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Unusual growth macrolayers on {100} faces of diamond crystals from magnesium-based systems

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ABSTRACT

We studied unusual growth macrolayers on the {100} faces of diamond crystals grown in Mg-C and $Mg_{0.9}Ge_{0.1}$-C systems at 7.0 GPa and in the temperature range of 1800–1900 °C. The layers were shaped as rectangles highly elongated in one of the [110] directions. The layer elongation (length to width ratio) was different, but did not exceed 23. We found that the ends of the macrolayers in most cases were composed of {111} microfacets, and their growth occurred by layers along these microfacets. Using selective etching, we found that the macrolayers were not associated with outcrops of dislocations and any planar defects on the {100} faces. It is supposed that the formation of these highly elongated layers occurs by two-dimensional nucleation that becomes possible at high carbon supersaturation under conditions of kinetically limited diamond growth in Mg-based systems.

1. Introduction

Growth and dissolution sculptures on crystal faces can have different shapes, depending on process conditions; however, in most cases they reflect the symmetry of a face on which they are located. Diamond is not an exception. Square or octagonal growth hillocks, layers, or etch pits are typical of {100} faces, while triangular or hexagonal ones are typical of {111} faces. The shape of face patterns always corresponds to the ***m3m*** point group of diamond. Recently, we published studies on diamond crystallization in Mg-C and $Mg_{0.9}Ge_{0.1}$-C systems at 7.0 GPa in the temperature range of 1500–1900 °C [1,2]. The morphology of diamond crystals from these systems corresponds to the cube-cuboctahedron series. An analysis of the crystal morphology demonstrated that growth macrolayers on {100} faces were often shaped as rectangles highly elongated in the [110] directions at crystallization temperatures above 1700 °C. Hereafter, we will use the abbreviation HEL's for these highly elongated layers. HEL's are unusual structures for diamond crystals. We have found no references to these layers on the {100} faces of both natural and synthetic diamond as well as on the {100} faces of other substances with a similar structure (Si, Ge). HEL's have the ***mm*** two-dimensional point symmetry that does not match the symmetry of {100} diamond faces. We previously supposed that the HEL's source might be outcrops of planar defects, such as microtwins or stacking faults, on the face surface [2]. However, planar defects in diamond crystals grown on seeds in the Mg-C system were not detected during analysis of the crystals by X-ray topography and selective etching [3]. Indeed, the planar defects (microtwins and stacking faults) are absent usually in the {100} sectors of synthetic diamond crystals. They are characteristic of {111} growth sectors diamond [4–7].

In the present study, we investigated the highly elongated growth macrolayers and analyzed possible causes of their development.

2. Experimental details

Synthetic diamond crystals studied in this work were grown in Mg-C and $Mg_{0.9}Ge_{0.1}$-C systems at a pressure of 7.0 GPa and temperature in the range of 1800–1900 °C using the high-pressure split-sphere apparatus [1,2]. To produce diamond crystals, a graphite capsule with a pressed Mg (Mg-Ge) cylinder and seed crystals was placed in the center of a high pressure cell. As seeds, cuboctahedral diamonds (ca. 0.4–0.5 mm) were used. Spontaneous diamond crystallization occurred predominantly at the graphite-melt interface. Also, spontaneous diamond crystallization in the $Mg_{0.9}Ge_{0.1}$-C system occurred directly in the melt, in the central part of a reaction chamber. A detailed description of the high-pressure cell design and growth technique is presented in our recent papers [1,2].

Diamond crystals grown on seeds (1.0–2.0 mm in size), and spontaneous diamond crystals (100–900 µm in size) were studied using a Carl Zeiss Axio Imager Z2m optical microscope and a Tescan

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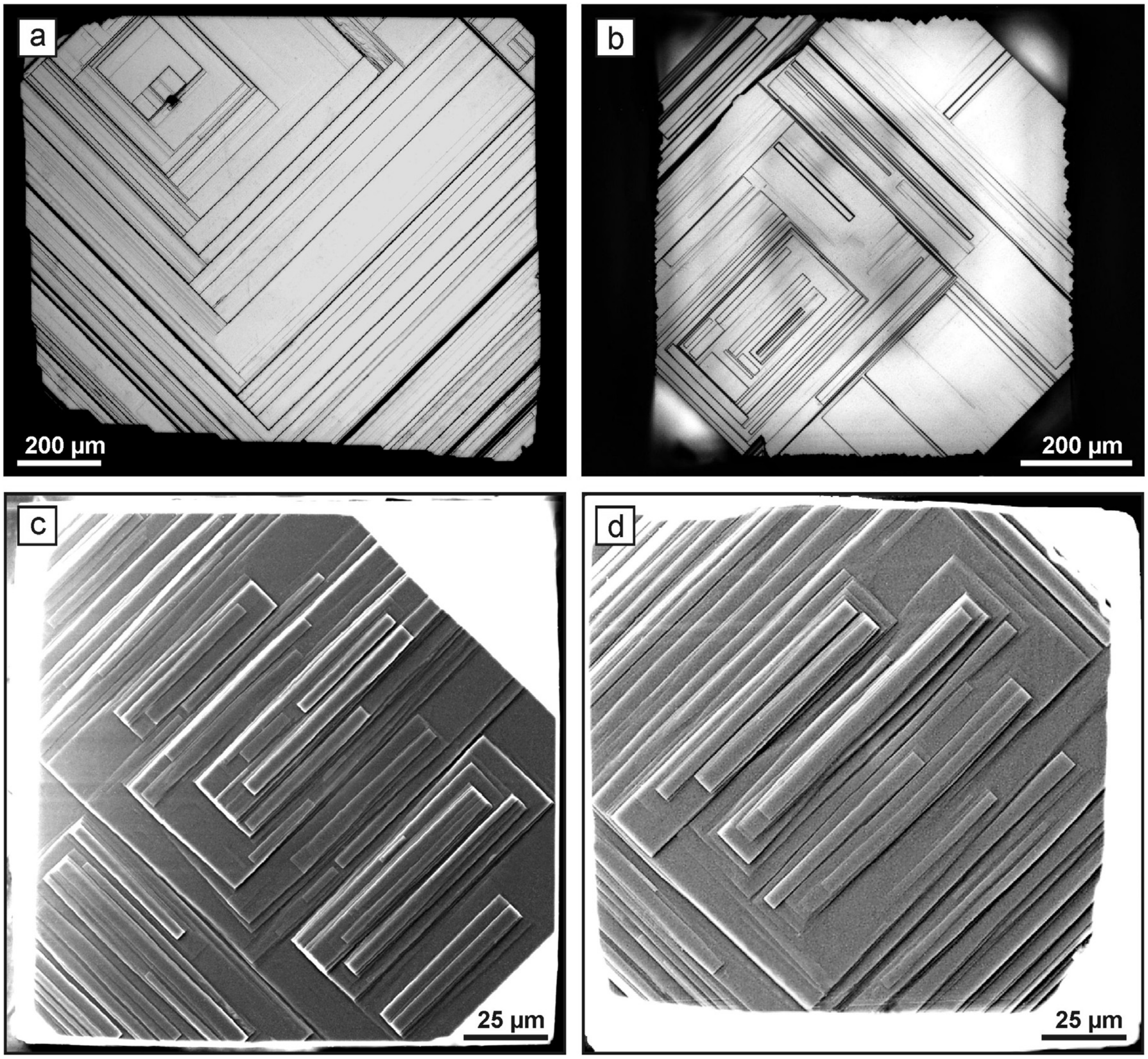

Fig. 1. Growth patterns on a {100} faces: (a, b) diamond crystals grown on a seed in the Mg-C system, optical micrographs; (c, d) spontaneous diamond crystals grown in the $Mg_{0.9}Ge_{0.1}$-C system, SEM micrographs..

MIRA3 LMU scanning electron microscope. Diamond crystals were etched to elucidate the relationship between HELs and extended defects (dislocations and planar defects) outcropping on faces. Selective etching of diamond crystals was performed according to previously established procedures in a potassium nitrate melt at a temperature of 700 °C [3,8,9]. The etch pits were measured using a double-reflecting interference microscope. The light wavelength used in the measurements was 0.55 µm. The etch figures were characterized by the inclination angle between the etch side wall and the (100) face, $\alpha_{(100)}$ [8]. The error in the inclination angle measurements did not exceed ± 0.5° due to the small size of the etch pits.

3. Results

3.1. Morphology of HELs

Diamond crystals grown in Mg-C and $Mg_{0.9}Ge_{0.1}$-C systems have a habit of the cube-cuboctahedron series. Most of the diamond crystals have predominantly the cubic morphology with minor {111} faces. Spontaneous diamond crystals that have formed in the central part of the reaction chamber, directly in the $Mg_{0.9}Ge_{0.1}$-C melt, often have a cuboctahedral habit. The {111} crystal faces are flat and do not have layers detectable by the used analysis methods. The {100} faces of diamond crystals always have rectangular macrolayers with their sides oriented in the [110] directions. On seed-grown diamond crystals, macrolayers, up to 15 µm in height, often form a stepped surface with one or more centers of layers propagation, which are apparently related to dislocation bundles or other crystal imperfections (Fig. 1a). As noted previously [1,2], the ends of the growth layers were always formed by the {111} microfaces. In addition, spontaneous diamond crystals, and sometimes diamonds grown on seeds, have highly elongated layers (HEL's) with a thickness of from 200 nm to 10 µm on {100} faces (Fig. 1b–d). HEL's are shaped as rectangular macrolayers elongated in one of the [110] directions. The ends of short HEL's sides are usually formed by {111} microfacets and sometimes by {hkk} microfacets of a trapezohedron (Fig. 2). The long sides of HEL's have a different structure. The ends of long sides can be flat and in this case they are formed by {111} or {hkk} microfacets (Fig. 2b, c and g). Most HEL's have stepped long sides composed of thinner macrosteps (Fig. 2d–f). In this case, long edges of the layers are not strictly linear. The octahedral microfacets forming the HEL's often have a layered structure (Fig. 2c, f and h). These layers are parallel to the {111} microfacets and have zigzag or straight ends oriented in the [110] directions. Trapezohedron microfacets of HEL's always have a fine stepped structure…

HEL's are usually elongated in two possible [110] directions on each {100} face. However, most or all HEL's on some faces are oriented in one [110] direction. Fig. 3 shows a diagram of the length (L) to width (W) ratio for individual HEL's measured on images obtained using