Single crystal diamond deposition by laminar and turbulent acetylene-oxygen flames

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The homoepitaxial deposition of diamond layers on {111} and {001} type-IIa natural diamond substrates, by both laminar and turbulent acetylene-oxygen flames, is described. Using the same gas flows, temperatures, and supersaturations of 4%, a higher growth rate was obtained on a {001} substrate with a turbulent flame than with a laminar flame. Layers grown at the same temperature on {111} substrates with a supersaturation of 3% show no significant difference in growth rate. Due to the large differences in geometry between both types of flames it is not possible to relate the substrate positions in the acetylene flames to each other and compare the growth results at any location. However, it is shown that the application of turbulent flames for single-crystal growth does not lead to a dramatic change in quality of the diamond as was previously reported in the literature. It is demonstrated by microscopic and spectroscopic techniques that the crystallographic orientation of the substrates, the deposition temperature, and the gas velocity all have a larger influence on the crystal morphology and impurity incorporation of the grown single crystals than the introduction of turbulence. © 1995 American Institute of Physics.

I. INTRODUCTION

In recent years the homoepitaxially deposition of diamond crystals from a laminar acetylene-oxygen combustion flame has only been studied by a limited number of research groups,1,2 despite the fact that with this relatively simple and inexpensive deposition technique good quality single crystals comparable to type-IIa natural diamond can be obtained at high growth rates.3 Snail and Craigie argued that the growth rate could be increased significantly by the introduction of turbulence if diamond growth in laminar flames is transport limited.4 The laminar or turbulent nature of a gas flow in a tube is within certain limitations determined by its dimensionless Reynolds number (Re) defined as 

$$\text{Re} = \frac{4 f_{\text{tot}}}{\pi D v}$$

with $f_{\text{tot}}$ the total gas flow, $D$ the tube diameter, and $v$ the kinematic viscosity of the gas mixture. For a mixture at 300 K with an acetylene-to-oxygen ratio close to 1, which is used in flame deposition, $v$ can be calculated to be 0.129 cm$^2$/s.5 Reynolds numbers below 2300 are associated with laminar flows and above 3200 turbulent flows.6 Between these two limits the flow is regarded to be in a transition state. As argued before by one of the authors,7 it is hard to obtain a turbulent flame with a commercial burner since the exit tube is by far not long enough to establish a turbulent flow. Although the Reynolds number calculated at the exit opening is well above 3200, the flame obtained is still laminar. Therefore, in this case Re should be related to the diameter of the gas tube leading to the tip; however, a turbulent flame can be obtained with a commercial burner by the use of extremely large flow rates and larger exit openings as compared to the laminar situation. A diamond layer deposited in a turbulent flame obtained in this way8 was shown to have a better quality but a lower growth rate than specimens grown in a laminar flame.6 This gain in quality at the cost of growth rate is a common phenomenon in crystal growth by chemical-vapor deposition (CVD); see, e.g., Ref. 9.

Recently, researchers at the CSEM succeeded in designing a burner for which a fully turbulent flame is stabilized at the same total gas flow as for a laminar flame obtained by a commercial burner with the same exit diameter. Alers and co-workers7 reported that in such a turbulent flame the polycrystalline diamond deposition rate on molybdenum substrates is twice as high as in a laminar flame under similar conditions. In the present study an upscaled burner tip of the same design with an exit opening of 1.4 mm in diameter is used to generate a turbulent flame. The results of homoepitaxial deposition on {111}- and {001}-oriented natural diamond substrates with this burner are compared with those obtained by a commercially available laminar burner with the same exit opening. The {111} samples are discussed in detail, while the {001} samples are considered briefly as the growth of these samples by the flame technique was previously described.3

II. EXPERIMENTAL DETAILS

The flame deposition setup has been described in detail in previous work.3,10 The cooling system developed at the University of Nijmegen allows regulation of the deposition temperature to within ±20 °C absolute and ±10 °C relative. The flows of the high-purity source gases oxygen (99.995%) and acetylene (99.6%) are regulated by mass flow controllers within ±0.05 standard liter per minute (slm). A commercially available welding torch equipped with a 1.4-mm-diameter orifice tip was used to generate the flame. Whenever a turbulent flame was required this tip was exchanged by a CSEM-designed turbulent tip with the same exit diameter.
The turbulent burner, which basically consists of a turbulence-inducing orifice mounted inside a commercially available burner tip a few millimeters before the exit opening, was designed for total gas flows around 6 slm. Because diamond deposition takes place in a narrow composition region around a 1:1 mixture of acetylene and oxygen, the oxygen flow during all experiments was fixed at 3 slm. The deposition temperature $T_d$ was kept around 1150 °C for most experiments. At such high temperatures good quality diamond single crystals with growth rates up to 130 $\mu$m/h were obtained with a laminar flame before. The position of the sample in the acetylene feather is determined by the distance $d$ from the inner cone of the flame or the distance $b$ from the burner tip (see Sec. III). The gas composition is defined by the acetylene supersaturation ($S_{ac}$) or the acetylene-to-oxygen ratio $R$. The deposition times varied between 2 and 3 h. The growth conditions and a number of characteristics of the samples are listed in Table I. The samples grown in the turbulent and laminar flame are denoted T and L, respectively. The second character in the notation indicates whether the type-IIa natural diamond substrate has a cubic (C) or octahedral (O) top face. These (within $\pm 4^\circ$) {001}- and {111}-oriented substrates are cylindrically shaped with a diameter of 2 mm and a thickness of 250 $\mu$m. To ensure a good thermal contact during deposition the substrates were soldered onto the water-cooled substrate holder.

After flame deposition the surface morphology of the single crystals was investigated by scanning electron microscopy (SEM) and optical differential interference contrast microscopy (DICM). The orientations of the facets developed along the sides of the samples were determined by measurement of their angles $\theta$ relative to the top face of the sample using a two-circle optical-reflection goniometer. The diameter of the in-drawn circle of these faces is used as a measure of their morphological importance (M) relative to each other. In addition the differences in crystalline perfection of the deposited layers were analyzed by various techniques such as cathodoluminescence (CL) topography, and Raman and photoluminescence (PL) spectroscopy. The PL spectra presented in this study were obtained at 87 K using the 514.5 nm line of an Ar$^+$ laser as the excitation source. The luminescence was dispersed by a 0.6 m double monochromator with 1200 lines/mm gratings and detected by a cooled photomultiplier tube with a GaAs photocathode. The equipment used for Raman spectroscopy and CL topography have been described elsewhere.

III. FLAME CHARACTERISTICS

An important feature of a premixed flame is the flame front. For the acetylene-oxygen flame this is the zone in which the primary combustion of the premixed gases and oxygen to CO and H$_2$ takes place. This reaction zone propagates opposite to the outflowing source gases with the burning velocity $v_b$ which equals the gas flow component normal to the zone. For a laminar flame the primary combustion process is reasonably well understood and the burning velocity and the shape of the flame front can be described in terms of gas composition, total flow rate, and the dimension of the burner orifice. The flame fronts in Fig. 1 can be recognized as the brightest parts of the flames due to emission of thermally or chemically excited C$_2$ and CH radicals. Figure 1(a) shows that the front of a laminar flame (Re≈2000) is a conically shaped zone with a thickness of about 40 $\mu$m. Inside this cone the gas mixture is heated up slightly but does not react. Apart from side effects at the rim and the rounded tip of the cone, $v_b$ is constant over the flame front. Therefore, the burning velocity of a flame can be determined from the measurement of the area of the flame from $A_f$ and the total gas flow $f_{tot}$ by $v_b = f_{tot}/A_f$. Approximating the flame front of the flame in Fig. 1(a) by a cone with height $h$ and base radius $r$, which in general is about 10% larger than the radius of the burner opening, $A_f = \pi r \sqrt{r^2 + h^2}$ and $v_b$ is found to be 5.8 m/s.

Outside the cone the combustion proceeds in a diffusion flame in which the CO and H$_2$ formed in the flame front react to CO$_2$ and H$_2$O by in-diffusion of oxygen from the ambient. In case an excess of acetylene is present in the gas mixture, this reacts outside the flame front in the diffusion flame forming the acetylene feather [see Fig. 1(a)]. This feather, in which all kinds of hydrocarbons exists, is visible due to radiation of C$_2$ and CH radicals. If the excess of acetylene is diminished the feather decreases until a neutral flame is obtained as the feather just disappears. This situation can be clearly recognized in a laminar flame and defines the zero point in the acetylene supersaturation ($S_{ac}=0$%).

![FIG. 1. Free-burning (a) laminar and (b) turbulent acetylene-oxygen flames obtained with the same gas composition (f$_{ac}=3$ slm, R=1.005, S$_{ac}=5\%$) and burner opening which is 1.4 mm in diameter. The same (c) laminar and (d) turbulent flames directed on a cooled substrate.](image)
The turbulent nature of the CSEM-designed burner (Re \( \approx 7000 \)) was confirmed by the loud hissing sound of the burner\(^{4,6} \) and the shape of its flame front which is shorter and more rounded than the laminar one [see Fig. 1(b)]. The center of the front is not sharply defined but is blurred and therefore usually referred to as the flame brush. In contrast to the center, the rim of the flame front remains steady indicating that the amount of turbulence decreases radially with the distance from the center of the flame. For turbulent flames obtained with commercial burners by the application of high flow rates,\(^{17} \) the flame front is more elongated and the part which remains well defined is larger than for the turbulent flame which is used in the present study. The appearance of such a flame is a kind of intermediate between the laminar flame and the turbulent flame shown in Fig. 1. The brush appears to be a time average of a rapidly fluctuating wrinkled and sometimes even fragmented flame front, as was also confirmed by Marks et al.\(^{18} \) using dark-field shadow photography. These fluctuations indicate that the burning velocity varies both in time and with the position of the flame front. This is caused by turbulent eddies of the same dimensions as the thickness of the flame front leading to sharp curvatures in the front and an increased transfer of heat and radicals.\(^{6} \) Approximating the mean area of the front by a truncated cone with a hemispherical top, the average value of the burning velocity of the flame in Fig. 1(b) is estimated to be 7.5 m/s.

Not only the flame front but also the acetylene feather of the turbulent flame is smaller. This shows that the combustion of the excessive acetylene proceeds faster by the enhanced in-diffusion of oxygen from the ambient due to the turbulence. Diamond deposition takes place if a cooled substrate is placed in the reducing acetylene feather [see Figs. 1(c) and 1(d)]. Outside the feather in the oxidizing outer flame, diamond will be etched rather than grown. In previous studies\(^{3,10} \) the quality of the deposited material among others appeared to be dependent on the excess of acetylene used to create the feather and the position of the substrate in it. Using a laminar flame these features were described by \( S_{\text{ac}} \) and \( d \) [see Fig. 1(c)], for which the flame front directly or indirectly is used as a reference. However, as the turbulent flame front is not sharply defined the accurate determination of the values for \( d \) and \( S_{\text{ac}} \) in a turbulent flame is not possible. This problem is "solved" by using the substrate to burner distance \( b \) [see Fig. 1(d)] and the acetylene-to-oxygen ratio \( R \) in a turbulent flame as an alternative reference for \( d \) and \( S_{\text{ac}} \), respectively.

### IV. GROWTH RESULTS AND DISCUSSION

Due to the specific graphitelike appearance of the \{111\} surface and its easy disturbance of stacking order,\(^{19} \) crystal volumes grown via this face usually suffer from several defects such as stacking faults, graphitelike inclusions, and, perhaps most of all, microtwinning. These defects obstruct the step growth mechanism of the face, which therefore easily becomes polycrystalline after growth of a few micrometers.\(^{15} \) Janssen et al. demonstrated the occurrence of this phenomenon for a flame-grown specimen at a temperature of approximately 940 °C.\(^{20} \) Results of a recent study on flame-grown polycrystalline diamond layers indicate that the occurrence of these defects increases with decreasing activation level of the gas phase.\(^{13} \) Samples grown at a distance larger than 2 mm from the flame front or with supersaturations above 6% show a fast deterioration of the \{111\} faces. It was discussed that this is probably related with the formation of larger hydrocarbon compounds and possibly soot in the gas phase which, upon deposition easily induces the formation of twins or other defects. To avoid these problems the \{111\} samples in the present study were grown at about 1 mm from the flame front using a somewhat lower value for \( R \) (\( S_{\text{ac}} \)) than the \{001\} samples (see Table I). This strategy appeared successful because the single-crystal nature of the samples was maintained, although the deposition rate was much lower than that of the \{001\} samples. Table I shows that for the \{111\} samples grown at 1150 °C the introduction of turbulence did not result in an increase in growth rate; however, the \{001\} sample grown by the turbulent flame was obtained with a higher deposition rate than the one grown by the laminar flame. Polycrystalline layers grown on molybdenum substrates, using the same flames as described in the present study, reveal a similar behavior of the growth rate as a function of the supersaturation. At low \( S_{\text{ac}} \) diamond layers grow faster in the laminar flame in the turbulent flame, at high \( S_{\text{ac}} \) the layers grow faster in the turbulent flame. This phenomenon could be described by the higher mixing rates in the turbulent flame, resulting in a less localized flame front and a smaller acetylene feather due to a faster completion of the combustion process.\(^{13} \) Compared to the total length of the turbulent feather, growth proceeds relatively close to the flame front for high \( S_{\text{ac}} \). For low \( S_{\text{ac}} \) growth proceeds relatively close to the periphery of the turbulent feather where the combustion of excessive acetylene is almost completed. A more detailed description of this process is given in Ref. 13.

### Table I. Growth conditions and results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LO</th>
<th>TO1</th>
<th>TO2</th>
<th>LC</th>
<th>TC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Burner tip</strong></td>
<td>laminar</td>
<td>turbulent</td>
<td>turbulent</td>
<td>laminar</td>
<td>turbulent</td>
</tr>
<tr>
<td><strong>Substrate</strong></td>
<td>{111}</td>
<td>{111}</td>
<td>{111}</td>
<td>{001}</td>
<td>{001}</td>
</tr>
<tr>
<td>( T_{e} \approx 20 ) (°C)</td>
<td>1150</td>
<td>1150</td>
<td>1250</td>
<td>1150</td>
<td>1150</td>
</tr>
<tr>
<td>( f_{\text{ac}} \approx 0.03 ) (slm)</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>( S_{\text{ac}} \approx 0.5 ) (%)</td>
<td>3.0</td>
<td>...</td>
<td>...</td>
<td>4.0</td>
<td>...</td>
</tr>
<tr>
<td>( R \approx 0.005 )</td>
<td>0.985</td>
<td>0.985</td>
<td>0.985</td>
<td>0.995</td>
<td>0.995</td>
</tr>
<tr>
<td>( d \approx 0.1 ) (mm)</td>
<td>1.0</td>
<td>...</td>
<td>1.0</td>
<td>1.0</td>
<td>...</td>
</tr>
<tr>
<td>( b \approx 0.3 ) (mm)</td>
<td>8.0</td>
<td>5.0</td>
<td>5.0</td>
<td>8.0</td>
<td>5.0</td>
</tr>
<tr>
<td>( h_{\text{ac}} \approx 5 ) (µm)</td>
<td>43</td>
<td>38</td>
<td>38</td>
<td>85</td>
<td>97</td>
</tr>
<tr>
<td>( a_{\text{ac}} \approx 3 ) (µm/h)</td>
<td>14</td>
<td>13</td>
<td>21</td>
<td>34</td>
<td>49</td>
</tr>
</tbody>
</table>

Schermer, Gilling, and Alers
of the {111} samples, resulted in the development of a wealth of additional facets such as {337}, {7 7 13}, and {9 9 19}. The sources are overgrown by larger ones generated by twins or twins27 can account for the observed appearance of the "double" growth hillock. Alternatively, the triangular features might be generated by extended dislocations along (112), consisting of two closely spaced partial dislocations with a stacking fault in between.28 In that case the twins between the summits of these elevations could be formed at any time during the deposition process. The relatively small number of hillocks compared to the dislocation density of type-IIa natural diamond (10⁶ cm⁻²) is explained by the fact that most of the smaller hillocks from individual dislocation sources are overgrown by larger ones generated by twins or extended, more active, dislocation sources. The presence of the triangular hillocks indicates that the growth rate is limited by the growth rate. The slopes of the hillocks are opposite to those expected from a first-order periodic bond chain (PBC) analysis,29 but can satisfactorily be explained by the assumption of step reconstruction by dimer formation.30 In the center of the sample the triangular features are somewhat less distinct and the hillocks are a bit rounded. There are two

A. Morphology of specimen grown on {111}-oriented substrates

Sample LO grown using a laminar flame shows a number of interesting features which are discussed in detail followed by a comparison with the characteristics of the {111} samples grown with a turbulent flame. Figure 3(a) shows that the (111) top face of the sample is covered by triangular hillocks. These elevations are bounded by vicinal faces of the "positive"24 form {111} + δ with 0 < δ < 1 which are stepped toward the [112], [121], and [211] directions. The inclination of the vicinal faces with the exact (111) face is 4° as was determined by the goniometer. Close examination with DICM reveals that most of the large elevations consist of two individual hillocks with closely spaced (between 5 and 15 μm) summits which have one slope in common. The summits are connected by a peculiar line-shaped feature typically 2 μm wide, perpendicular to the in-plane (112) directions. Several of them could be identified as penetration twins.25,26 Accumulation of steps generated by contact nucleation at both ends of the low inclination side (twin plane) of the twins can account for the observed appearance of the "double" growth hillock. Alternatively, the triangular features might be generated by extended dislocations along (112), consisting of two closely spaced partial dislocations with a stacking fault in between.28 In that case the twins between the summits of these elevations could be formed at any time during the deposition process. The relatively small number of hillocks compared to the dislocation density of type-IIa natural diamond (10⁶ cm⁻²) is explained by the fact that most of the smaller hillocks from individual dislocation sources are overgrown by larger ones generated by twins or extended, more active, dislocation sources. The presence of the triangular hillocks indicates that the growth rate is limited by integration of growth units into the kink positions in a step. The slopes of the hillocks are opposite to those expected from a first-order periodic bond chain (PBC) analysis,29 but can satisfactorily be explained by the assumption of step reconstruction by dimer formation.30 In the center of the sample the triangular features are somewhat less distinct and the hillocks are a bit rounded. There are two

TABLE II. Angles of the side faces with the top face of the {111} specimens and the smallest lateral width of these faces as an indication of their morphological importance.

<table>
<thead>
<tr>
<th>Sample LO</th>
<th>Sample TO1</th>
<th>Sample TO2</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ±2 (deg)</td>
<td>M±3 (μm)</td>
<td>θ±2 (deg)</td>
<td>M±3 (μm)</td>
</tr>
<tr>
<td>71.2</td>
<td>140</td>
<td>70.4</td>
<td>150</td>
</tr>
<tr>
<td>89.5</td>
<td>40</td>
<td>87.5</td>
<td>80</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>127.1</td>
<td>50</td>
<td>126.0</td>
<td>50</td>
</tr>
<tr>
<td>35.6</td>
<td>38</td>
<td>36.4</td>
<td>40</td>
</tr>
<tr>
<td>56.2</td>
<td>30</td>
<td>56.2</td>
<td>15</td>
</tr>
<tr>
<td>71-76</td>
<td>95</td>
<td>72-82</td>
<td>145</td>
</tr>
<tr>
<td>109.9</td>
<td>70</td>
<td>110.3</td>
<td>75</td>
</tr>
</tbody>
</table>
In addition to the triangular features the top face exhibits about ten clearly distinguishable parallel twins of approximately 30 μm in diameter [see Fig. 3(b)]. None of these twins is perfectly shaped, they all show evidence for additional twinning due to the increased local strain in the diamond lattice. This process eventually leads to the complete deterioration of the octahedral surface since the growth steps cannot pass the twin boundary. At the same time it is clear from their limited appearance that formation of twins can be suppressed by deposition close to the flame front using a relatively low supersaturation and a high deposition temperature. From the fact that their presence does not seem to interfere with the macrosteps located nearby on the crystal surface, it can be deduced that they were nucleated in a final stage of the growth experiment. Whatever induced their appearance, which is not restricted to a certain part of the octahedral top face, in this stage remains unclear.

Inspection of the sample by DICM reveals that the center of the sample exhibits a large number of cracks along the octahedral cleavage planes [see Fig. 3(c)], i.e., perpendicular to the {112} directions in the plane of the top face. The cracks are confined to the grown layer and were formed after growth since the cracks do not interfere with the growth features at the surface. Van Enckevort et al. reported similar crack patterns which are a manifestation of stress release of homoepitaxial {111} samples grown by the hot filament technique. The stresses arise from a lattice mismatch between the grown layer and the substrate. Near the rim of the top face the sample is not cracked since the strains in this region are expected to be released by elastic deformation of the side faces of the crystal. This picture is supported by the fact that previously investigated flame-grown samples on {110} substrates show an increasing amount of cracks along the {111} cleavage planes with increasing lateral dimensions of the crystal.

Along the rim of the top face a curved band of macrosteps has developed which is interrupted by six sets of broad connected facets more or less vertical along the sides of the sample [see Fig. 4(a)]. Some of the faces are not shown in the stereographic projection of Fig. 2 because their angle with the top face is more than 90°. These faces have developed in spite of the fact that they are not directly facing the main gas flow. The faceted sets, which are of two different types, are shown in detail in Figs. 4(b) and 4(c). The large side facet visible in Fig. 4(c) is identified as a {111} face since it shows exactly the same growth features as described for the top face. Together with the top face the position of this side face completely fixes the orientation of the sample. The arrows in Fig. 2 indicate the direction in which the photographs of Fig. 4 were taken. The goniometer measurements reveal that the faces in the set shown in Fig. 4(b), and to be referred to as the (cubic) C set hereafter, are {111}, {001}, {11X}, and {111} from top to bottom. The other set [see Fig. 4(c)], to be referred to as the (octahedral) O set, exhibits {111}, {112}, and {001} faces from top to bottom. Figure 4(d) is a schematic representation of both sets showing the relative dimensions of the observed faces averaged over the three symmetry-equivalent counterparts (also see Table II). From the cross section it becomes clear that,
though reported by others, the observed \{112\} faces in the O sets most probably are the “translated” sides of the original cylindrical substrate which have not grown out of the crystal form yet. The morphological importance of the \{112\} faces in the three O sets of the specimen differ significantly (between 17 and 60 \(\mu m\)). Because the angle between both faces adjacent to the \{112\} orientation in the C sets (\(\approx 37^\circ\)) is smaller than in the O sets (\(\approx 55^\circ\)) (see Table II), the face has already disappeared from all C sets. The gradual transition to the rough, cobbled orientations on both sides of the \{112\} faces [see Fig. 4(c)] illustrates their relatively low degree of stabilization compared to the other side faces. In addition the cross section shows that the morphological importance of more stable faces with equivalent Miller indices in both sets changes with their distance from the top face. This is related with the typical gas-phase geometry of the flame technique of which the composition changes significantly between the top and the bottom of the samples.

A comparison between Figs. 4(b) and 4(c) reveals that close to the O sets the curved band shows a high density of macrosteps parallel to the \{110\} PBCs, while it exhibits more flattened features close to the C sets. This indicates that most of the surfaces with orientations in the curved band are stabilized in one direction (parallel to the in-plane PBCs) but that close to the C sets a discrete number of them are stabilized in two directions. The difference in stabilization, indicated by the solid and dashed lines in Fig. 2, can be described by a model based on an orientation-dependent broken bond analysis of the surfaces, with additional considerations about dimer formation perpendicular to the \{110\} PBCs which is presented elsewhere. The model shows that due to the formation of dimers, stabilization in at least one direction is expected for orientations corresponding to Miller indices \(\{hkk\}_{h<k}\) in the \{110\} zones which, according to the PBC theory, should be rough (kinked) \(K\) faces. Except for the \{111\} facets which are stabilized by three connected \{110\} PBCs, all the faces and the curved bands with macrosteps observed in the present study belong to these zones. Other orientations, including the \(\{hkk\}_{h<k}\) which should be stepped \(S\) faces according to the PBC theory, have a rough appearance [see Figs. 4(b) and 4(c)]. From this it can be concluded that the presence of \(\{110\}\) PBCs, consisting of nearest-neighbor covalent bondings only, in one direction is not sufficient to stabilize the surface.

About half of the \(\{111\}\) top face of the substrate used to grow sample TO1 in the turbulent flame was misoriented toward \(\{112\}\) resulting in a strong elongation of the growth hillocks in that direction. The other half of the top face has approximately the same density of triangular hillocks as observed for sample LO although most of them do not reveal the described line-shaped features at their summits. The phenomena observed along the sides of sample TO1 are less pronounced but also similar to those on sample LO (see Table II). This shows that the application of turbulence does not lead to large differences in the crystallographic habit of the grown samples. Sample TO2, which is grown in a turbulent flame at a 100 °C higher deposition temperature, shows some remarkable differences compared to the other two \(\{111\}\) samples and is therefore discussed in more detail Figure 5(a) shows that the top face of the sample is covered by a small number of large growth hillocks which have overgrown all the others. The summits of most of them are badly shaped showing steep irregular pits [see Figs. 5(a) and 5(b)]. Possibly similar inclined twins as observed on sample LO have locally hampered the growth of the \(\{111\}\) top face inducing the pits. No twins are observed on the final surface which is cracked although to a lesser extent that sample LO.

Figure 5(c) shows that for sample TO2 the occurrence of \{112\} faces in the O sets is “obscured” by the development of faces with \{11X\} orientations (see also Table II). The C sets, of which one is shown in Fig. 5(b), differ completely from those of the other \(\{111\}\) samples. The \{001\} faces have disappeared and at the positions they would be expected the width of the sets perpendicular to the plane of the cross section is strongly reduced. The \{11X\} faces closest to the top face of the sample now definitely are identified as \{113\} facets. In contrast to this, the \{11X\} facets further away from the top have shifted toward the \{117\} orientations. The shallow rim indicated by the arrow in Fig. 5(b) shows that these \{11X\} faces even tend to break up into two separate facets, most probably \{113\} and \{115\} or \{117\}. At both sides of the waist in the C set, flat faces started to develop which likely correspond to the \{11X\} faces originally laying in the curved band along the rim with the top face of the sample (see Fig. 2). These faces just started to develop from this band and were not observed on the other \{111\} samples. This is explained by the fact that in the band with a relatively low curvature (radius\(\approx 1\) mm), the \{11X\} faces and orientations close to them, which are only slightly less stabilized, hardly hamper each others development. In regions of higher curvature as between the \{111\} and \{001\} within the faceted sets (radius\(\approx 0.2\) mm) the more stable \{11X\} faces have a pronounced appearance since they have competed and survived their neighboring orientations. The \{11X\} faces in the C sets originating from the straight corner between the top and the
side wall of the substrate have the most pronounced appearance.

In addition to the large curved band along the top face, a smaller but similar band has developed along the octahedral bottom face of the sample [see Fig. 5(c)]. Note that this band also shows flattened areas close to the (001) orientation in the O set just as the band along the top face does close to the (001) orientation in the C set.

B. Morphology of specimen grown on (001)-oriented substrates

Diamond layers grown in a laminar flame on cylindrically (001)-oriented type-IIa natural diamond substrates were thoroughly investigated in a previous study. These samples, referred to as C series are compared with the samples investigated in this study. They (001) top faces of the samples in the C series are flat and grow via steps due to the (2×1) surface reconstruction. They show no sign of twinning or crack formation. Along the rim (111) and (001) side faces have developed giving the samples an octahedral shape as was also reported by Snail and Hamssen.

The top and side faces of both (001) samples presented in this study reveal the same features, except for some occasional cracks on the LC samples related with minor inclinations that were induced by inappropriate cleaning before growth. Because of this, sample TC—grown in the turbulent flame—looks somewhat smoother and has sharper boundaries with its side faces than sample LC. Figure 6(a) shows that several square growth hillocks have developed on sample TC with macrosteps aligned along the (011) directions as expected from the 2×1 surface reconstruction. DCM reveals that the hillock located more or less in the center of the sample originates from a three-dimensional nucleus or penetration twins. Such features which are common for hot-filament-grown {001} single crystals are rarely observed on flame-grown specimens. Like the other hillocks on sample TC they generally have sharp point-shaped summits which are usually located near the rims of the top face. These hillocks are most probably generated by bundles of screw dislocations originating from the substrate. In addition to the (111) and (001) facets, eight (113) facets are observed on the perimeter of the samples [see Fig. 6(a)]. Figure 6(b) gives a detailed view of one of these facets. The rims of this (311) facet are parallel to the (011) and (130) directions. The features shown in the photograph with steps parallel to the in-plane (011) PBC might be considered as extremely elongated hillocks which were able to expand rapidly along (011) since in this direction no energy barrier exists for the addition of growth species. Possibly these hill-
ocks are nucleated in the central region of the facets by dislocations originating from the straight corner of the cubic top face with the side wall of the substrate. In that case the hillocks might coalesce further away from the center causing the decreased step density observed toward the top and bottom of the facet [see Fig. 6(b)]. An alternative explanation of this effect is that the hillocks are generated at the rims of the facet which for {001} facets were found to be preferred nucleation sites during flame deposition.27 Hillocks nucleated at the top and bottom rims of the {113} facets interfere with each other somewhere in the middle of the facet resulting in a higher density of macrosteps in this region.

Surprisingly, in the first instance {113} facets were not observed on the previously examined samples of the C series.3 Reinspection of these samples revealed that only the sample with the thinnest epitaxial layer of these specimens exhibits very small {113} facets. For this sample the average growth rate of these {113} faces (v_{113}) relative to that of the {111} side faces on the sample (v_{111}) was found to be about 2.2. For the other samples it could be deduced that v_{113}/v_{111}<1.9 since no {113} facets were present any more. This indicates that under the applied growth conditions, the minimum in the surface energy of the {113} face is only local.34 Finally, the diamond crystal will be bounded by the more stable {111} and/or {001} faces, dependent on their relative growth rates.25,26,39 For the samples LC and TC, which are grown at a 50 °C lower temperature than the previous obtained samples,3 v_{113}/v_{111} is 1.7 and 1.6, respectively. Apparently relatively small differences in the deposition temperature influences the crystallographic appearance of the samples to a larger extent than the introduction of turbulence in the flame. The wealth of growth features observed on the {111} samples is not present on the {001} samples because they are overgrown by the (under the applied growth conditions more stable) {111}, {001}, and {113} facets.

C. Impurities

The main impurities expected in flame-grown diamond single crystals are nitrogen, nondiamond carbon phases such as graphitic inclusions, and hydrogen which is chemically bonded to carbon as CH₂. Previously investigated {110} samples, flame deposited at 1200 °C, show that an increase in hydrogen concentration is reflected by an increase in background fluorescence as well as in the full width at half-maximum (FWHM) of the diamond peak in the Raman spectrum (see Table I of Ref. 3). However, similar to the {001} samples of the C series (see Sec. IV B) investigated in the same study all the {111} and {001} samples presented in the present study show Raman spectra that are identical to the natural type-IIa substrates with a FWHM≤3 cm⁻¹. This indicates the absence of nondiamond carbon phases and incorporated hydrogen.

The PL spectra of the flame-grown diamond layers are usually dominated by two vibronic systems that have been attributed to nitrogen-vacancy pairs with their zero phonon lines at 2.156 eV (575 nm) and 1.945 eV (638 nm).1,40 The spectra of the samples considered in the present study, however, are dominated by their Raman lines (indicated by R) to which they are normalized (see Fig. 7). The spectra reveal an extremely low density of luminescent defects with a marginal presence of the 575 nm (indicated by N−V) system and almost no sign of the other nitrogen-related system mentioned above. Therefore, it can be concluded that, under the present growth conditions, incorporation of nitrogen as nitrogen-vacancy pairs from the ambient in the crystals, which grow via the F faces (111) and {001}, is low. No significant differences are observed between samples grown by a laminar and a turbulent flame.

This picture is supported by CL topographic investigations: All samples reveal blue-band A luminescence characteristic for natural type-IIa diamond. In contrast to this, the previously investigated samples from the C series revealed some orange luminescence from the 575 nm system, indicating a small amount of nitrogen incorporation. However, these small amounts could not be detected by infrared spectroscopy3 so the grown diamond layers have to be classified as type IIa. It is well possible that the decrease in signal of the 575 nm system is caused by higher gas velocities used in the present experiments. The samples of the C series were grown using a burner orifice of 1.6 mm in diameter and a total gas flow of 6.8 slm giving a gas velocity v_0 of 56 m/s at the burner opening, while the specimens in this study were grown at v_0=65 m/s. The high quality of the {001} diamond single crystal grown with a turbulent flame as reported by Snail et al.,8 in our opinion, is mainly caused by the same effect, i.e., improved shielding from the ambient air due to a high gas flow rate, which can be calculated to be 127 m/s in their experiment (20.5 slm total flow with an 1.85 mm burner opening). This shows that the incorporation of nitrogen in flame-deposited single crystals in the first place is determined by the applied gas flows. Obviously the generated turbulence is not sufficient for a significant increase of the amount of nitrogen mixed in from the ambient up to the center of the feather where the single crystals are located.

FIG. 7. PL spectra of the flame-grown diamond single crystals normalized to the first-order Raman phonon line (R). The peak indicated by N−V is the zero phonon line of the nitrogen-vacancy-related 575 nm system. The spectra are not corrected for the system response and the increasing intensity observed at the high-energy end of several of them is caused by reflections of the laser light.
Results obtained by a detailed investigation of the influence of the applied supersaturation at the position of the sample in the feather for turbulent and laminar flames on diamond growth, point in the same direction.

V. CONCLUSIONS

In the present study it is demonstrated that laminar and turbulent flames can be obtained using the same gas flows and burner openings by the addition of a turbulence-inducing step inside a commercially available burner tip. The flames show significant geometrical differences due to a higher reaction rate (burning velocity) in the turbulent flame as a result of the enhanced mixing of heat and radicals. The flame front of the turbulent flame is blurred and more rounded than that of the laminar flame.

Due to the large differences in geometry it is not possible to relate the positions in the acetylene feathers of both flame types to each other and compare the growth results at any location in the flames. In order to determine which type of flame is better suited for diamond deposition, the performance of both over a large range of growth conditions should be compared. Recently, the influence of the growth parameters $S_{ac}$ and $d$, which are most closely related to the gas-phase geometry, on diamond deposits grown by both flame types has been investigated. The results of this study are presented elsewhere. However, this preliminary study already shows that the application of turbulent flames for single-crystal growth does not lead to a dramatic change in quality of the diamond as previously reported in literature. The crystallographic orientation of the substrates, the deposition temperature, and the gas velocity have a larger influence on the crystal morphology and impurity incorporation of the grown single crystals.

In addition it was demonstrated that the single-crystalline nature of diamond layers exceeding 50 $\mu$m thickness deposited on {111} substrates can be maintained in a highly activated gas phase. This is obtained by deposition with the substrates close to the flame front at a high temperature and a relatively low supersaturation. All faces and the curved bands with macrosteps, observed on the {111} and {001} single crystals, belong to the $\{hhk\}_{h<k}$ parts of the $\{110\}$ zones. The stabilization of these orientations can be explained by the formation of disson bonds between the surface atoms. Other orientations have a rough appearance due to the occurrence of microfacetting. No faces or other signs of stabilization appeared for the $\{hhk\}_{h>k}$ parts of the $\{110\}$ zones which according to the PBC theory are $S$ faces and should be stabilized in one direction.

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