Growth mechanisms and defects in boronated CVD diamond as identified by scanning tunneling microscopy

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Boron-doped CVD-diamond films were grown in a simple hot filament reactor. A set of samples grown using various methane-in-hydrogen concentrations has been examined by scanning tunneling microscopy in air. On the diamond (111) crystal faces monoatomic steps could be observed giving evidence for layer growth. At low CH₄ concentrations the layers form triangular growth spirals. Screw dislocations in the middle of the spirals serve as continuous sources of steps for the layer growth producing (111) faces of high crystal perfection. At higher methane concentrations the crystal perfection declines and the (111) crystal faces exhibit a mosaic structure. The size of the subgrains in the mosaic pattern decreases with increasing CH₄ concentration. Nucleation of new layers takes place at the subgrain boundaries. The topography of (001) crystal faces did not significantly change with the methane-in-hydrogen concentration and did not allow the determination of the underlying growth mechanism.

I. INTRODUCTION

Due to its extreme properties, diamond is a very interesting material for various applications. In particular, the incorporation of boron during growth allows the formation of *p*-type semiconducting diamond¹ with outstanding electronic properties.^{2,3} Since the early 1980's, chemical vapor deposition (CVD) methods have been studied intensely, but still the underlying growth mechanisms are not fully understood.⁴

In this paper, we report on scanning tunneling microscopy (STM) investigations of boron containing hot filament CVD diamond films. We will elucidate details of the growth mechanisms and discuss defect structures. The STM is excellently suited for such purposes, because it provides quantitative topographical information in three dimensions together with extremely high lateral and vertical resolution. However, the great roughness of most polycrystalline diamond (PCD) films leads to strong convolution effects with the STM tip. Therefore, great care had to be taken interpreting the STM topographs.

II. EXPERIMENT

A. Chemical vapor deposition film growth

The diamond samples were grown in a simple hot filament reactor with a carburized tungsten wire as a filament.⁵ A mixture of methane and hydrogen was used as the feed gas. The gas flow rate was adjusted to 50 std. cm^3/min while the pressure in the growth chamber was 5300 Pa.

Si(001) wafers were used as substrates. In order to achieve a high and uniform nucleation density, these were scratched with a 20- μ m diamond abrasive in an ultrasonic bath before deposition. During the CVD process the substrate temperature was held constant at 980°C, while the filament temperature was 1995°C; both determined with an optical pyrometer without further corrections.

Boron doping⁶ was achieved by placing powder of elemental boron next to the substrate on the sample holder. The samples were grown for 16 and 64 h, respectively.

B. Scanning tunneling microscopy investigations

The diamond films were examined by scanning tunneling microscopy in air using a commercial STM.⁷ There was no post-deposition treatment applied to the samples before the STM investigations. All images were taken in the constant current mode with bias voltages around -300 mV (negative bias on the sample) and tunneling currents of about 0.35 nA. Crystallographic planes and directions were assigned according to the geometry of the crystallites.

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III. RESULTS

All samples grown were polycrystalline diamond films without a pronounced texture, as could be seen in scanning electron micrographs (SEM) and in large-area STM topographs. Figure 1 shows an SEM and an STM image of a sample grown at 0.3% methane in hydrogen. Comparing scanning electron micrographs of samples grown in the presence of boron and samples grown under the same conditions, but in a boron-free environment, we found strong morphological differences.⁸ Thus, it appears that boron can significantly change the diamond growth.

The electrical conductivity of boron-free samples was too low for stable imaging with the STM. Whichever tunneling conditions we chose, on boron-free samples, charging effects always occurred.

From film thickness measurements in the SEM, we obtained the following growth rates (film thickness/growth time) after 16 h of growth: 0.3% methane in hydrogen: 0.13 μ m/h; 0.5%: 0.31 μ m/h; 0.8%: 0.41 μ m/h; 1.2%: 0.75 μ m/h; and 1.6%: 0.94 μ m/h.

A. (111) crystal faces

For methane-in-hydrogen concentrations of up to 1.2%, (111) crystal faces could be identified in the PCD



FIG. 1. Topographic overview of a boron-doped PCD sample grown at 0.3% methane in hydrogen. An SEM image is shown on top (magnification ≈ 3000), the image size of the STM measurement below is $\Delta x \Delta y \Delta z = 11 \times 11 \times 1.6 \, \mu \text{m}^3$.



FIG. 2. Scanning tunneling microscopy topograph of a part of a (111) face on a sample grown at 0.3% methane in hydrogen. A single growth spiral propagates the layer growth leading to a flat (111) face of high crystalline perfection. Terrace widths: 21.2 nm; step heights: 1 or 2 ML (image size $\Delta x \Delta y \Delta z = 420 \times 420 \times 8 \text{ nm}^3$).



FIG. 3. Layer growth on a (111) face grown at 0.3%, shown at different magnifications. Two left-handed spirals propagate the growth. The terrace widths are 22 nm, the step heights 1 or 2 ML. The upper image shows some big steps, which are attributed to the evolving mosaic structure (image size top: $\Delta x \Delta y \Delta z = 500 \times 500 \times 12$ nm³; bottom: $\Delta x \Delta y \Delta z = 160 \times 160$ $\times 1.5$ nm³).

films. All those faces were stepped with step heights of the order of one monolayer (1 ML=0.206 nm). But otherwise the topography of the (111) faces varies significantly with the methane-in-hydrogen concentration.

At the lowest CH₄ concentration of 0.3%, the steps were wound up to spirals (growth pyramids), see, e.g., Fig. 2. The terrace widths were 20 ± 2 nm and the step heights 1 or 2 ML. The steps run parallel to the face boundaries, i.e., along the $\langle 110 \rangle$ directions. Between 1 and 5 spirals were found on a single (111) face. There existed left- as well as right-handed spirals, but on one (111) face only one handedness was found. Figure 3 shows two left-handed spirals on a (111) face at different magnifications.

From 0.5 to 1.2% CH_4 in H_2 the crystal perfection of the (111) faces declines, and the faces are made up of little "blocks" (Fig. 4). The size of these "blocks" decreases with increasing methane concentration. 0.5% methane in hydrogen: 60-400 nm linear dimension; 0.8%:



FIG. 4. Mosaic structure on diamond(111). The steps which confirm layer growth can mostly still be resolved. Step sequences always begin at places where subgrains touch each other. The samples were grown at methane-in-hydrogen concentrations of 0.5% (top) and 1.2% (bottom), the image sizes are $550 \times 550 \times 7$ nm³ and $420 \times 420 \times 12$ nm³, respectively. Subgrain sizes are given in the text. (The high elevation in the middle of the lower topograph is attributed to contamination of the sample.)



FIG. 5. Nucleation of growth layers on (111) CVD diamond. The image shows impressively how new growth layers are nucleated at subgrain boundaries. It can also be seen that for this layer-nucleation mechanism, the layer nucleation frequency and therefore the terrace widths may vary considerably even within a single (111) face. Methane concentration: 0.5% (image size $\Delta x \Delta y \Delta z = 240 \times 240 \times 4 \text{ nm}^3$).

30-150 nm; and 1.2%: 40-70 nm. The surfaces of the blocks are stepped with step heights ranging from 1 to 4 ML and terrace widths between 4 and 14 nm. The terrace widths vary strongly within one sample, so that no significant dependence on the methane-in-hydrogen concentration can be detected. The uppermost terraces and therewith the starting points of the layer sequences are always at an edge of a block and were never found in the middle of a block. See for example Fig. 5.

The form of the blocks is triangular or hexagonal with edges aligned within a few degrees parallel to the edges of the (111) face, i.e., along the $\langle 110 \rangle$ directions. The blocks are tilted by 0.5° to 3° against each other (with respect to the $\langle 111 \rangle$ directions). Mostly, the steps on the blocks also run along the $\langle 110 \rangle$ directions, but sometimes rounded terraces occurred.

Onsets of the block structure can already be found on samples grown with 0.3% methane in hydrogen. The blocks observed here are 300 to 600 nm in linear dimension.

B. (001) crystal faces

On the (001) faces, no growth spirals and no growth steps could be resolved. Significant changes in the topography with a variation of the methane-in-hydrogen concentration could not be observed either. The (001) faces were flat within 5-10 nm over 500×500 nm² areas. Mostly, there was one ridge (sometimes several) dividing the (001) face into two (or more) flat domains. Figure 6 shows an example.

Within a few degrees, the ridges were always parallel to the face edges, i.e., they ran along the $\langle 001 \rangle$ or $\langle 110 \rangle$ directions. Whether, in fact, both or only one of these directions occurred cannot be definitely decided, because of the complicated crystallite arrangements in the PCD films.

The flat domains are aligned to each other by angles



FIG. 6. Scanning tunneling microscopy topograph showing a part of a (001) crystal face in a film grown at 0.3% methane in hydrogen. The angle between the two adjacing flat domains is 4.3°. The corrugations on the flat domains are about 0.1 nm deep (image size $\Delta x \Delta y \Delta z = 360 \times 360 \times 12 \text{ nm}^3$).

between 1° and 10°. They exhibit corrugations, mostly in the form of somewhat irregular ridges with heights between 0.1 and 0.8 nm running parallel to each other with separations between 1 and 10 nm. But bigger roundish elevations and valleys exist also. The small ridges are mostly parallel to the big ridge along the $\langle 001 \rangle$ or $\langle 110 \rangle$ directions.

On a near-atomic scale (001) and (111) faces both showed irregular structures. With heights between 0.1 and 0.5 nm and widths between 1 and 5 nm, the corrugations on the terraces of (111) crystal faces are similar to those on (001) faces. Using normal tunneling parameters, we could not achieve atomic resolution on any of the samples.

IV. DISCUSSION

As has been indicated before, the presence of boron in the hot filament CVD process significantly changes the growth of the PCD films. Therefore, it should be kept in mind that the following conclusions might only apply to diamond growth in the presence of boron.

A. (111) crystal faces

The existence of steps with heights of the order of 1 ML shows that the (111) faces of the samples grew in a layer-by-layer growth mode. This applies to all methane-in-hydrogen concentrations between 0.3 and 1.2%. However, new growth layers were nucleated in different ways.

At 0.3% the layer growth produced growth spirals. This can be explained in terms of nucleation at screw dislocations as already described by Burton, Cabrera, and Frank:⁹ During growth, the step intrinsically connected to a screw dislocation winds up to a spiral (growth pyramid). The screw dislocations act as continuous sources of growth steps, and crystals grown that way are of high perfection. That diamond (111) faces can grow according to this mechanism is remarkable since the (111) faces are usually considered to be highly defective, in particular, due to microtwinning.¹⁰ The Burton-Cabrera-Frank theory⁹ cannot be quantitatively applied to CVD systems, because here the growing surface is covered with a dense adsorption layer during the growth process.¹¹ Yet the high uniformity of the terrace widths at the growth spirals (20 nm \pm 10% for all samples grown at 0.3% methane in hydrogen and 980 °C substrate temperature) is to be expected for this nucleation mechanism.

For 0.5% or more methane in hydrogen, the observed topography reveals that the (111) faces grow with a mosaic structure, i.e., the crystals consist of small subgrains ("mosaic blocks"), which are tilted against each other by up to a few degrees in all three directions. There are also reports on natural diamond with mosaic structure,¹² but the grain sizes we observed are two to three orders of magnitude smaller than those described there. The structures on (111) faces described in Ref. 13 as microtwins appear to be basically the same as the features observed here. We interpret these as mosaic structure, and we do not have any reason to assume that they have anything to do with twinning phenomena.

The steps on the subgrains with heights of 1-4 ML show that layerwise growth still took place, moreover growth can obviously take place multilayerwise. At the higher methane concentrations ($\geq 0.5\%$), there is no more nucleation at screw dislocations. And there is also no two-dimensional nucleation, because if there were, step sequences originating somewhere in the middle of a subgrain should have been found. Instead, nucleation at subgrain boundaries took place: New steps are nucleated where two crystals or subgrains touch each other. Figure 5 shows this clearly. Those places can provide energetically or sterically preferred adsorption sites.

This layer-nucleation mechanism can explain the wide variation of terrace widths (4-14 nm): The energy necessary for originating a new layer at such a contact nucleation place, and therefore the layer-nucleation frequency and terrace widths, depends strongly on the orientation of the subgrains with respect to each other. Since various subgrain orientations may occur, the terrace widths will vary, too.

The decrease of the subgrain size in the mosaic structure and thus the decline of crystal perfection with increasing methane-in-hydrogen concentration may be understood by a simple argument: At higher methane concentrations (and constant temperature) the balance between desorption and adsorption is shifted such that there are more carbon species adsorbed at defect sites or in a defective manner than at lower concentrations. The nucleation of new subgrains will, therefore, be enhanced for higher methane concentrations resulting in more and smaller subgrains.

B. (001) crystal faces

The observed topography on (001) crystal faces does not allow definite conclusions about the growth mechanism. It is likely that the (001) faces grow layerwise, as also proposed in Refs. 13 and 14, since the well-defined crystallographic alignment of the observed ridges would not occur in pure normal growth. With the alignment angles between the flat domains being 1° to 10° and assumed step heights of 1 or 2 ML (89 and 178 pm, respectively) the expected terrace widths in case of layerwise growth should be of the order of 2 nm.

The similarity of the topography on near-atomic scale on (001) and (111) faces can be explained if there are irregularly distributed adsorbates on the PCD films. Nondiamond carbon phases have been shown to exist on CVD-diamond films.^{15,16} It is likely, that such adsorbates form during the switch off of the CVD process.¹⁵ During the initial cool-down period after the production of our samples, there were still some carbon species in the gas phase, which might have been adsorbed. Thus, low growth steps (1 or 2 ML) with small terrace widths (≈ 2 nm) may have existed on the (001) faces, which just could not be resolved by the STM because of adsorbates on the surfaces.

V. SUMMARY

Polycrystalline boron-doped CVD-diamond films have been examined by means of scanning tunneling microscopy in air. We gave direct proof that the (111) faces grew in a layer-by-layer growth mode by imaging the growth steps. Step heights were found to range from 1 to 4 ML and terrace widths from 4 to 20 nm.

For low methane-in-hydrogen concentrations, nucleation of new growth layers occurs at screw dislocations resulting in growth spirals leading to high crystal-

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⁷The STM we used was a Nanoscope II from Digital Instru-

line perfection. This is a noteworthy fact, because usually (111) faces are considered highly defective.

With increasing methane concentration in the feed gas, the crystal perfection declines and a mosaic structure evolves more and more. The linear dimensions of the subgrains range from 600 nm at 0.3% methane in hydrogen down to 40 nm at 1.2%. At 0.5% and higher concentrations, the layer nucleation was shown to take place at subgrain boundaries. The dependency of the subgrain sizes and of the terrace widths on the methane-inhydrogen concentration could be explained.

The (001) crystal faces mostly consisted of two or more angled domains. These show irregular structures on the nanometer scale. Since the nanotopography of (111) faces is similar, it is assumed that adsorbates existed on the PCD films. Whether the (001) faces grow layerwise or not cannot be concluded from the observed topography.

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FIG. 1. Topographic overview of a boron-doped PCD sample grown at 0.3% methane in hydrogen. An SEM image is shown on top (magnification ≈ 3000), the image size of the STM measurement below is $\Delta x \Delta y \Delta z = 11 \times 11 \times 1.6 \, \mu \text{m}^3$.



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