Relation between gas phase CN radical distributions, nitrogen incorporation, and growth rate in flame deposition of diamond

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Controlled amounts of nitrogen were added during oxyacetylene flame deposition of diamond to investigate the possible role of the CN radical in the effects of nitrogen addition. CN radical distributions were visualized using two-dimensional laser induced fluorescence (LIF) and compared with nitrogen incorporation into the layer and with the diamond growth rate, which were measured by means of cathodoluminescence (CL) and optical microscopy, respectively. For the studied range of nitrogen flows, it was found that the CN LIF signal in the center of the flame is linearly dependent on the added amount of nitrogen. Diamond deposition in the central region is mainly influenced by the deposition parameters, whereas deposition in the outer zone is largely determined by the interaction of the flame with the ambient; the annulus of enhanced growth is affected by both the deposition parameters and the ambient. By a simple consideration, in which the growth rate is separated in nitrogen dependent and independent contributions, an observed positional difference between CN LIF and growth rate maxima can be explained. Comparison of the CN LIF signal, the CL signal and the diamond deposition rate indicates that CN (or a closely related species) may be *the* species or one of the main species responsible for the effects of nitrogen addition during oxyacetylene flame deposition of diamond. © *2000 American Institute of Physics.*
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INTRODUCTION

For centuries, diamond has been regarded as a fascinating material with many interesting and useful properties. Diamond layers suitable for specific applications can, in principle, be tailored by means of chemical vapor deposition (CVD). The properties of CVD diamond layers are determined by a number of experimental parameters, such as the deposition temperature and the composition of the reaction mixture used. The amount of nitrogen present in the reaction mixture has a large influence on the deposition process and the deposited diamond. Several authors have studied the effect of nitrogen addition during diamond CVD[1–7] and it has been found that the addition of small amounts of nitrogen leads, among other things, to an increase of the deposition rate[4,7] and a preferred {100} texture.[1,2,5,7,8] Despite the considerable number of studies on the effects of nitrogen addition during diamond CVD processes, it is not clear what nitrogen-containing species is or are reponsible for the observed changes. Candidates mentioned frequently in literature are CN and HCN. Bohr *et al.*[9] have found from thermodynamic calculations that these species can abstract H from the diamond surface during growth and in this way create new growth sites, a role of CN and HCN upon which Badzian *et al.*[10] have speculated as well. According to Butler,[11] CN may very well be the nitrogen-containing species that is active at the growing diamond surface, despite the fact that HCN is probably more dominant in the gas phase. He gives a possible explanation of the influence of nitrogen addition on, e.g., the growth rate and the value of the alpha parameter, in which the CN radical enhances the next layer nucleation on the diamond {111} face.[12] In the case of oxyacetylene flame CVD, Klein-Douwel *et al.*[13] have shown a relation between the presence of gas phase CN close to the deposition substrate and the diamond deposition rate, diamond morphology, and nitrogen incorporation into the deposited diamond layer. In their experiments, no nitrogen has been added intentionally: nitrogen from the ambient air has entered the flame by indiffusion or entrainment.

In the present work, controlled amounts of nitrogen are added during oxyacetylene flame CVD of diamond to study the effect of nitrogen on the growth process and deposited diamond and to obtain information about the role of the CN radical in the growth process. Hereto, gas phase CN distributions close to the deposition substrate are measured, together with the diamond growth rate and the incorporation of nitrogen. In studies by other authors, several techniques such as optical emission spectroscopy[14] and conventional absorption spectroscopy[15] have been employed to measure CN in different diamond CVD reactors. In this work, two-dimensional laser induced fluorescence (LIF) is used to visualize spatial distributions of gas phase CN during the deposition process, in a way similar to the method applied by Klein-Douwel *et al.*[13] LIF is a highly sensitive, species specific, nonintrusive laser spectroscopic technique which is very suitable for gas phase diagnostics. Because of colli-
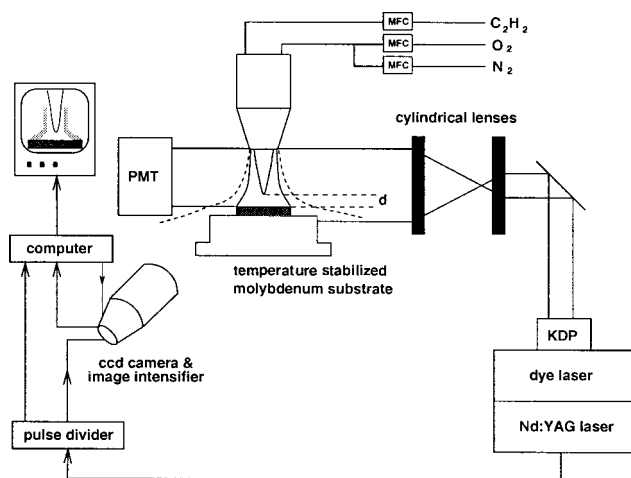
FIG. 1. The setup used for the diamond deposition and two-dimensional laser induced fluorescence (LIF) experiments; MFC=mass flow controllers.

sional quenching, LIF measurements performed at atmospheric pressure do in general not yield quantitative results. Fortunately, the quenching should be nearly constant under similar experimental conditions, and since all experiments presented in this work are done under very similar conditions, the LIF measurements can be regarded as semi-quantitative.

The incorporation of nitrogen into the deposited diamond layers is studied by means of cathodoluminescence (CL), which is very sensitive for the determination of nitrogen related and other defects in diamond.[7,16] The effect of nitrogen addition on the diamond deposition rate is measured by means of optical microscopy. By comparison of the gas phase measurements to the nitrogen incorporation and diamond growth rate, more insight can be gained into the importance of CN in the diamond deposition mechanism.

EXPERIMENT

Diamond deposition

A detailed description of the diamond deposition setup has been given by Schermer *et al.*[17] Here, only some important features, experimental parameters, and differences with respect to that setup are mentioned. The setup, which consists of a welding torch and a temperature controlled substrate, is depicted in Fig. 1. The torch, a commercial welding torch with an orifice of 1.3 mm in diameter, is used to burn acetylene (99.6% purity, Indugas) with oxygen (99.995%, Indugas). To remove the residual nitrogen contamination present in the acetylene bottle, an initial amount of acetylene is released before the start of a measurement series.[7] Throughout the experiments described here, the oxygen flow is kept constant at 2.5 standard liters per minute (slm); the acetylene flow is set to give an acetylene supersaturation S_{ac} of 4%, where S_{ac} is defined as the difference between the acetylene flow used and the acetylene flow of a neutral flame relative to the flow of the latter. The resulting total flow is about 5.5 slm. Both flows are regulated by mass flow controllers (MFC).

For nitrogen addition, a mixture of 29.5% nitrogen in oxygen is used, instead of pure nitrogen. If pure nitrogen were used, the MFC that regulates the nitrogen flow would have to be operated in the lower part of its range for the nitrogen additions applied during the experiments. This would result in a reduced accuracy of the added nitrogen flow, since the relative error in flows produced by an MFC is rather large in the lower part of its operating range. With the mixture, small nitrogen flows can be added while the MFC is used in the central and higher part of its range, where the relative error is smaller. In the deposition setup, the nitrogen line is coupled to the oxygen line and the nitrogen flow is regulated by means of a MFC with a maximum flow of 100 standard cubic centimeters per minute (sccm), which results in a maximum flow of 29.5 sccm. The extra oxygen flow that goes together with the use of the nitrogen/oxygen mixture for addition is corrected for by decreasing the flow coming from the oxygen bottle.

A molybdenum square of approximately $12 \times 12 \, \text{mm}^2$ and a thickness of 0.5 mm is used as a substrate, the surface temperature T_s of which is kept constant by means of a pulsed water spray. All experiments described here are performed at a T_s of $1050 \, °C \pm 20 \, °C$. The distance d between the flame front and the substrate is between 2.0 and 2.2 mm for all growth experiments; d is determined using a CCD camera in the manner described by Klein-Douwel *et al.*[18] Prior to a growth run, the substrate is prepared by scratching it with sandpaper and, consecutively, with a slurry of micrometre sized diamond powder and glycerol, to enhance diamond nucleation. Shortly before the run, the substrate is cleaned with iso-propanol and etched for about 1 min in the oxidizing outer part of the flame. All growth runs lasted 1 h, except for the one with an added nitrogen flow of 5 sccm. This was stopped after 55 min because of problems with the cooling of the substrate. These have not affected the LIF measurements and it is unlikely that they have significantly influenced the growth rate.

Laser induced fluorescence

The setup used for the LIF measurements, which is similar to the one described by Klein-Douwel *et al.*,[13] is shown in Fig. 1. For detection of the CN radical, laser light from a Nd:YAG pumped dye laser (Quantel YG 781 C10 and Quantel TDL 50, respectively), which runs on Pyridine 1, is frequency doubled by means of a KDP crystal. The repetition rate of the resulting 5 ns laser pulses is 10 Hz; the laser bandwidth is $0.2 \, \text{cm}^{-1}$. Cylindrical lenses are used to shape the laser beam into a sheet, which is directed through the flame. The laser power at the position of the flame is about 50 μJ/pulse. Sufficient laser power close to the substrate is ensured by aligning the sheet in such a way that its lower edge is just below the substrate. Detection of CN is done by inducing the $B \, ^2\Sigma^+(v'=1) \leftarrow X \, ^2\Sigma^+(v''=0)$ transition at 359.1 nm and collecting the fluorescence at right angles by means of an image intensified Peltier cooled CCD camera (La Vision Flame Star II). Four reflection filters (Laser Optik, bandwidth about 13 nm) are placed in front of the camera, to select only the fluorescence coming from the

$B\,^2\Sigma^+(v'=1)\rightarrow X\,^2\Sigma^+(v''=1)$ transition and to block reflections of the laser beam and the major part of the natural flame emission and nonresonant background fluorescence. The camera is triggered by the Q-switch of the laser and collects signal for 20 ns after each trigger pulse, thus reducing the natural flame emission by a factor of 5×10^6. Saturation during the excitation of CN[19] is avoided. Correction for background luminescence from the flame and nonresonant fluorescence transmitted by the filters is achieved by subtracting an off-resonant LIF image from the resonant image at 359.1 nm. The resulting fluorescence signal is corrected for the inhomogeneous intensity distribution of the laser beam, which is necessary because the fluorescence is linearly proportional to the laser power. All resonant and off-resonant images are averages of 10 images, each of which is integrated over 100 laser shots. The spatial resolution of the LIF measurements is about 40 μm; spectrally, rotational resolution is obtained.

Cathodoluminescence

Cathodoluminescence (CL) topography is performed using a cold-cathode luminescence unit (8200 MKII) equipped with an optical microscope for low and medium magnifications. During examination, the pressure in the CL chamber is kept at 0.1 Torr and the acceleration voltage at 15 keV, resulting in a current density of about 6 μA/mm^2 and a penetration depth between 1 and 2 μm.[20] Due to a slight heating up by the electron beam the temperature of the specimens increases from room temperature to a maximum of 50 °C. Because the spatial distribution of the luminescent point defects in the diamond layers has a strong circular symmetry, images are taken along a single, circa 1.2 mm wide line across the center of the sample. This line is located around and in the direction of the cross section of the sample with the LIF laser sheet used for gas phase CN detection. The CL signal is recorded photographically.

RESULTS AND DISCUSSION

The upper graph of Fig. 2 shows an excitation spectrum of CN, measured in an oxyacetylene flame without the presence of a substrate. The signal is the fluorescence from the $B\,^2\Sigma^+(v'=1)\rightarrow X\,^2\Sigma^+(v''=1)$ transition of CN, which was maximized by adding the maximum amount of nitrogen (100 sccm) to the flame. In the spectrum, rotational resolution can be observed. Because the KDP crystal was tracked manually, the measured intensities of the (rotational) peaks in the spectrum may be slightly different from the actual intensities. The strongest signal, however, undoubtedly results from the excitation of the (1,0) bandhead, which is therefore used for excitation in the LIF measurements. The spectrum is in correspondence with the one measured by Klein-Douwel *et al.*[13] To ascertain that the measured spectrum is indeed that of CN, the CN spectrum was simulated using the LIFBASE software developed by Luque and Crosley.[21] The resulting spectrum is shown in the lower graph of Fig. 2. From the good agreement between the measured and simulated spectrum, it
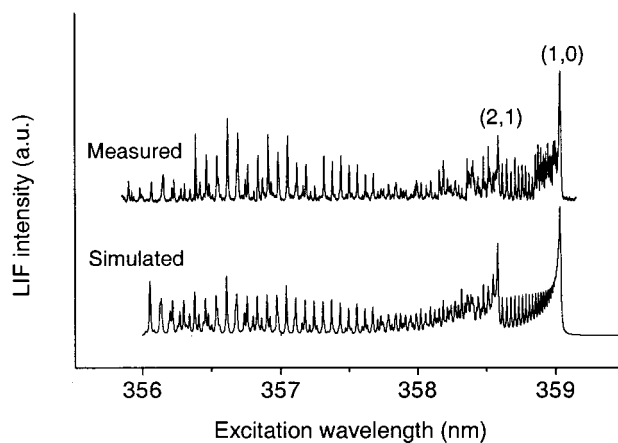

FIG. 2. Measured and simulated excitation spectrum (upper and lower graph, respectively) of the $B\,^2\Sigma^+\leftarrow X\,^2\Sigma^+$, $\Delta v=1$ transition of the CN radical; the fluorescence signal comes from the $B\,^2\Sigma^+(v'=1)\rightarrow X\,^2\Sigma^+(v''=1)$ transition of CN; in the measured spectrum, the (1,0) and (2,1) bandheads are indicated, the former of which is used for excitation in the LIF measurements.

is clear that the measured spectrum is that of CN; differences in the relative peak intensities are mainly due to the manual tracking of the KDP crystal.

Figure 3 displays a LIF image recorded during a growth run with an added nitrogen flow of 25 sccm. In this image, the LIF intensity is represented by false colors: blue corresponds to a low, red to a high intensity. It can be seen that the signal left and right of the flame axis is higher than that in the center of the flame. Figure 4 shows CN LIF profiles constructed from a LIF image of a growth run without nitrogen addition. The profiles represent the average LIF signal in an approximately 100 μm wide strip centered at three different heights above the substrate, viz. 100, 400, and 800 μm. In all three profiles, almost no signal is observed in the center, meaning that practically no CN is present there; maxima in LIF intensity can be observed on both sides of the center. The CN present is formed out of nitrogen that has entrained or indiffused from the ambient into the hydrocarbon rich
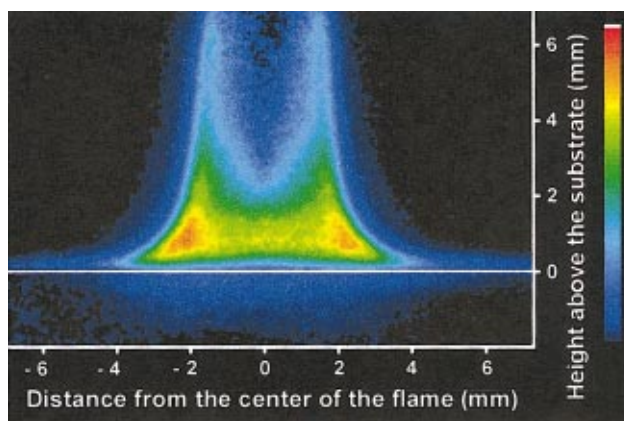

FIG. 3. LIF image of the CN distribution in the oxyacetylene flame during diamond deposition with a nitrogen addition of 25 sccm; the colors represent the intensity of the LIF signal, as indicated by the color scale on the right side of the image; the white line indicates the position of the molybdenum substrate.
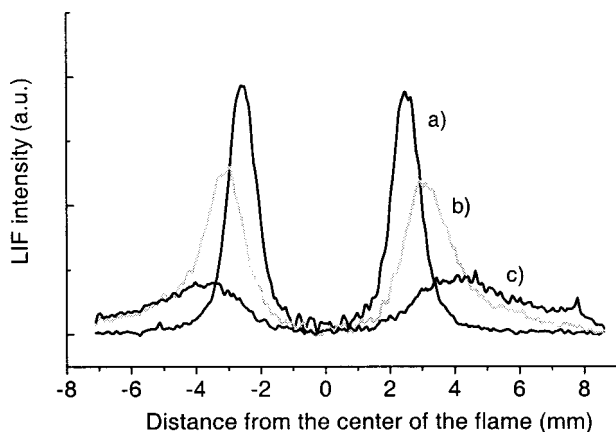
FIG. 4. Profiles of the LIF intensity measured in the oxyacetylene flame without nitrogen addition; the profiles were taken at 800 (a), 400 (b), and 100 μm (c) above the substrate and are averages over a strip with a height of about 100 μm.

FIG. 5. The average LIF intensity of a 2.1 mm wide central area of the flame at 100 μm above the substrate, as a function of the amount of nitrogen added to the flame; the solid squares give the LIF intensity, the error bars indicate the standard deviation; the solid line is a best linear fit through the data points.

acetylene feather of the flame and interacted with it.[22] The profiles obtained are similar to profiles reported by Klein-Douwel *et al.*[13] It can be noticed in Fig. 4 that, with a decrease in height above the substrate, the LIF maxima broaden and become less intense and the position of the maxima lies further away from the center of the flame. The broadening and the positional shift are caused by the fact that species are moving radially outward along with the flame, when they come closer to the substrate. The decrease of the peak intensity is caused by spreading of CN over a larger area and possible removal from the flame by reactions with flame species and/or interaction with the growing diamond layer. Other factors, such as differences in temperature and the temperature dependent quenching of the CN LIF signal at different positions in the flame, may also play a role in weakening the LIF signal. Because the profile at 100 μm above the substrate is likely to bear the most direct correlation with the growing diamond surface, LIF profiles at 100 μm are used for further analysis of the measurements.

With the addition of pure nitrogen (99.999%), an experiment is performed in which LIF images are recorded for a range of nitrogen flows in one single experimental run. In this run, the nitrogen flow is varied between 0 and 100 sccm in steps of 10 sccm. The LIF images are obtained by averaging over 5 images of 75 laser shots each. Figure 5 shows the intensity of the central CN LIF signal, which is the average LIF intensity of a 2.1 mm wide central area at 100 μm above the substrate, as a function of the added nitrogen flow. From the linear relation between the LIF signal and the added nitrogen flow, it can be concluded that for nitrogen additions between 0 and 100 sccm, a fixed fraction of nitrogen is transformed directly or indirectly into CN. This means that the CN concentration in the flame can be regulated by adding a well-defined amount of nitrogen to the flame and, vice versa, that the added amount of nitrogen can be monitored by measuring the CN LIF signal. Furthermore, the relation between the CN LIF signal and the added amount of nitrogen can be applied to scale LIF images recorded during different growth runs with respect to one another. Scaling is necessary to account for small run-to-run differences which
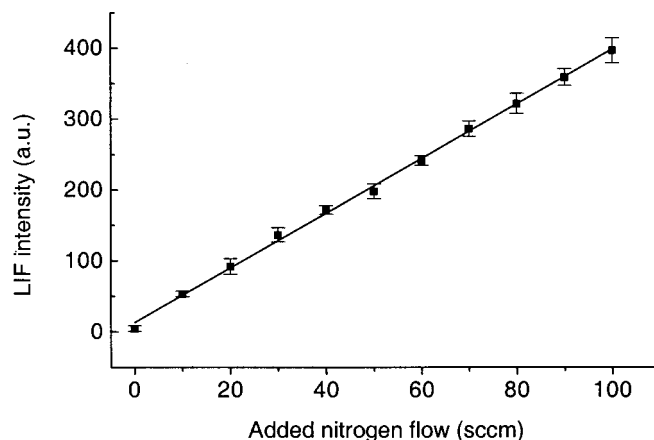
influence the LIF signal, such as a slightly different optical alignment. The observed linear relation between the CN LIF signal and the nitrogen flow is in correspondence with results reported by Vandevelde *et al.*[14] These authors have applied optical emission spectroscopy to characterize a plasma during microwave assisted CVD of diamond with controlled nitrogen addition, and observed a linear relation between the CN emission and the added nitrogen flow. Since the LIF measurements are semi-quantitative, they must be calibrated if absolute concentrations are required. This can be done by measuring species distributions with techniques other than LIF that do not suffer from collisional quenching, e.g., conventional absorption spectroscopy[15] and cavity ring down spectroscopy,[23] which have both been applied before for measuring radical number densities in oxyacetylene flame deposition of diamond.

Figures 6(a)–6(d) display the LIF profiles at 100 μm above the substrate (solid lines), CL signals (shown above each graph and in the background) and diamond deposition rates (dashed lines with square symbols) for samples grown with 0, 5, 15, and 25 sccm nitrogen addition. The LIF profiles were scaled with respect to each other. For the samples grown with nitrogen addition, this was done as follows: the LIF profile as measured was divided by a factor given by the ratio of the average LIF signal of the flat central area and the signal for the same nitrogen addition as given by Fig. 5. Because of the low LIF intensity in the center of the sample grown without nitrogen addition, this profile was scaled by its left-hand LIF maximum (i.e., the maximum on the side of the incoming laser beam). To do so, the height of the left-hand LIF maxima of the samples grown with different nitrogen flows was determined, after which a value for the maximum at zero nitrogen flow was found by extrapolation. Scaling was done by dividing the measured LIF profile by the ratio of its measured left-hand LIF maximum and the maximum obtained by extrapolation. As can be seen in Fig. 6, the central LIF signal increases gradually with increasing nitrogen flow. The height of the maxima located radially outward from the center, increases with increasing nitrogen
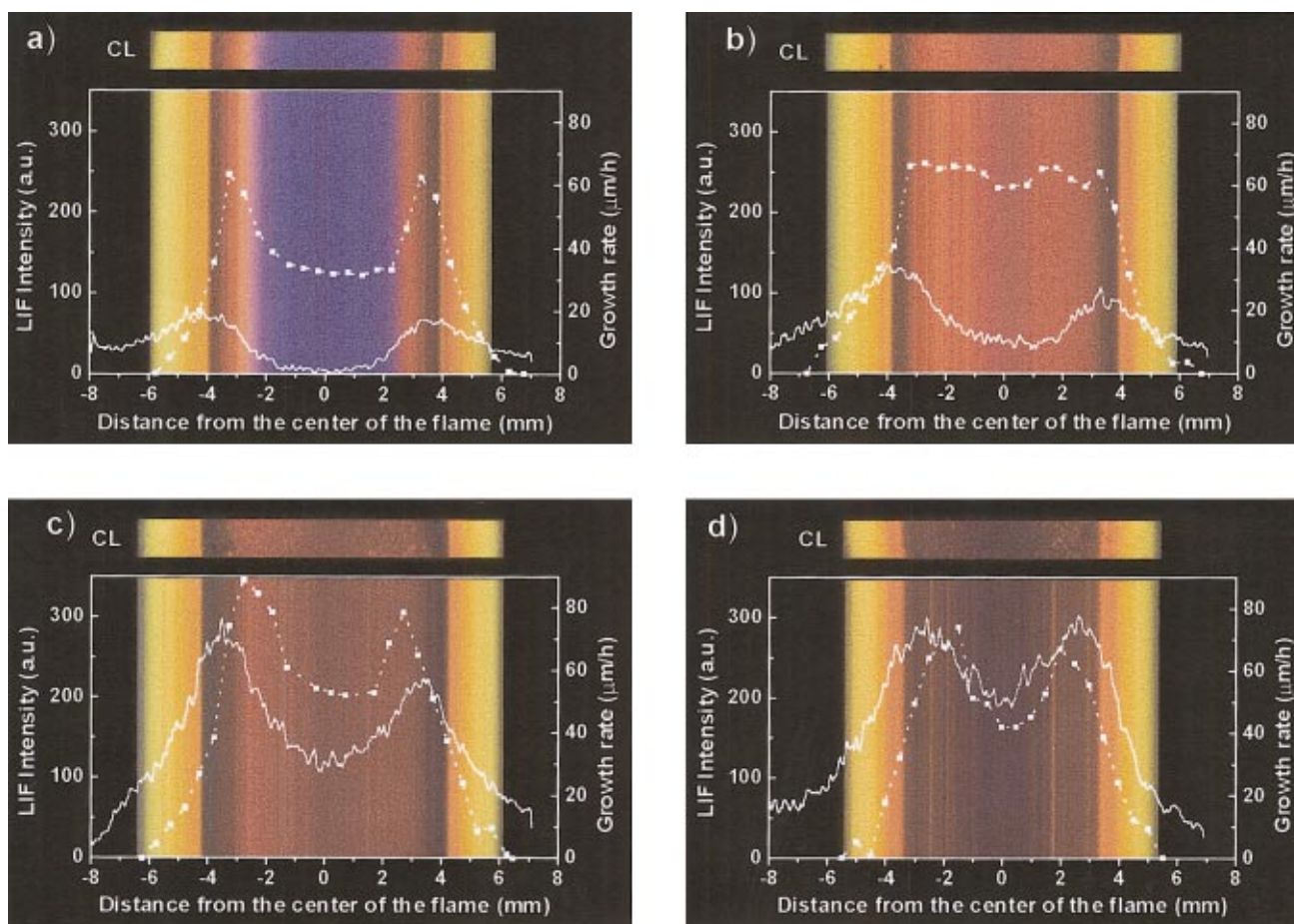
FIG. 6. Images of the combined CN LIF, growth rate, and CL measurements as a function of the distance from the flame center for nitrogen additions of 0 (a), 5 (b), 15 (c), and 25 (d) sccm; the solid line is an LIF profile taken at 100 μm above the substrate and measured during diamond deposition; the dashed line with solid squares is the diamond growth rate; the colored horizontal bar above the graph is the CL signal, which is also represented by the colors in the background of the plot.

addition. In Figs. 6(b) and 6(c) (a nitrogen addition of 5 and 15 sccm, respectively) and also for the sample grown with 10 sccm of nitrogen (not shown), the left-hand peak is considerably larger than the right-hand one. It is not quite clear what caused this difference. A reasonable explanation may be the decrease in laser power while the beam traverses the flame, because this results in a weaker LIF signal after the flame. If this effect causes the intensity difference between the LIF maxima, it is strange that the LIF maxima of the sample grown with 25 sccm of nitrogen addition are equally high.

CL topography measurements after growth display a radially changing luminescent behavior of the diamond layers as shown in Figs. 6(a)–6(d). The sample grown without nitrogen addition has a blue emitting central area. This blue emission is known as band A luminescence,[16,24] which has been argued to be dislocation related;[25,26] it is indicative for highly pure diamond. At some distance from the center, orange-red luminescence is observed, which, with an increasing distance from the center, gradually turns to yellow in the outer zone. Previously reported CL spectroscopy measurements on flame-deposited samples[16,27] indicate, that this orange-red to yellow emission must be attributed to the well-known 2.16 eV system[28] and an accompanying broad lumi-

nescent band around 2 eV. The 2.16 eV system was found to be related to the incorporation of nitrogen as nitrogen vacancy (N-V) pairs,[16,29] while the band around 2 eV is probably induced by the presence of sp^2-bonded carbon.[30] The color shift from orange-red to yellow is caused by the fact that the peak of the luminescent band lies at wavelengths decreasing with increasing radial distance,[27] as a result of a decreasing amount of incorporated nitrogen.[7] In between the blue emission in the central area and the orange-red luminescence, some pink luminescence occurs, which is probably due to the combination of orange-red luminescence from the 2.16 eV system and blue band A emission. At the outer rim of the diamond layer, green luminescence[22,27] can be observed, which is attributed to a nitrogen-vacancy complex which emits at 2.33 eV.[28,29] Within a certain part of the orange-red region, the signal is largely quenched. This region corresponds to the well-known annulus of enhanced growth and roughness generally encountered in flame CVD diamond layers grown at relatively low values of d.[22,31–33] Quenching occurs as a result of a change in morphology of the diamond layer. Whereas most of the layer consists of strongly interconnected randomly oriented diamond crystallites bounded by {111} as well as {100} facets, the annulus shows some large isolated crystallites in a matrix of amor-

phous features usually referred to as diamond-like carbon (DLC). A more detailed discussion of the morphology of the diamond layers will be given in a forthcoming paper.[34]

Since no nitrogen was added during the deposition of the sample shown in Fig. 6(a), the nitrogen incorporated in the layer originates from the ambient.[22] During the deposition process, nitrogen enters the acetylene feather, is transformed into several nitrogen containing species by reactive collisions with other flame species and/or thermal dissociation, becomes adsorbed at the diamond surface, and eventually incorporates into the diamond lattice. In the gas phase above the outer boundary of the deposits, only a small fraction of the nitrogen is decomposed because of the relatively low local temperature and gas phase activation. Closer to the center of the acetylene feather, more nitrogen is transformed, which leads to a larger incorporation into the diamond lattice and a change in CL signal from yellow to orange-red. Directly above the annulus, the amount of reactive nitrogen in the gas phase probably reaches a maximum, resulting in a maximum incorporation of nitrogen into the diamond crystal lattice and a quenching of the CL signal. Further inside the flame, the indiffusion of nitrogen sharply decreases to zero, which results in blue band A luminescence in the central area.

All samples grown with nitrogen addition do not show blue luminescence in their central area. At nitrogen flows of 5 [see Fig. 6(b)] and 10 sccm (not shown), the entire central area shows orange-red luminescence which is only slightly weaker in the center. With increasing nitrogen flows, the intensity of the CL signal from the central area decreases, finally resulting in a confluence of the central area and the annulus [Figs. 6(b)–6(d)] for the sample grown with a nitrogen flow of 25 sccm. The total region (center and annulus) appears dark with a large concentration of isolated orange spots, as shown in Fig. 5(d). From the change of the CL signal as a function of the nitrogen addition, it can be said that the incorporation of nitrogen in the central region is strongly influenced by the amount of nitrogen added to the oxyacetylene flame. Contrary to this, the incorporation in the outer zone of the deposits, i.e. the region outside the annulus, seems to be unaffected by nitrogen addition: the radial variation of the CL signal in the outer zone does not change upon nitrogen addition.

In Fig. 6, it can be seen that with an increasing nitrogen addition, the diamond deposition rate in the central region of the flame first increases and then decreases again. This corresponds to results reported previously by one of the authors[7] for flame deposition carried out under similar conditions. With a nitrogen addition of 5 sccm, the maximum central growth rate of about 60 μm/h is observed, which is more than 1.5 times the rate of the undoped sample. In the previous report, an increase in growth rate by more than a factor of 2 was found. This difference in maximum deposition rate enhancement may be caused by the larger flame front-to-substrate distance and the lower substrate temperature used in the present work. The growth profiles in Figs. 6(a), 6(c), and 6(d) have a shape different from that in Fig. 6(b): the latter profile is nearly flat, whereas the others display maxima away from the center as is generally observed for

undoped samples.[22,31–33] On close observation, it can be seen that the growth rate in the center reaches a maximum value at 5 sccm of added nitrogen, whereas the growth rate in the annulus does so at 15 sccm. Apparently, the growth rates of center and annulus behave differently as a function of the added amount of nitrogen. Assuming a different behavior, the evolution of the growth profiles in Fig. 6 can be described as follows. In the case of the sample grown without nitrogen addition, nitrogen coming from the ambient enhances the growth rate at a radial distance of about 3 mm from the center, resulting in the formation of the annulus; in the center, no nitrogen is present. Upon the addition of 5 sccm of nitrogen, the growth rate at 3 mm from the center does not change much; the central growth rate, on the other hand, increases and becomes as large as the rate in the annulus, resulting in a flat growth profile. With an addition of 15 sccm, the central growth rate decreases significantly and the rate in the annulus increases, which results again in an overall growth profile with maxima on both sides of the center. Finally, the addition of 25 sccm of nitrogen leads to a decrease of the growth rate in both the annulus and the center. Very likely, a different behavior of the growth rate in the center and annulus as a function of the added amount of nitrogen is related to differences in local gas phase composition and chemistry.

Following the behavior of the CL signal in the outer zone, the growth rate in the outer zone does not seem to be influenced by the added amount of nitrogen. Both observations indicate that the deposition process in the outer zone is almost fully determined by the interaction of the flame with the ambient. In the central area, the diamond deposition depends strongly on the applied growth conditions, as follows from the changes in growth rate and CL signal as a function of the added nitrogen flow. Based upon these findings and in agreement with previous work,[7] the area of diamond deposition can be divided into three zones: the central area, the outer zone, and, in between, the annulus. Whereas the diamond deposition in the other two zones is influenced by either the growth parameters or the ambient, the annulus is determined by both. Therefore, the annulus can be regarded as a marker, which indicates how far the influence of the ambient stretches into the flame and how large the area is in which the deposition is controlled by the growth conditions.

In Fig. 6, it can be seen that both the maxima in the CN LIF signal and the growth rate [except for Fig. 6(b)] move radially inward with an increasing nitrogen addition. Furthermore, in all cases the growth rate maxima are further inside the flame than the LIF maxima. The latter can be explained by considering the diamond growth rate as being composed of two separate contributions: one that represents the growth rate without the presence of nitrogen and one that represents an additional growth rate caused by nitrogen (added or coming from the ambient air). In the case of diamond growth without nitrogen addition, this existence of two contributions to the growth rate has already been suggested by Klein-Douwel and Ter Meulen.[35] From LIF and growth rate measurements, they found a good match between the radial H distribution close to the deposition substrate and the growth rate profile in the whole area of diamond deposition except
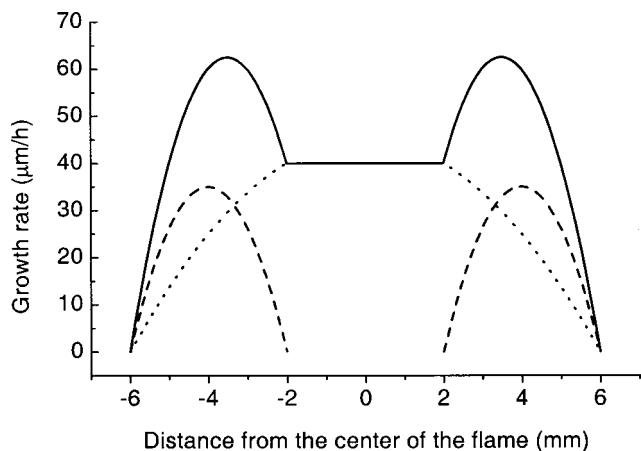
FIG. 7. Explanation of the inward shift of the growth rate maxima with respect to the CN LIF maxima; the growth rate is considered to be the sum of two contributions, viz. the rate without nitrogen (dotted line) and the rate due to the presence of nitrogen (dashed line); the solid line represents the sum of the two contributions and shows that the maxima in the overall profile are shifted with respect to the maxima in the rate due to nitrogen (which are located at the position of the CN LIF maxima).

for the annulus. Based on the results of earlier work,[13] they ascribed the disproportionately high growth rate in the annulus to the presence of nitrogen-containing species, which positively influence the diamond growth rate. Following the relation between the growth rate and the H distribution as obtained by Klein-Douwel and Ter Meulen,[35] the shape of a suitable H LIF profile can be used as a representation of the growth rate profile in the absence of nitrogen. Since Klein-Douwel and Ter Meulen performed their measurements under experimental conditions similar to the ones applied in the present paper, the H LIF profiles recorded at a distance d of about 2 mm, which look like a flattened parabola, can be used for this purpose. In Fig. 7, the growth rate in the absence of nitrogen is given by a dotted line. The contribution of nitrogen to the growth rate is assumed to be represented by two parabolas (dashed line), which approximately describe the measured CN LIF profile. Unlike this profile, the parabolas go to zero at a radial distance of 6 mm, because this is as far as the outer rim of the deposited diamond layer stretches. The overall growth rate, which is the sum of the two contributions, is given by the solid line. It can be seen that the maxima of the overall rate are shifted in the direction of the center by about 0.5 mm, which is the behavior observed in Fig. 6(a) for the positional difference of the growth rate and LIF maxima. This simple analysis shows that CN or a closely related species can very well be responsible for the enhanced growth rate, because the observed inward shift of the growth rate maxima with respect to the LIF maxima is expected for a species responsible for the influence of nitrogen addition. It is necessary to mention ''closely related species'' here, because the distance of 100 μm above the substrate at which the CN profiles are measured is large enough to allow for, possibly reactive, collisions of CN with other gas phase species. A similar analysis can be made for layers deposited with nitrogen addition. Because of the above mentioned possible difference between the nitrogen dependent contribution to the growth rate in the center and that in the

annulus, the growth rate profiles of layers grown with nitrogen addition are described by three contributions instead of two: one for the growth rate in the absence of nitrogen, one for the influence of nitrogen on the central growth rate, and one for the influence of nitrogen on the growth rate in the annulus. By means of this description with three contributions, the inward shift of the growth rate maxima in Figs. 6(c) and 6(d) and the flat growth rate profile of Fig. 6(b) can be explained.

To investigate to what extent the description of the growth rate as a sum of different contributions corresponds to reality, it would be very interesting to study the influence of nitrogen addition in a flame shielded from the ambient by a coflow. This coflow should consist of a mixture of 20% oxygen in an inert gas (e.g., argon), which allows the secondary combustion processes in the flame to happen and excludes the possibility of ambient nitrogen entering the flame. In this way, a diamond growth rate profile without any influence of nitrogen can be determined and the influence of nitrogen addition on the growth (rate profile) can be studied without the disturbance by nitrogen from the ambient. A study of the influence of nitrogen addition on diamond deposition in a low pressure flat oxyacetylene flame has been conducted by Wolden *et al.*[36] Their results, however, are not comparable to the ones presented in the current paper, because of the large difference in the CVD reactors used.

In earlier work, Klein-Douwel *et al.*[13] have reported measurements on an oxyacetylene flame, which show that the position of the maxima in CN LIF profiles taken at 365 μm above the substrate and that of the annulus of enhanced growth coincide. As discussed above, this is not the case for LIF profiles taken at 100 μm. This demonstrates the importance of performing the LIF measurements and, in general, measurements to determine the role of species in the diamond deposition process, as close to the deposition substrate as possible. The conclusion of Klein-Douwel and co-workers that the presence of CN or a closely related species may strongly influence the diamond growth rate, is supported by the results described in the present paper.

As mentioned above in the discussion of the CL measurements, the nitrogen incorporation into the central area of the diamond layer increases with the added amount of nitrogen. Figure 5 shows that the CN LIF signal in the center of the flame increases linearly with the added amount of nitrogen. Since the LIF signal is linearly proportional to the CN concentration, it follows that, in the central area, the nitrogen incorporation in the layer increases with the CN concentration. From a comparison of the positions of the CN LIF maxima and the region where the CL signal quenches, it follows that the LIF maxima are at or slightly outside the outer rim of this region for the sample grown without nitrogen addition and move closer towards the center of the flame with increasing nitrogen addition. So, in this region there is no clear relation between the incorporation of nitrogen and the presence of CN. It is remarkable that the quenching of the CL signal in the annulus occurs at a lower CN LIF signal than the quenching in the central region: one can compare, e.g., the LIF signal in the annulus of the sample grown with 0 sccm nitrogen addition (CL quenching) to the central LIF

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signal of the sample grown with a 15 sccm addition (less CL quenching). This may support the statement made earlier that the influence of nitrogen addition on the diamond growth mechanism in center and annulus may be different. Care must be taken, however, that the collisional quenching of the CN LIF signal in the two regions mentioned may be different and that the difference in CN concentration may be smaller than the difference suggested by the CN LIF signal.

With respect to the relation between the CL signal and the growth rate maxima, it can be noticed that the maxima are closer to the center of the flame than the region in which the CL signal is largely quenched. Apparently, the amount of incorporated nitrogen in this region has deteriorated the crystal structure to such an extent that the growth rate has decreased. It is noticeable that the growth rate at the outer rim of the region with the quenched CL signal is never larger than about 50 μm/h and is about 40 μm/h or lower in most cases. This may be related to the observation that the central growth rate of the sample grown with 25 sccm of nitrogen, where the central CL signal is quenched, is also 40 μm/h.

CONCLUSIONS

In this work, the influence of nitrogen addition on oxyacetylene flame deposition of diamond and the role of the CN radical therein was studied. To do so, gas phase distributions of the CN radical were measured and compared to the radially changing growth rate and nitrogen incorporation into the deposited diamond layer. It was found that the relative CN concentration around the center of the flame is linearly proportional to the amount of nitrogen added to the flame in the flow range from 0 to 100 sccm of nitrogen. This means that the amount of CN present in the flame can be regulated by controlling the added amount of nitrogen. Furthermore, the added amount of nitrogen can be monitored by measuring the CN LIF signal, a result which can be of importance for tailoring diamond layers with specific properties.

Nitrogen addition to the source gases greatly influences diamond growth in the central zone of the diamond layer, whereas the features in the outer zone appear to be unaffected by the added nitrogen and seem to depend mostly on indiffusion and entrainment of air from the ambient. The annulus, which marks the transition between the central region and the outer zone, is influenced by both the applied growth conditions and interaction with the ambient. The evolution of the growth rate profile as a function of the added nitrogen flow and the observation that the growth rate maxima lie further inside the flame than the LIF maxima, can be explained by a description of the growth rate with three contributions: one for the growth rate in the absence of nitrogen, one for the influence of nitrogen on the central growth rate, and one for the influence of nitrogen on the growth rate in the annulus. The possibly different influence of nitrogen on the diamond growth process in center and annulus is very likely to be caused by differences in local gas phase composition and chemistry.

Conclusively, it can be said that the measurements described in this paper strongly indicate that CN (or a closely related species) may be *the* major species or one of the major species responsible for the effects of nitrogen addition during flame deposition of diamond. Additional research is necessary to determine whether nitrogen-containing species other than CN can be responsible for the effects of nitrogen addition during flame CVD of diamond. Interesting challenges for the future are the determination of absolute gas phase CN concentrations and the amount of nitrogen incorporated into the diamond layer. Information from such measurements would enable a quantification of the influence of nitrogen addition during flame CVD of diamond, on both the gas phase and the deposited diamond.

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