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CRYSTALLOGRAPHY

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ON THE ORIENTED CRYSTALLIZATION OF α-SiC ON DIAMOND

(Presented by Academician N. V. Belov on 30 IV 1966)

In studying the internal morphology of natural diamond crystals, one of the authors concluded that the zoning of diamonds manifested in anomalous birefringence is due to hexagonal silicon carbide, periodically overgrown epitaxially on the faces {111}.

To verify the fundamental possibility of epitaxial overgrowth of hexagonal silicon carbide on diamond, we studied the interaction of pure silicon with diamond in a vacuum of 10^{-4} mm Hg and at a pressure of 60 kbar in the temperature range 1000—1550°. A diamond crystal was immersed in silicon powder (silicon from semiconductor diodes was used) filling a graphite crucible. The material of the crucible was chosen deliberately: graphite prevented a possible reaction between the diamond and the vapors of the metals of the vacuum furnace. The crucible was closed with a graphite lid and placed, in turn, in an alumina cup installed in the vacuum furnace. The vacuum furnace was made of tungsten wire 1 mm in diameter, on the principle of a freely suspended spiral surrounded by molybdenum screens. The temperature was measured with a platinum-rhodium —platinum thermocouple, the working junction of which was located in the wall of the alumina cup. At a temperature of 1430°, a diamond crystal of octahedral habit, weighing 10.95 mg, became covered within 20 min with a pale yellow-green film and increased in weight by 0.4 mg. From this crystal, oriented with the L_3 axis parallel to the primary beam of x-rays, two Laue photographs were taken: before the experiment and after the experiment (Fig. 1, see insert to p. 571). The recording conditions in both cases were identical. A comparison of the indicated Laue photographs shows that on the second of them, taken from the crystal covered with the film, there are additional spots (in Fig. 1b marked by arrows), not belonging to diamond and associated with the L_6 axis. These spots and their arrangement indicate the single-crystalline character and the regular orientation, with respect to diamond, of the film that formed. The latter is also evidenced by the reflection of light from the entire surface of the

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

film at the same positions of the crystal at which the diamond faces {111} covered by it reflect, as was established goniometrically.

For diagnosis, the film was separated from the diamond in the following way. Several diamond crystals treated with silicon by the method described were heated in air in a muffle furnace to 1000—1200°. Heating for 30 min at 1000° caused no changes in the diamond or in the film. At a temperature of 1200° for 30 min, the diamonds partially burned away, this process proceeding most intensively on the edges and vertices of the crystals (Fig. 2, see insert to p. 571). Increasing the duration of heating at 1000° to 2 h, and at a temperature of 1200° to 1 h, led to complete combustion of the diamonds with preservation of the film in the form of a shell repeating the shape of the crystal. We note that the indicated intervals of time and temperature may vary and depend on the size and quality of the crystals and the film. The film separated from the diamonds was ground, and a Debye photograph was taken from the resulting powder. The lines of the Debye photograph correspond to hexagonal silicon carbide.*

* S. G. Shchelchkova participated in the x-ray diagnosis.

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Fig. 1. Laue patterns of a diamond single crystal without an α-SiC film *(a)* and of the same single crystal with an epitaxial α-SiC film *(b)*

Fig. 2. Diamond single crystal with an epitaxial α-SiC film after heating at 1200° in air for 30 min. 26×

Fig. 3. Area of the surface of an α-SiC film. Reflected light. 300×

It is known that the distance between silicon and carbon atoms in the basal planes of hexagonal silicon carbide is constant and is 3.07 Å, while the corresponding parameter of the {111} nets of diamond is 2.52 Å ([1]). The closeness of these values is in sufficiently good agreement with one of the conditions permitting regular intergrowth of different crystalline substances ([2,3]). To this should be added the complete analogy of the geometry of the corresponding nets and of the character of the C–C bonds in diamond and the Si–C bonds in hexagonal silicon carbide. Taking into account what has been said and the features of the

Figure 3

Figure 3: Figure 3

arrangement of the additional spots on the Laue pattern in Fig. 1b, it may be concluded that, during the interaction of diamond with silicon, α-SiC is formed epitaxially on the $\{111\}$ plane of diamond.

It was established by 30 experiments that the reaction of diamond with silicon begins in vacuum at a temperature of 1200°, but proceeds most intensively near the melting point of silicon (1410°) and above. The duration of the experiments (not more than 20 min.) at temperatures above the melting point of silicon was limited by the complete disappearance of the latter from the reaction volume. Repeated treatment with silicon, under the same conditions, of a diamond covered with a film, and the introduction of graphite powder into the silicon, did not produce an increase in the weight of the crystal. Experiments carried out beforehand with the same crystals under analogous conditions, but without silicon, showed that the diamonds do not graphitize in this case. All this gives grounds for asserting that the formation of hexagonal silicon carbide on diamond occurs only at the expense of the carbon of the diamond and practically ceases as soon as the entire surface of the crystal becomes covered with a film. Owing to the imperfection of the surface of the crystals, the rate of crystallization of silicon carbide at different points of this surface is different, which apparently leads to inhomogeneity of the film formed (Fig. 3, see insert to p. 571). An estimate of the film thickness, made after each experiment, gave values not exceeding 2–4 μ.

The second stage of the experiments was to determine the possibility of the reaction of diamond with silicon in the region of thermodynamic stability of diamond. The interaction of diamond with silicon was carried out in a high-pressure chamber with a graphite heater at a temperature of 1500—1550° and a pressure of 60 kbar. In this case the silicon powder and the diamond were placed in a container made of pressed aluminum oxide and were thus isolated from the heater. Under these conditions the diamonds, within 10–15 min., became covered with a film of hexagonal silicon carbide completely analogous to the film obtained in the reaction of diamond with silicon in vacuum.

Under the same conditions the reaction of graphite with silicon was carried out. As a result of this reaction, synthetic diamonds and hexagonal silicon carbide were obtained.

Summing up the foregoing, the following conclusion may be drawn. The interaction of diamond with silicon at a temperature above 1200° in a vacuum of 10^{-4} mm Hg and at a pressure of 60 kbar and a temperature of 1500—1550° leads to the formation of hexagonal silicon carbide, epitaxially growing on the $\{111\}$ plane of diamond.

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CITED LITERATURE

1. B. F. Ormont, *Structures of Inorganic Substances*, Moscow–Leningrad, 1950.

2. L. S. Palatnik, I. I. Papirov, *Oriented Crystallization*, Moscow, 1964.

3. V. A. Frank-Kamenetskii, *The Nature of Structural Impurities and Inclusions in Minerals*, Leningrad, 1964.

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

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