
CRYSTAL GROWTH

Growth Nature of Negative Relief Forms of Diamonds from Ural Placer Deposits

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Abstract—The morphology and anatomy of diamond crystals with tetragonal depressions on their surface have been studied. Based on the study of the interrelation between tetragonal depressions and the internal structure of diamond crystals, it is concluded that tetragonal depressions are related to the relics of surfaces of polycentric regeneration growth along the $\langle 100 \rangle$ direction. For all investigated crystals of cubic habit, including dissolved ones, surfaces of $\{111\}$ faces appear in the form of combination hatching in the last growth stage. It is shown that tetragonal depressions have a growth nature in most cases.

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INTRODUCTION

Diamond crystals from Ural deposits are characterized by overwhelming dominance of rounded dodecahedra [1]. Diamonds take this form as a result of dissolution or etching [2, 3]. During dissolution (etching), with rounding off crystal vertices and edges, an octahedron begins to transform into an octahedroid and then into a dodecahedron; a crystal of cubic habit transforms into a cuboid and then into a tetrahexahedroid. The final dissolution form is the dodecahedron of “Ural” type with constant curvature parameters [4, 5]. It was shown in numerous experiments that triangular and tetragonal negative sculptures are formed on the crystal surface during etching and dissolution. Tetragonal sculptures are formed along the $\langle 100 \rangle$ direction, and triangular sculptures are formed along the $\langle 111 \rangle$ direction; they develop on the $\{100\}$ and $\{111\}$ faces, respectively. The number, size, and morphology of these depressions depend on the P – T – $f(\text{O}_2)$ mode and composition of the medium [3, 5–7]. Triangular depressions are often related to dislocation outcrops on the crystal surface [8]. Tetragonal depressions occur less frequently on the surface of natural diamonds; they are also assigned to etching figures [9, 10] and they also may be related to dislocation outcrop [11, 12].

When studying the collection of diamond crystals from modern alluvial placers of Krasnovishersky district, Urals [13], 12% crystals (cuboids, tetrahexahedra, and dodecahedra) with tetragonal depressions were noted. These depressions, localized on surfaces that were affected by dissolution, are relics of growth forms. These depressions are absent on curvilinear

surfaces of dodecahedra and tetrahexahedra. In this paper, we report the results of studying the interrelation between the tetragonal depressions on crystal surface with the internal structure of diamond crystals.

EXPERIMENTAL

After preliminary study of a collection of 155 crystals, 10 samples with tetragonal depressions on their surface were selected for further research. The crystals were extracted from modern alluvial deposits of Krasnovishersky region, Urals (collection from the Karpinsky Russian Geological Research Institute (VSEGEI)). Photographs were obtained with a Leica M205 optical microscope (OM). Cathodoluminescence (CL) images and surface morphology secondary electron images (SEI) were obtained with a scanning electron microscope CamScan MX2500 S. Plane-parallel $\{100\}$ plates were prepared from crystals to visualize their anatomy; laser-cut preforms were polished on diamond wheels.

RESULTS

Concerning morphology, there were three cuboids, one tetrahexahedron, one octahedron, and five dodecahedra among the crystals studied (Fig. 1). According to Orlov’s classification [9], five crystals belong to I kind and five belong to II kind.

Tetragonal depressions exist on the surface of all crystals. Triangular and tetragonal depressions are observed on six crystals. Step depressions in some crystals have clear edges and flat walls. In some crys-

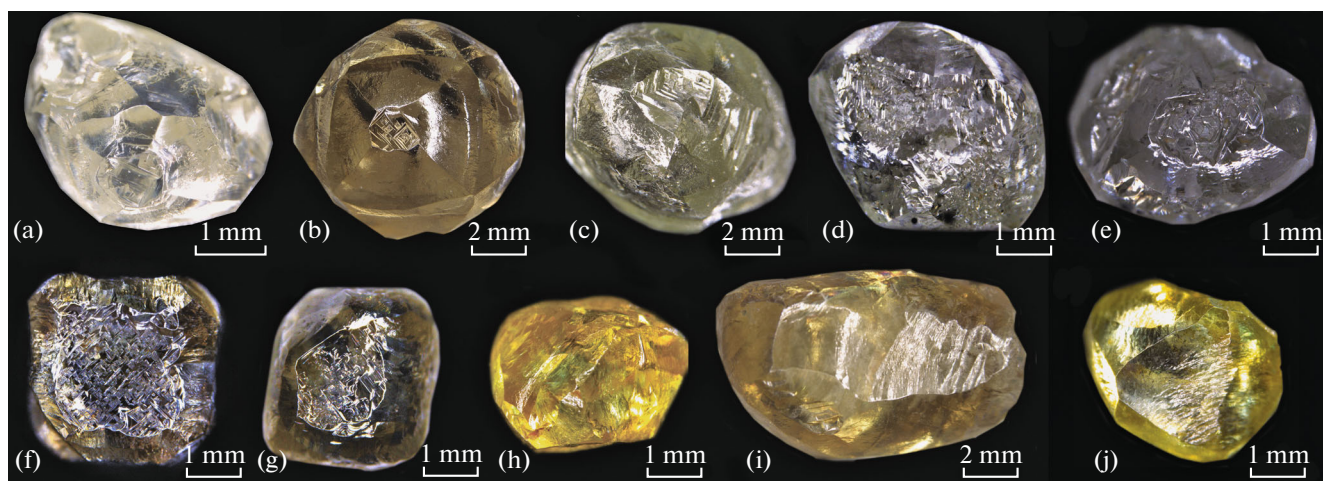


Fig. 1. General view of crystals with tetragonal depressions. The top row contains I-kind crystals [8]: (a) cuboid 29-76, (b) tetrahexahedron 123-76, (c) dodecahedron 122-76, (d) dodecahedroid 615-66, and (e) octahedron 612-66. The bottom row contains II-kind crystals [8]: (f) cuboid 600-66, (g) cuboid 601-66, (h) dodecahedron 610-66, (i) dodecahedron 123-76, and (j) dodecahedron 158-76.

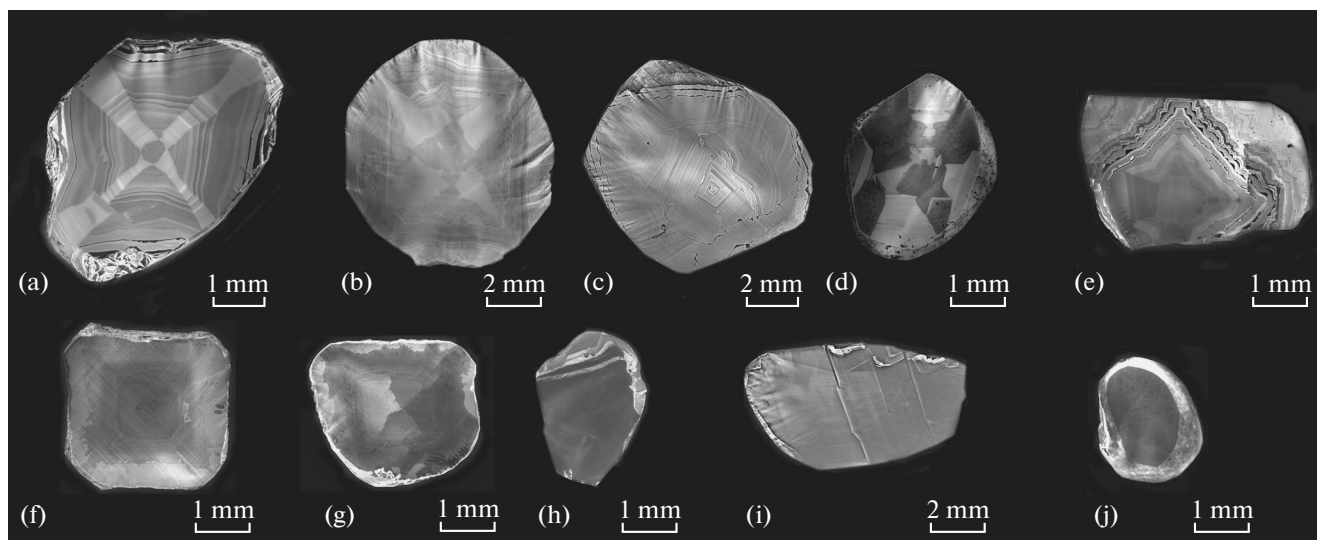


Fig. 2. CL images of crystals. The top row contains (a) cuboid 29-76, (b) tetrahexahedron 123-76, (c) dodecahedron 122-76, (d) dodecahedroid 615-66, and (e) octahedron 612-66. The bottom row contains II-kind crystals [8]: (f) cuboid 600-66, (g) cuboid 601-66, (h) dodecahedron 610-66, (i) dodecahedron 123-76, and (j) dodecahedron 158-76.

tals walls are curvilinear and flat out when outcropping on the surface. In some cases, the secondary character of depressions is obvious: these are etching channels penetrating deep into the crystal.

All plates cut through the crystal center in the $\{100\}$ plane exhibit wavy growth layers in the general direction $\langle 100 \rangle$ or, as an extreme case of these layers, concentric zonality (Fig. 2). For simplicity, parts of diamond crystals with wavy growth zonality along the $\langle 100 \rangle$ direction are referred below as $\langle 100 \rangle$ pyramids [14].

Coexistence of pyramids of $\{111\}$ faces and $\langle 100 \rangle$ pyramids was observed in three crystals. They are

referred to as “mixed-habit” in English scientific literature [15]. The internal structure of four crystals is characterized by dominance of $\langle 100 \rangle$ pyramids. These samples have a cubic habit, and their surface is formed by irregular surfaces similar to $\{100\}$ planes. A successive change was observed for crystal 122-76: layers $\{111\}$ are replaced with concentric zonality of $\langle 100 \rangle$ pyramids in the center, and plane-parallel $\{111\}$ layers appear again at the periphery.

Plane-parallel $\{111\}$ layers in the $\langle 100 \rangle$ direction are observed at the periphery of all plates. The end fragments of plates cut from crystals 123-76 and 122-76 are shown in Figs. 3a and 3b, and a fragment of crystal

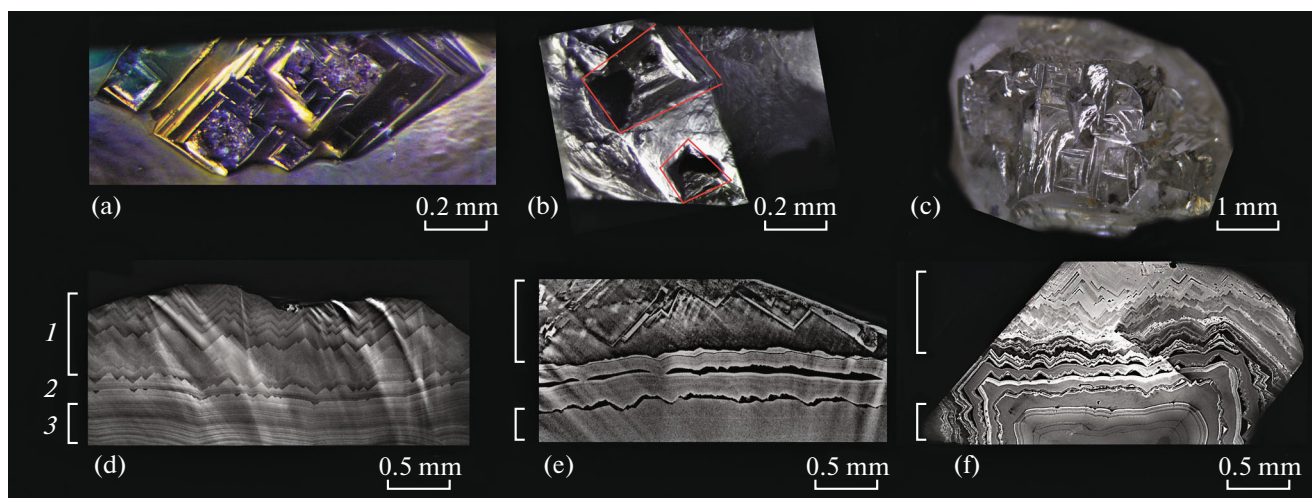


Fig. 3. (a–c) OM and (d–f) CL images of surface fragments with tetragonal depressions and the internal structure of peripheral regions in the cross section of crystals (a, d) 123-76, (b, e) 122-76, and (c, f) 612-66: (1) octahedral zonality, (2) intermediate stage, and (3) curvilinear zonality.

612-66 scanning along the $\langle 100 \rangle$ direction is shown in Fig. 3c. These images demonstrate clearly tetragonal depressions; CL images of surface layers are also presented for comparison. As can be seen from Figs. 3d, 3e, and 3f, the external part of the crystals consists of $\{111\}$ layers. Note that there are no tetragonal depressions in the crystal parts free of octahedral zonality. The zone thickness and the number of layers of polycyclic growth of $\{111\}$ faces change in a wide range.

Crystals of Kind I: 29-76, 123-76, 122-76, 615-66, and 612-66

The internal structure of crystals 123-76 and 122-76 was described in detail in [16]. These crystals contain only relics of the central parts of surfaces of cubic habit crystals with tetragonal depressions. The depressions are step ones, with rounded edges. Both triangular depressions along the $\langle 111 \rangle$ direction and tetragonal depressions along the $\langle 100 \rangle$ direction are observed in crystals 123-76, 615-66, and 612-66.

In the surface part of crystal 123-76 the wavy zonality of $\langle 100 \rangle$ pyramids is replaced with clear multilayer zonality over $\{111\}$ (Figs. 3a, 3d). The transition is gradual: the smooth line is interrupted by triangular steps in several layers, after which completely “zigzag” layers begin to be formed over $\{111\}$. This zonality is seen on the CL surface of many dissolved crystals (Figs. 4a, 4b). The depressions have a clear shape and stepwise character only at the hypsometric level of octahedral zonality development; below, where curvilinear cubic zonality occurs, they are transformed into a highly corroded and rough surface.

A very contrast zonality can be seen in the surface CL image of crystal 29-76 in the $\langle 100 \rangle$ direction. It corresponds to the cross section by the growth relief dissolution surface. The tetragonal depressions on this

surface only partially correspond to the surface CL image of zonality (Figs. 4g, 4h). Secondary tetragonal etching depressions are imposed on the primary growth relief in this crystal.

Two black CL bands can be seen in the cross section of crystal 122-76. Thin layers over $\{111\}$ are observed in only some near-surface regions. Tetragonal depressions can be seen in only the region with zonality over $\{111\}$ (Figs. 3b, 3e).

Crystal 615-66 contains also growth pyramids of $\{111\}$ faces and $\langle 100 \rangle$ pyramids. The areas with triangular depressions on the crystal surface almost join with the areas having tetragonal depressions (Fig. 1d).

Crystal 612-66 is a colorless octahedron with identical (in area) development of triangular and tetragonal depressions (Fig. 1e). Preferred development of $\langle 100 \rangle$ pyramids can be seen in the crystal cross section. In this stage the crystal had a form of skeletal cube. Afterwards, alternation of layers with concentric zonality of $\langle 100 \rangle$ pyramids and plane-parallel zonality of $\{111\}$ layers began. Then layers with multiple dissolution and regeneration signs can be seen. External bands are composed of low-step plane-parallel $\{111\}$ layers (Figs. 3c, 3f). The alternation of growth and subsequent dissolution stages led to the formation of a crystal that corresponded to octahedron when viewing along the $\langle 111 \rangle$ direction and to cuboid when viewing along the $\langle 100 \rangle$ direction.

Crystals of Kind II: 600-66, 601-66, 610-66, and 126-76

Samples 601-66 and 600-66 are entirely cuboids; dissolution affected only their edges, and the crystal surface is covered with tetragonal depressions. Samples 126-76 and 610-66 are dissolved fragments. The external part of 601-66 and 600-66 exhibits fine zonal-

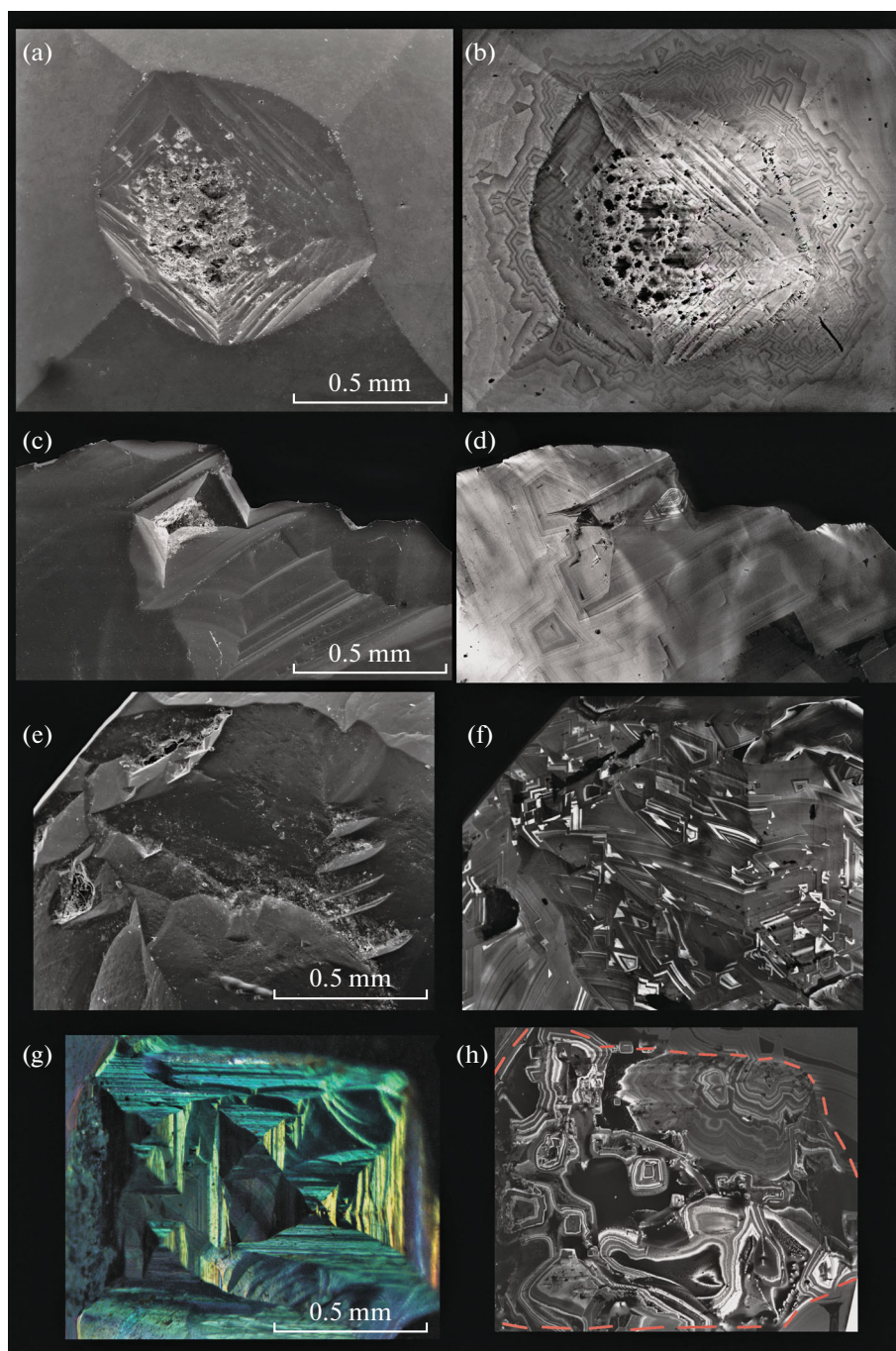


Fig. 4. (a, c, e) SEI, (b, d, f, h) CL, and (g) OM images of fragments of relief and natural surface of crystals with tetragonal depressions: (a, b) 123-76, (c, d) 126-76, (e, f) 610-66, and (g, h) 29-76.

ity, which has a weak CL contrast. The 126-76 sample surface contains only two tetragonal depressions (Fig. 1i). The homogeneous internal structure of the main volume, yellow color (due to the C centers), and the presence of low-step zonality $\{111\}$ suggest that this crystal is a fragment of large cuboid. Contrast linear zonality $\{111\}$ was observed only in the region with tetragonal depressions (Figs. 4c, 4d).

Sample 610-66 (Fig. 1h) has an irregular shape; there are only few tetragonal and triangular depressions on its surface. CL analysis of the plate reveals $\langle 100 \rangle$ pyramids and (in the external part) linear zonality $\{111\}$. Tetragonal depressions on the surface correspond to the plate region with zonality $\{111\}$ (Fig. 2h). Vicinal layers with octahedral zonality can be seen in the surface CL image (Figs. 4e, 4f). The smooth crys-

tal surface in the CL image has a very contrast zonal-ity, formed by the growth relief cross section.

DISCUSSION

There are two main growth mechanisms for crystals (in particular, diamonds): normal and tangential [17]. Diamonds of cubic habit grow according to the normal mechanism, with a characteristic irregular lumpy surface, close to $\{100\}$ planes. Octahedral crystals grow according to the tangential mechanism, with atomically smooth surface and generally without any defects or steps. The limiting stage of tangential mechanism is generally two-dimensional nucleation [17]. In the case of regeneration growth, the rate is limited by diffusion rather than two-dimensional nucleation. Therefore, the growth rate of regeneration surfaces is much higher than the growth rate of singular faces $\{111\}$. The crystal parts that grew according to the tangential mechanism have a clear plane-parallel zonality along the $\langle 111 \rangle$ direction. The crystal parts that grew according to the normal mechanism have wavy zonality in cross sections in the general direction $\langle 100 \rangle$ and concentric zonality in the limit. The dominance of a particular mechanism is determined mainly by the supersaturation of growth medium. Thus, cubic and octahedral diamonds grew at high and low supersaturations, respectively [18]. Skeletal crystals are formed in the intermediate (with respect to supersaturation) stage, between the stages of flat-face octahedral and rough cubic growth [19, 20].

There are regions of both normal and tangential growth in the internal structure of all crystals studied. Many low growth step of $\{111\}$ layers in the general direction $\langle 100 \rangle$ are formed at the onset of tangential regeneration growth. In this stage combination hatching appears in the crystal faceting. Crystals have a cubic habit, but their surface is formed by the relief of $\{111\}$ layers, which includes pyramids, depressions, and low-step positive octahedral forms. During further growth of $\{111\}$ layers regeneration surface of polycentric growth is formed, and then the crystal becomes decorated by deceleration faces $\{100\}$. Therefore, the occurrence of tetragonal depressions is a manifestation of polycentric growth of $\{111\}$ faces in the surface relief along the $\langle 100 \rangle$ direction. The formation of tetragonal pits along the $\langle 100 \rangle$ direction was demonstrated in numerous etching and dissolution experiments. Therefore, dissolution of crystals with polycentric growth relief leads to complication of their surface: etching pit are imposed on the growth relief.

A schematic diagram of the evolution of internal structure of rounded crystals with tetragonal depressions, composed on the basis of the analysis performed, is presented in Fig. 5. The crystals of the first group grew according to the normal mechanism with a transition to a short stage of tangential regeneration growth. The crystals retained cubic habit in this stage, their surface was formed by the combination hatching

of $\{100\}$ surfaces. The combination of positive relief forms is perceived visually as a set of tetragonal pits. Than the surface is complicated as a result of superposition of dissolution and etching processes: tetragonal etch pits may appear, and the crystal becomes rounded. Cube is transformed into a cuboid with tetragonal depressions and, finally, into a dodecahedron.

The crystals of the second group were formed as a result of joint growth of pyramids of $\{111\}$ faces and $\langle 100 \rangle$ pyramids. The crystals grew according to the tangential mechanism in the last stage. These individuals were skeletal cubes or cuboctahedra in the first growth stage. Combination hatching of $\{100\}$ surfaces arose after the transition to tangential regeneration growth, with development of deceleration faces crystals passed to the octahedral habit. Eventually, a complex combination surface with tetragonal depressions was formed. During dissolution this crystal has a shape of tetrahexahedron with triangular depressions (in the regions of outcrop of the growth pyramids of $\{111\}$ faces to the surface) and tetragonal growth pyramids $\{100\}$.

The third-group crystals are characterized by long-term regeneration growth according to the tangential mechanism. As a result, an octahedron with depressions instead of vertices is formed. The final stage in the evolution series of these crystals should be the formation of a full-fledged octahedron with a step relief and vertices with tetragonal depressions. Crystals with regeneration growth after partial dissolution should have the same morphology. This situation was described for octahedral diamond crystals with a cloudy cubic core from the Internatsional'naya kimberlite pipe (Yakutia) [21, 22]. The crystal becomes octahedron and then dodecahedron during dissolution.

The occurrence of $\{111\}$ steps in the final formation stage of all crystals obeying normal growth mechanism can be considered as a specific feature of Ural diamonds. The long-term stage of crystal formation by $\langle 100 \rangle$ pyramids may indicate peculiar formation conditions for Ural diamonds. For example, the transition from cube to octahedron occurred more rapidly in Yakutsk bedrock deposits, and cubes in these deposits are only small cores of octahedra, as was shown in [8].

CONCLUSIONS

Concentric zonality is occurs often in the bulk of diamond crystals, which is indicative of normal growth mechanism. A crystal acquires a cubic habit during normal growth of $\langle 100 \rangle$ pyramids. However, concentric zonality is not observed in the surface morphology, in the overwhelming majority of cases it is replaced by linear zonality of regeneration tangential polycentric growth of $\{111\}$ faces. The relief with set of platforms of $\{111\}$ faces arises on the crystal surface

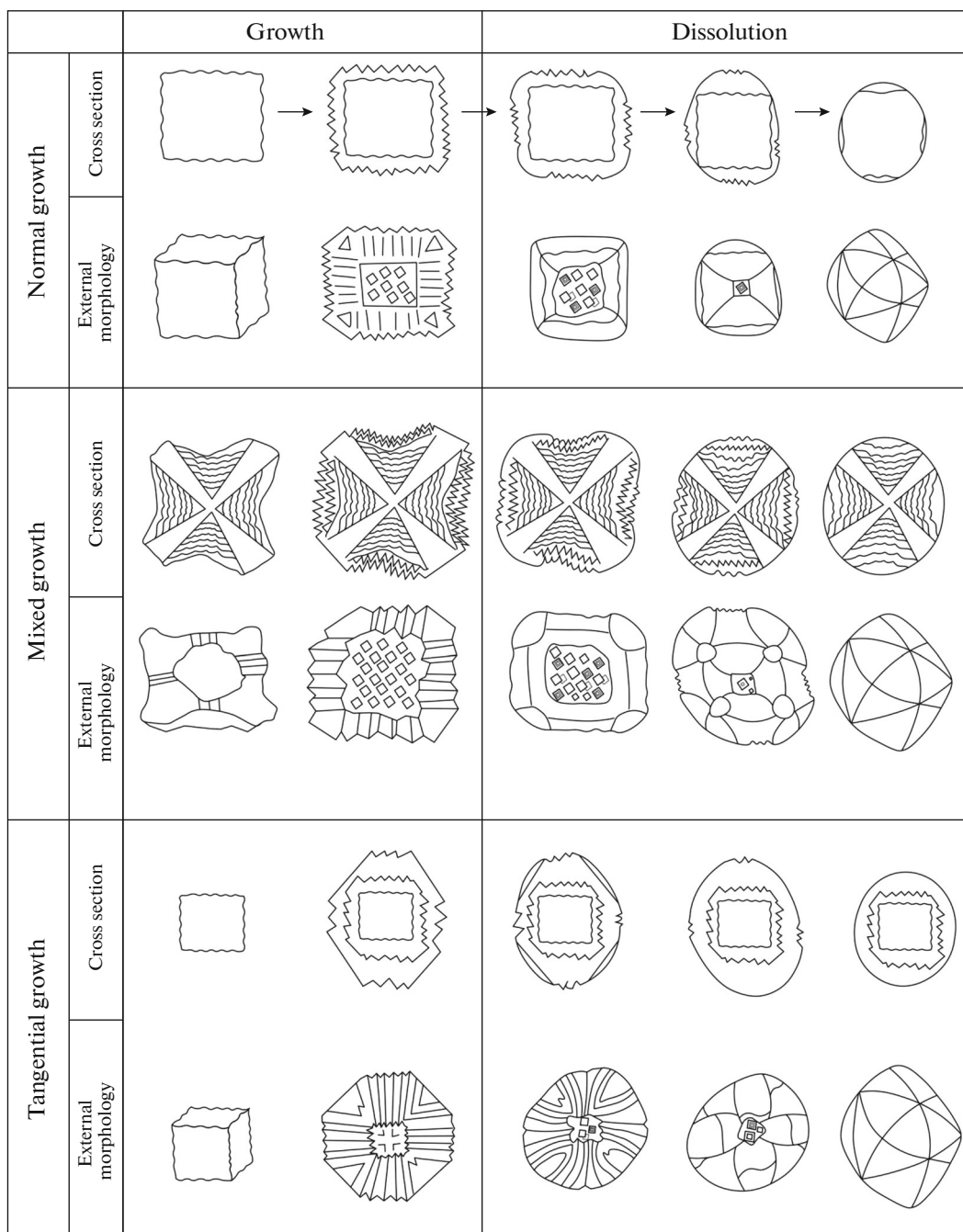


Fig. 5. Schematic of the growth and dissolution of diamond crystals with tetragonal depressions. Rows 1 and 2: growth according to the normal mechanism with transition to tangential in the final growth stage and subsequent dissolution. Rows 3 and 4: joint growth of the $\langle 100 \rangle$ and $\langle 111 \rangle$ faces with transition to the tangential mechanism in the final stage and subsequent dissolution. Rows 5 and 6: growth according to the normal mechanism with transition to the long-term growth stage according to the tangential mechanism with subsequent dissolution.

when the growth mechanism changes. The crystal acquires octahedral faceting during further growth, but portions with polycentric growth relief may remain on vertices. Thus, portions with relief of polycentric regeneration growth along the $\langle 100 \rangle$ direction serve as indicator of complex internal structure of crystal. During post-growth changes etching sculpture over

dislocations in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions and surface dissolution are imposed on the growth relief.

Regeneration growth of $\{111\}$ faces was observed in the last growth stage for all investigated crystals with cubic habit and in their derivative dissolution forms from the placer deposits of the Krasnovishersky district.

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