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Fig. 1

Figure 1: Fig. 1

Abstract

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CRYSTALLOGRAPHY

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ON THE SECTORIAL STRUCTURE OF β-SiC CRYSTALS

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Pure silicon carbide of the cubic modification is transparent and yellow in color, owing to the fact that the edge of its absorption band lies in the visible region of the spectrum (4400 Å) ([1]). However, a number of impurities give it a dark coloration (from olive-green to black), which makes it possible to trace clearly the distribution of impurities and shows that, during the growth of β-SiC crystals from the gas phase, their sectorial structure is very strongly manifested ([2]). We have investigated the sectorial distribution of nitrogen

Fig. 1. *a*—ideal form of β-SiC crystals grown from the gas phase by thermal decomposition of methyltrichlorosilane in hydrogen (combination of the positive and negative tetrahedron, the negative trigonal-tritetrahedron $\{\bar{2}11\}$, and the cube); $O = \{111\}$; $O' = \{\bar{1}\bar{1}\bar{1}\}$; $m' = \{\bar{2}11\}$; $a = \{100\}$; *b*—schematic representation of a real plate-type crystal with an entering dihedral angle at the site of one of the faces $\{\bar{1}\bar{1}\bar{1}\}$. Growth direction $\langle\bar{1}10\rangle$; $A = \bar{1}\bar{1}\bar{1}$; $p = \{\bar{3}31\}$; $m' = \{\bar{2}11\}$; $m = \{311\}$; $a = \{100\}$

and boron in β-SiC crystals obtained by thermal decomposition of methyltrichlorosilane in hydrogen on a graphite substrate heated to 1500–2000° ([3]).

The crystals have natural faceting. Goniometric measurements of a large number of crystals showed that the faces $\{111\}$, $\{331\}$, $\{\bar{1}\bar{1}\bar{1}\}$, $\{\bar{2}11\}$, and $\{100\}$ of the crystallographic zone $\langle 1\bar{1}0\rangle$ appear most often on β-SiC crystals. Figure 1a shows the ideal form of β-SiC crystals. Real crystals are rarely isometrically developed. β-SiC, like compounds $A^{III}B^{V}$, crystallizes in the zinc-blende lattice, $F\bar{4}3m$. The polarity of the β-SiC structure in the $\langle 111\rangle$ direction determines a number of features of the structure of β-SiC crystals. Thus, it was found that in β-SiC single crystals the growth rate of the faces of the positive tetrahedron is many times less than the growth rate of the faces of the negative tetrahedron. This leads to the fact that β-SiC single crystals have a plate-like form (Fig. 1b), and in place of the faces $\{\bar{1}\bar{1}\bar{1}\}$ there are formed roughened faces $\{h\bar{1}h\}$ (where

Fig. 2. Sectorial structure of a plate-like β-SiC crystal doped with nitrogen (photographed in transmitted light, after grinding and etching in a Na_2O_2 melt)

Figure 2: Fig. 2. Sectorial structure of a plate-like β-SiC crystal doped with nitrogen (photographed in transmitted light, after grinding and etching in a Na_2O_2 melt)

$h \geq 2$) and, in many cases, even an entering dihedral angle bounded by the planes $\{\bar{h}1\bar{h}\}$ and $\{hh1\}$. We shall call the most developed and most perfect face (111) of plate-like crystals the face B, and the face $(\bar{1}\bar{1}\bar{1})$ parallel to it, of somewhat smaller size, the face A.

The faces B (111) and A $(\bar{1}\bar{1}\bar{1})$ have not only different size and different perfection, but also different etchability. When crystals are etched in a melt of $KOH + KNO_3$ $(1 : 4)$ for 3–5 min at a temperature of $\sim 500^\circ$, well-defined triangular etch pits appear on the A faces (and the other $\{\bar{1}\bar{1}\bar{1}\}$ faces); on the B faces (and the other $\{111\}$ faces) such pits do not arise. All this makes it easy to distinguish the A and B faces.

Figure 2 shows a photograph of a plate-like β-SiC crystal doped with nitrogen. It is clearly seen that the nitrogen is not distributed uniformly through the crystal, but forms sectors*. The distribution of impurities visible to the eye is confirmed by measurements of the specific resistance, which in the regions of the crystal corresponding to the dark-colored sectors is one to two orders of magnitude lower than in neighboring, light-colored sectors. The investigation showed that the dark coloration is observed in the growth pyramids of the faces (111) and $\{\bar{2}1\bar{2}\}$–$\{\bar{3}1\bar{3}\}$, while the growth pyramids of the cube faces $\{100\}$, of the negative tetrahedron $\{\bar{1}11\}$, and of the negative trigon-tritetrahedron $\{\bar{2}11\}$ are not colored**.

Fig. 2. Sectorial structure of a plate-like β-SiC crystal doped with nitrogen (photographed in transmitted light, after grinding and etching in a Na_2O_2 melt)

Growing crystals in an atmosphere containing boron showed that in this case the growth pyramids of the cube faces are not colored, and those of the positive and negative tetrahedron are colored most intensely; the pyramids of the trigon-tritetrahedron are somewhat weaker.

In Fig. 3 the distribution of nitrogen and boron in β-SiC single crystals is shown schematically by means of sections of the crystal by a plane perpendicular to the faces (111) and $(\bar{1}\bar{1}\bar{1})$. Ideal plate-like β-SiC crystals have a hexagonal shape and a third-order axis of symmetry; therefore sections of only two different types are possible: 1) through the point of the beginning of growth along

Fig. 3. Schematic representation of the distribution of nitrogen and boron over the growth pyramids of plate-like β-SiC crystals

* Since the crystals are attached to the substrate at one end, the sectors converge

Fig. 3. Schematic representation of the distribution of nitrogen and boron over the growth pyramids of plate-like β-SiC crystals

Figure 3: Fig. 3. Schematic representation of the distribution of nitrogen and boron over the growth pyramids of plate-like β-SiC crystals

Fig. 4

Figure 4: Fig. 4

not at the center of the crystal but at its "root," where the point of the beginning of growth is located.

** In those cases where an incoming dihedral angle is formed on the crystal, one face of the positive trigon-tritetrahedron $\{\bar{1}1\bar{3}\}$ usually arises (Fig. 1b). The growth pyramid of this face is also colored.

growth pyramids of any of the faces of the positive tetrahedron $\{\bar{1}1\bar{1}\}$, and 2) through the point of the beginning of growth along the growth pyramids of the cube faces and of the negative trigonal tritetrahedron. The growth pyramids of the (111) faces are not shown in the diagrams, since the growth rate of these faces in the normal direction is negligible and, consequently, their thickness is also negligible.

Fig. 4. Projection of the atomic structure of a lamellar β-SiC crystal onto the $\{1\bar{1}0\}$ plane
• –atoms of type B; ∘ –atoms of type A

Since the sectorial structure of crystals is associated with the individual surface properties of the faces of different simple forms, let us consider the atomic structure of the surface of those faces of the $\langle 1\bar{1}0\rangle$ zone which are formed on β-SiC crystals during growth from the gas phase (Fig. 1b).

Figure 4 shows a projection of the atomic structure of a lamellar β-SiC crystal onto the $\{1\bar{1}0\}$ plane, and Table 1 gives a comparison between the absorption of impurities and the number of bonds by which surface atoms on different faces are connected with the bulk of the crystal.

Table 1

Simple form	{111} {$\bar{2}$21}	{$\bar{1}\bar{1}\bar{1}$} {$\bar{3}$31}	{$\bar{3}$11}	{3$\bar{1}$1}	{100}	{$\bar{1}$00}	{2$\bar{1}$1}	{$\bar{2}$11}	{$\bar{1}$11}	{1$\bar{1}$1}
Type of atoms	B	A^*	B	A	B	A	B	A	B^*	A

Simple form	{111} {$\bar{2}$21}	{111} {$\bar{3}$31}	{$\bar{3}$11}	{$\bar{3}$11}	{100}	{100}	{$\bar{2}$11}	{$\bar{2}$11}	{$\bar{1}$11}	{$\bar{1}$11}
Number of bonds holding an atom of the given type on the surface of the face	3	2	3	2	2	2	2	3	2	3
Absorbed impurity	nitrogen	nitrogen	nitrogen	nitrogen	—	—	boron	boron	boron	boron

* On a step.

As can be seen, the difference between the faces {111} and {$\bar{3}$11} and the faces {$\bar{1}$11} and {$\bar{2}$11} consists in the fact that on the former the B atoms are bound by three bonds and the A atoms by two,* while on the latter the reverse is true. Since the cube faces, on whose surface both B atoms and A atoms are held by only two bonds, practically absorb neither boron nor nitrogen, we may conclude that in the present case nitrogen atoms replace B atoms, and boron atoms replace A atoms.

The introduction of aluminum into the reactor atmosphere shows that it, like boron, is absorbed mainly by the growth pyramids of the faces of the negative tetrahedron. Such selectivity in the absorption of boron, aluminum, and nitrogen—

* Generally speaking, such an orientation of steps on the {111} faces is also possible when both B and A atoms are bound by three bonds; however, the orientation of the vicinal hillocks and other growth figures speaks in favor of the first assumption.

between different faces of β-SiC crystals makes it possible to draw a conclusion

about the chemical nature of atoms B and A.

In the formation of true mixed crystals (substitutional solid solutions), the equivalence of atoms with respect to substitution of one another depends mainly on the relatedness of the given chemical elements ([4,5]). The most important coordination parameters of the atoms Al, B, Si, C, and N, and their tendency to form isotypic compounds (see, for example, ([5]), Fig. 224; ([6])) indicate a great similarity in the chemical properties of nitrogen with carbon, aluminum with silicon, and boron—with both carbon and silicon.

Table 2

Element	B	Al	Si	C	N
r	0.89	1.26	1.17	0.77	0.70
x	2.0	1.5	1.8	2.5	3.0

Table 2 gives the values of the tetrahedral radii r and electronegativities x of the elements under consideration. Comparison of these parameters, the indicated closeness of the properties of N to C and Al to Si, and the fact that boron and aluminum are absorbed by the same faces compel one to suppose that in the crystals we studied nitrogen atoms replace carbon atoms in the β-SiC lattice, while boron and aluminum replace silicon atoms, i.e., atoms of C emerge on the surface of faces $B\{111\}$, and Si on faces $A\{\bar{1}11\}$.

The phenomenon of nonuniform distribution of impurities in the process of crystal growth has long been known and has been described in a number of Russian and foreign books and articles ([2,7]); however, in most cases the examples refer to crystals grown from solution. Recently a number of works have appeared reporting nonequilibrium and nonuniform distribution of impurities (the so-called "face effect") during pulling from the melt of single crystals of germanium ([8]) and indium antimonide ([9]), as well as dendrites of germanium ([10]) and indium antimonide ([11]). In our case the effect is expressed very sharply (as was indicated above, the resistivity, and consequently the impurity content, in neighboring growth pyramids of the crystal may differ by one or two orders of magnitude) and apparently can be explained only on the basis of the peculiarities of tangential growth, which, when crystals are grown from the gas phase, are probably manifested most strongly.

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Note: Figure translations are in progress. See original paper for figures.