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INVESTIGATION OF THE STRUCTURE OF BORON NITRIDE CRYSTALS BY THE METHOD OF CHEMICAL ETCHING

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Boron nitride crystals with a sphalerite-type structure, obtained by a phase transformation from hexagonal boron nitride under the conditions described in ([1]), were investigated. The crystals had reduced symmetry $3m$ and m and were represented by completely faceted, flattened twins of nearly perfect structure*. The most highly developed opposite faces (111) and $(\overline{1}\overline{1}\overline{1})$ had a visually mirror-smooth microrelief. The diameter of the crystals was 0.4–0.5 mm, their thickness not more than 0.1 mm. The color of the crystals was dark brown, sectorial. More darkly colored, often opaque, were the growth pyramids of developed faces with outlines close to a trigone, as well as the growth pyramids of lateral faces belonging to this same simple form. In accordance with ([2]), these faces were assigned to $\{\overline{1}\overline{1}\overline{1}\}$. The growth pyramids of the developed face with hexagonal outlines and the lateral trapezoidal faces belonging to the same simple form were weakly colored brownish or amethyst and transparent; these faces were assigned to {111}.

Chemical etching of the crystals was carried out with a KOH melt at 380°C for 30 min., 1, 2, 4 and more hours.

Micromorphological analysis of the etched surfaces (111) and $(\overline{1}\overline{1}\overline{1})$ and their photographing were performed with an MIM-8m. The analysis showed that the faces $(\overline{1}\overline{1}\overline{1})$, irrespective of the etching time, preserve their mirror surface; etch pits reveal only various defects of the crystal structure. On the faces $(\overline{1}\overline{1}\overline{1})$ of some crystals, the finest etch pits are arranged sectorially; the growth center of the sectors is more or less displaced relative to the center of the face (Fig. 1a, see insert to p. 1067).

Stepwise etching of the surface (111) reveals the sectorial and zonal structure of the crystals. With short-term etching, numerous etch pits appear on (111), covering the entire base of the growth pyramid of this face (Fig. 1b). Increasing the etching time is accompanied by gradual etching away of the layer of the growth pyramid of the developed face from the periphery toward the growth center. This reveals the sectors (pyramids) of growth of the lateral faces {111}

and $\{1\bar{1}1\}$, which differ from one another in the different concentration of etch pits on their surface (Fig. 1b, d). The etch pits have the form of pyramids, represented by combinations of negative trigonal pyramids of the first and second kinds with gently sloping, often terraced faces (Fig. 1d). In sectors resting on edges formed by the face (111) with lateral faces $\{\bar{1}11\}$, the etch pits are present in smaller numbers and are oriented parallel to the indicated edges; in sectors emerging on edges between the face (111) and the lateral faces {111}, the etch pits are very numerous and are oriented oppositely—parallel to the indicated edges (Fig. 1d). Within the sectors, etch pits are often collected into chains and grooves parallel to the edge, revealing the zonal structure of the crystal; it is especially clearly traced in the growth sectors of the lateral faces {111} (Fig. 1b, e).

Lines projecting the surfaces of growth of the edges of the lateral faces are clearly revealed after 2–4-hour, sometimes longer, etching, in the form of grooves composed of merged faces of pyramidal etch pits, the apices of which form the axis of the groove. These grooves be-

* X-ray diffraction patterns of the crystals were obtained by Yu. A. Alekseev.

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Fig. 1. Etched faces of tetrahedra of boron nitride crystals.

Fig. 1. Etched faces of tetrahedra of boron nitride crystals. Crystal 1: **a** – face {111}, **b** –face {111}, etched for 1 hour; **c** –face {111}, etched for 2 hours. Crystal 2: **d**, **e** –face {111}, etched respectively for 30 min and 4 hours. Crystal 3: **f** –face {111}, etched for 2 hours.

originate from the growth center, often displaced relative to the center of the face (Fig. 1g, e). The structure of the etch pits on different sides of the groove ridge is different and is close to the structure of the etch pits in the growth sectors of the lateral faces adjoining the given side of the groove. The grooves are curvilinear and are not constant in their cross section and outlines (Fig. 2). This indicates a mosaic structure of the crystal in the regions adjoining the surfaces of growth of the edges.

Fig. 2 Fig. 3

Fig. 2. Crystal 1, face {111}, etched for 4 hours. Growth center of the structural elements of the crystal; grooves along the surfaces of growth of the edges of the lateral faces. Reflected light. 350×

Fig. 3. Schematic position of crystal 3 in a unidirectionally directed feeding flux

Chemical etching also reveals near-edge regions along the periphery of the face (111). The edges {111} are etched at a higher rate, and the edges between (111) and the faces $\{1\bar{1}1\}$ at a lower rate. Thus, along the periphery of the (111) face of crystal 2, after 4-hour chemical treatment the etched near-edge regions with

faces {111} had a width of 20, while the near-edge regions with faces {$1\bar{1}1$} were 5-7 m (Fig. 1d).

The observations made show that boron nitride crystals obtained by (1) nucleate and grow under conditions of free growth of individuals, in contrast to the joint growth of its crystals in aggregates according to (3).

The reduced symmetry, flattened form, twinned structure, and eccentric development of individuals with asymmetric development of the growth pyramids of the lateral faces (Fig. 3) indicate the growth of boron nitride crystals of the spherulitic type in a feeding medium with symmetry $L_\infty \infty P$ (4), represented by powdered hexagonal boron nitride, impregnated by unidirectionally directed fluxes of a mobile melt.

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