{dt} = \tau_C^{-1} N_C - g_{Si} N_{Si}, \quad \frac{dN_{Si}}{dt} = \mp \frac{N_{Si}}{\tau_{Si}} - g_C N_C.
\]

(A.1)

Here, the coefficients \( g_C \) and \( g_{Si} \) describe the mutual influence of the temporal changes in \( N_C \) and \( N_{Si} \), with the upper signs related to the HPE process with \( D_2 > D_1 \), and the lower signs, to the opposite situation. We consider that \( g_{C, Si} < \tau_{C, Si}^{-1} \). Because \( N_C \geq N_{Si} \) for all the polytypes under consideration (see Fig. 2 b), it is clear that the direction in which the concentrations change is determined by the first terms in the right-hand parts of equations (A.1).

It can be shown that the solution to (A.1) has the form of the following functions

\[
N_C(t) = N_{1C} \exp(\mp t/\bar{\tau}_C), \quad N_{Si}(t) = N_{1Si} \exp(\pm t/\bar{\tau}_{Si}),
\]

(A.2)

where the lifetimes of carbon (\( \bar{\tau}_C \)) and silicon (\( \bar{\tau}_{Si} \)) vacancies in the transition layer are given, with consideration for their mutual influence, by

\[
\frac{1}{\bar{\tau}_{C, Si}} = \frac{R + 1}{2\tau_{C, Si}} + \frac{R - 1}{2\tau_{C, Si}},
\]

(A.3)

where

\[
R = \sqrt{1 + 4\alpha}, \quad \alpha = \frac{g_C g_{Si} \tau_C^2 \tau_{Si}^2}{(\tau_C + \tau_{Si})^2}.
\]

(A.4)

Assuming that \( \alpha << 1 \), we approximately obtain

\[
\frac{1}{\bar{\tau}_{C, Si}} \approx \frac{1}{\tau_{C, Si}} + \frac{1}{\tau^*}, \quad \tau^* = \frac{\tau_C + \tau_{Si}}{g_C g_{Si} \tau_C \tau_{Si}}.
\]

(A.5)

Now, the \( \tau_{Si} / \tau_C \) ratio in the left-hand part of expression (13) should be replaced with

\[
\frac{\bar{\tau}_{Si}}{\bar{\tau}_C} \approx \frac{\tau_{Si}}{\tau_C} \tau_C + \tau^*.
\]

(A.6)
For the case $\tau_{\text{Si}} / \tau_C > 1$, we have $\tau_{\text{Si}} / \bar{\tau}_C < \tau_{\text{Si}} / \tau_C$; if, however, $\tau_{\text{Si}} / \tau_C < 1$, then $\bar{\tau}_{\text{Si}} / \bar{\tau}_C > \tau_{\text{Si}} / \tau_C$. Since the width of the transition layer is now given by the formula

$$L_T^{12} = \frac{G}{N_1} \ln \left( \frac{N_{1C}}{N_{2C}} \right) = \frac{G_{\text{Si}}}{N_{1\text{Si}}} \ln \left( \frac{N_{1\text{Si}}}{N_{1\text{Si}}} \right),$$

and, according to (A.5), the lifetimes $\bar{\tau}_C$ and $\bar{\tau}_{\text{Si}}$ decrease as compared with $\tau_C$ and $\tau_{\text{Si}}$, the transition layer becomes narrower, i.e., $L_T^{12} > \bar{L}_T^{12}$.

**References**