

## Growth of Nano-Crystalline Diamond on Single-Crystalline Diamond by CVD Method

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**Abstract**—Nanocrystalline (NC) diamond films are grown by chemical vapor deposition on various single crystal diamond faces. Under conditions of NC diamond growth, the growing film morphology is reduced to two planes: {100} and {111}. The {100} planes are smooth and homoepitaxial layer-by-layer growth occurs on them, whereas the NC film formed by twin crystallites with sizes of several tens and hundreds nanometers grows on {111} planes. Nitrogen impurity sharply increases the diamond growth rate.

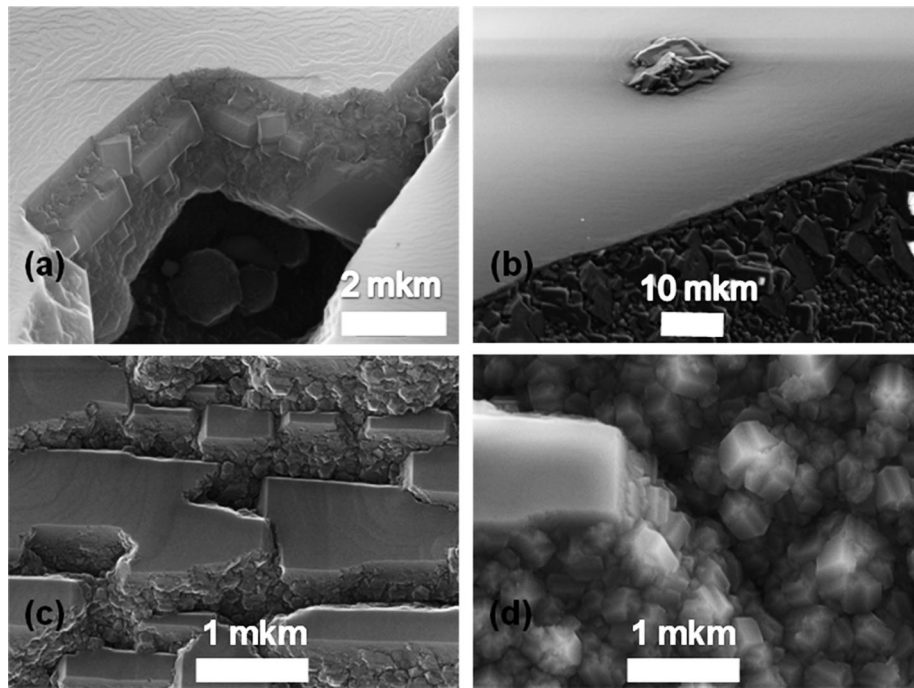
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Diamond is in demand for mechanical treatment of many materials due to its high hardness and abrasion resistance. To this end, synthetic diamond powders grown in high-pressure apparatuses are commonly used. However, diamond powder should be somehow glued to a tool or be pressed into a composite. The chemical vapor deposition (CVD) technology is free of this difficulty and allows growth of polycrystalline diamond coating immediately on the tool surface. In the CVD technology, diamond is deposited from an activated gas mixture of H<sub>2</sub> and hydrocarbon (usually CH<sub>4</sub>) with addition of other gases.

For particular instrumental problems, diamond crystallite sizes in the coating should be controlled in a wide range, including growth of nanocrystalline (NC) coatings on microcrystalline films. Variation of CVD conditions and addition of some gases (N<sub>2</sub>, O<sub>2</sub>, Ar) into a gas mixture make it possible to grow NC (with crystallite sizes of tens and hundreds of nm) and even ultrananocrystalline films. This raises the problem of secondary nucleation and growth of diamond nanocrystals on various single-crystal diamond faces.

During growth, the evolution of the diamond film crystallite morphology is controlled by growth rates  $V$  of main low-index crystal faces, first of all {100} and {111}, as well as {110} and {311} faces [1]. According to the laws of crystal growth in the form of crystallites, the fraction of the area of faces with the least growth rate gradually increases. For convenient analysis, dimensionless parameters characterizing the ratios of growth rates of low-index faces to the growth rate of one of them, e.g., {100} face, are introduced. Among them, the main parameter is  $\alpha = 3^{1/2}V_{100}/V_{111}$ . The higher  $\alpha$ , the larger the area fraction of {111} faces of crystallites. A decrease in the substrate temperature during CVD leads to an increase in  $\alpha$  and a decrease in the crystallite size [2]. An increase in the methane concentration

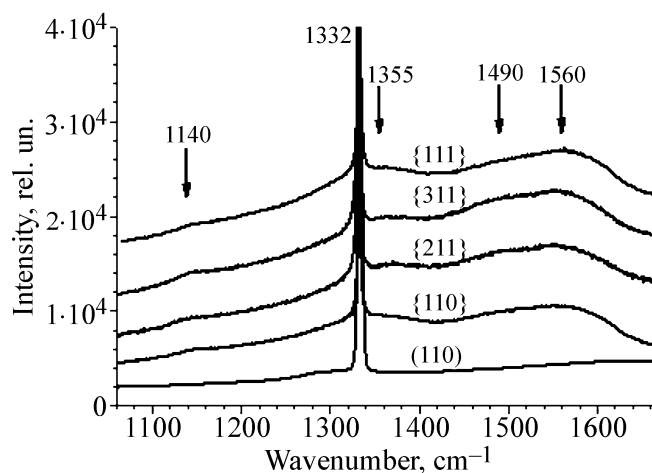


**Fig. 1.** SEM image of the (001) face; (a) after 5-min growth, the lacuna view at an angle of 45°; (b) after 70-min growth, the view at an angle near the face edge; (c) {311} faces after 5-min growth; and (d) after 70-min growth.

[CH<sub>4</sub>] in a gas mixture results in an increase in the diamond growth rate and parameter  $\alpha$ , a decrease in the crystallite size, and an increase in the probability of secondary nucleation, i.e., the formation of new diamond crystallite nuclei with the other crystal orientation on the surface [2]. This provides NC film growth. An increase in [CH<sub>4</sub>] increases the concentration of hydrocarbon radicals (CH<sub>3</sub>, CH<sub>2</sub>, CH, and others) and their adsorption rate on the growing diamond surface. This increases the probability of adjacent deposition of two growth radicals, including radicals with two (CH<sub>2</sub>) or three (CH) dangling bonds, which promotes the formation of growth defects and crystal nuclei with different orientation. A nitrogen addition to the growth mixture also increases the diamond growth rate [3], increases  $\alpha$  and the probability of secondary nucleation. The mechanism is similar, since the N atom incorporated on the diamond surface has two or more dangling bonds [2]. At high  $\alpha$ , {111} faces dominate in the nanocrystallite shape, which are inclined to twinning due to a low twin formation energy [4]. Therefore, multiple twinning on {111} planes controls the NC film morphology. The objective of this work is to study the nucleation mechanisms and NC coating development on various diamond crystal faces in the CVD technology.

*Experimental.* NC layers were deposited on substrates of a single crystal grown by the gradient growth method in a high-pressure apparatus. A crystal upper part containing growth faces such as {311}, {211}, {111}, {110}, and the (111) face was cut off along the (001) plane. The top (001) plane and the cut plane were polished on a polishing ring (with a roughness less than 10 nm). The substrate thickness was 0.9 mm which provided maximum possible growth conditions on its faces in the CVD reactor. NC films were synthesized in microwave plasma in an ARDIS-100 reactor (2.45 GHz, 5 kW) [5], in a “hydrogen/methane/nitrogen” gas mixture at the total gas flow of 500 stand.cm<sup>3</sup>/min (H<sub>2</sub>:460/CH<sub>4</sub>:20/N<sub>2</sub>:20), a chamber pressure of 130 Torr, and a microwave powers of 2.8 kW [6]. The substrate temperature was 800 °C. The temperature was measured using a Micron M770 two-beam pyrometer. The morphology of grown films was studied using a JEOL JSM7001F scanning electron microscope (SEM). Raman spectra were measured using a LabRam HR spectrometer (Horiba, France) upon light scattering excitation by a semiconductor laser with a wavelength of 473 nm. Laser radiation was focused on the object surface using an  $\times 100$  objective into a spot 2  $\mu$ m in diameter. The spectral resolution was 0.5 cm<sup>-1</sup>.

*Results and discussion.* Figure 1 shows the SEM images of several areas of the diamond substrate at various stages of NC film growth by the CVD method. Under NC diamond growth conditions, the



**Fig. 2.** Raman spectra on various faces after 5-min NC film growth. The spectra are shifted on the vertical scale for clarity.

morphology of films growing on substrate faces (Fig. 1 shows only  $\{100\}$  and  $\{311\}$  faces) is reduced to a combination of  $\{100\}$  and  $\{111\}$  crystal planes. The initial  $\{311\}$  and  $\{211\}$  substrate faces did not contain regions with emergence of  $\{100\}$  crystal planes; however, already at the initial growth stage, distinct flat  $\{100\}$  plane areas are formed on them at the tops of  $\{111\}$  layers (Fig. 1(c)). The film morphology on  $\{100\}$  and  $\{111\}$  substrate faces is principally different:  $\{100\}$  planes are smooth and homoepitaxial growth occurs on them, whereas nanocrystallites nucleate and develop on the  $\{111\}$  face. An addition of only 4%  $N_2$  to the gas mixture strongly increases the diamond growth rate [3]. In Fig. 1(a), the growth lacuna on the (001) face is seen, on which the thickness of the homoepitaxial film grown for 5 min was measured. It was  $3.5 \mu\text{m}$  which corresponds to the  $\{100\}$  face growth rate of  $42 \mu\text{m}/\text{hour}$ . In this mode without added  $N_2$ , the  $\{100\}$  face growth rate was  $8 \mu\text{m}/\text{hour}$  [5]. Figure 1 shows the images after 5-min growth (panels (a) and (c)) 70-min growth (panels (b) and (d)). Their comparison shows that the fraction of  $\{100\}$  plane areas decreases during growth. Hence,  $\{100\}$  faces grow with a maximum rate. Figure 1(a) shows the layered nature of the initial stage of the  $\{100\}$  face growth: in some regions, growth layers are sequential; sometimes, they form twisted screw structures (probably, around screw dislocations). During growth, polycrystalline regions are formed and grow at tops of such structures and in intersection regions of growth layers of different directions (i.e., in the regions of the most developed relief). One of the polycrystalline regions is seen at the top of Fig. 1(b).

On  $\{111\}$  and  $\{110\}$  substrate faces, an NC film is formed from the very beginning of growth. It is formed by crystallites from several tens to hundreds of nanometers in size. On  $\{311\}$  and  $\{211\}$  faces, 5-min growth results in the formation of a combination of smooth  $\{100\}$  surfaces (layer-by-layer growth) and NC coating regions on  $\{111\}$  planes (Fig. 1(c)). After 70-min growth on the  $\{211\}$  face, no smooth areas of layer-by-layer growth were observed, it was completely coated with the NC film; on the  $\{311\}$  face, smooth areas of layer-by-layer  $\{100\}$  growth surfaces are still observed (left side of Fig. 1(d)). Nanocrystallites are formed by the multiple twinning mechanism (Fig. 1(d)). The observations described above disprove the concept that nanocrystallites nucleate and develop on any growth surfaces under NC film growth conditions [6].

At the end of 5-min growth, Raman spectra of films deposited on all sample faces were measured (Fig. 2). The position of the main diamond line on studied faces varies from  $1331.8$  to  $1332.7 \text{ cm}^{-1}$ . The peak width at half maximum varies from  $3$  to  $4.5 \text{ cm}^{-1}$ . On the (001) face, a perfect homoepitaxial film was grown. Therefore, its spectrum contains only the main diamond line (at  $1332.4 \text{ cm}^{-1}$ , width is  $3.0 \text{ cm}^{-1}$ ). On all other faces, the spectrum also contains broad bands of unordered carbon (G and D bands have the maxima at  $1560$  and  $1355 \text{ cm}^{-1}$ , respectively) and the trans-polyacetylene bands characteristic of NC diamond (with maxima at  $1140$  and  $1490 \text{ cm}^{-1}$ ), caused by C–H bond vibrations [7]. Hydrogen in them is situated on the nanocrystallite surface.

*Conclusions.* In the technology of CVD growth of diamond, a decrease in the growth temperature, an increase in the hydrocarbon fraction, and a nitrogen addition to the gas mixture enhances the NC diamond film growth. A nitrogen impurity sharply increases the diamond growth rate, especially the {100} face growth rate. Under NC diamond growth conditions, the morphology of the film growing on all diamond crystal faces is a combination of {100} and {111} planes. At the initial growth stage, {100} planes are smooth and homoepitaxial growth by the layer-by-layer mechanism occurs on them. During growth, the area of {100} planes decreases, and polycrystalline areas are formed on them. On {111} planes, the NC film develops which is formed by crystallites of several tens and hundreds of nanometers in size. Nanocrystallites are formed due to multiple twinning. The NC film contains a graphite-like  $sp^2$  phase, and its crystallite interfaces are saturated with hydrogen.

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