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Growth of {100} textured diamond films by the addition of nitrogen

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Localized {100} fiber textured diamond films were grown by addition of 20-200 ppm nitrogen into the gas phase during hot-filament chemical-vapor deposition (CVD). Cathodoluminescence indicates the presence of the nitrogen-vacancy system in the {100} textured diamond, whereas a blue "band A" luminescence is normally observed in diamond films grown without nitrogen addition. The results demonstrate that the nature of the substrates used for growth has no appreciable influence on the {100} texture, which implies that this fiber texture is obtained by competitive growth and selection of facets. The interaction of nitrogen with the {100} surface is a highly important factor in this process. Homoepitaxial growth shows that the addition of a small amount of nitrogen greatly enhances the growth rate of the {100} faces, making (100) the fastest growth direction in comparison with the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions. This is attributed to breaking of a part of the dimers on the (2×1) reconstructed {100} surface by nitrogen compounds. The {100} texture in narrow, ring-shaped areas on diamond layers grown by the flame technique can also be attributed to the occurrence of a certain amount of nitrogen in the gas phase. It is demonstrated that the flame grown polycrystalline diamond layers have morphologies and cathodoluminescence features that are consistent with those observed in the hot-filament CVD diamond films grown with the addition of nitrogen. © 1996 American Institute of Physics. [S0021-8979(96)01003-6]

I. INTRODUCTION

Although the growth of diamond at low pressure using various chemical-vapor-deposition (CVD) techniques has been extensively studied, the nucleation and growth of heteroepitaxial diamond films remain a great challenge for the research community.¹⁻³ Recent successes in obtaining $\{100\}$ textured diamond films on single-crystal silicon substrates⁴⁻⁷ has presented a promising approach to heteroepitaxy, despite the fact that the actual cause of the textured growth is not yet clear. In principle there are two types of {100} textured diamond films, which according to the terminology introduced by Wild et al.⁷ are referred to as fiber textured and epitaxially textured films. Fiber textured growth according to the evolutionary selection theory introduced by van der Drift,⁸ requires that the textured direction is the fastest growth direction. In a theoretical study, Wild et al.⁹ have defined an α factor $\alpha = \sqrt{3} V_{\{100\}}/V_{\{111\}}$, where $V_{\{100\}}$ and $V_{\{111\}}$ are the growth rates of the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, respectively. An α value of 3 or higher is required to obtain fully {100} textured diamond films. On the other hand, epitaxially {100} textured diamond films are only obtained by formation of diamond nuclei with the same crystallographic orientation as the {100} silicon substrate. This is a situation close to heteroepitaxy.

carburization.¹⁵ It is speculated that a silicon carbide interfacial layer may play an important role to achieve epitaxially textured growth on {100} silicon. {100} fiber textured films were reported to grow on silicon as well as nickel¹⁶ and molybdenum^{17,18} substrates, because this kind of texture can be influenced by manipulation of the gas phase chemistry during the growth. It is well known that different growth conditions will greatly influence the growth rate, crystallinity, and morphology of the diamond films. In several publications Wild et al.^{7,9} demonstrated that, depending on the growth temperature and methane concentration, {100} fiber textured films can be obtained by microwave CVD. However, recently the same group reported that besides the growth parameters the addition of a small amount of nitrogen in the gas phase is responsible for the growth of {100} fiber textured films,¹⁹ which might also explain their previous results. Jin and Moustakas²⁰ have also shown that $\{100\}$ textured diamond film can be obtained when a certain amount of nitrogen is introduced to the system. Although Kania and Oelhafen²¹ have grown {100} textured films using a low concentration of methane without intentional addition of nitrogen during the growth, the photoluminescence spectra demonstrated the presence of the nitrogen-vacancy system in these films. Sun, Zhang, and Lin²² have reported a similar growth of {100} textured diamond films on silicon substrates at a low methane concentration. It might be possible that there was a small amount of nitrogen in their system. In flame CVD, {100} fiber textured films localized in a ringshaped area are often obtained on polycrystalline molybdenum substrates.^{17,18} It is clear that diamond films deposited by flame CVD always contain nitrogen in a radially changing concentration, which is due to in-diffusion from the ambient during growth.¹⁷ The above experimental results show that the presence of a small amount of nitrogen during CVD dia-

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1357

Bias-enhanced nucleation using microwave CVD is the

most widely used method to grow epitaxially textured films.^{10,11} However, bias-enhanced nucleation does not always result in epitaxially or even fiber textured growth.¹² A second approach is to grow on single-crystal β -SiC substrates^{13,14} or on silicon substrates via *in situ*

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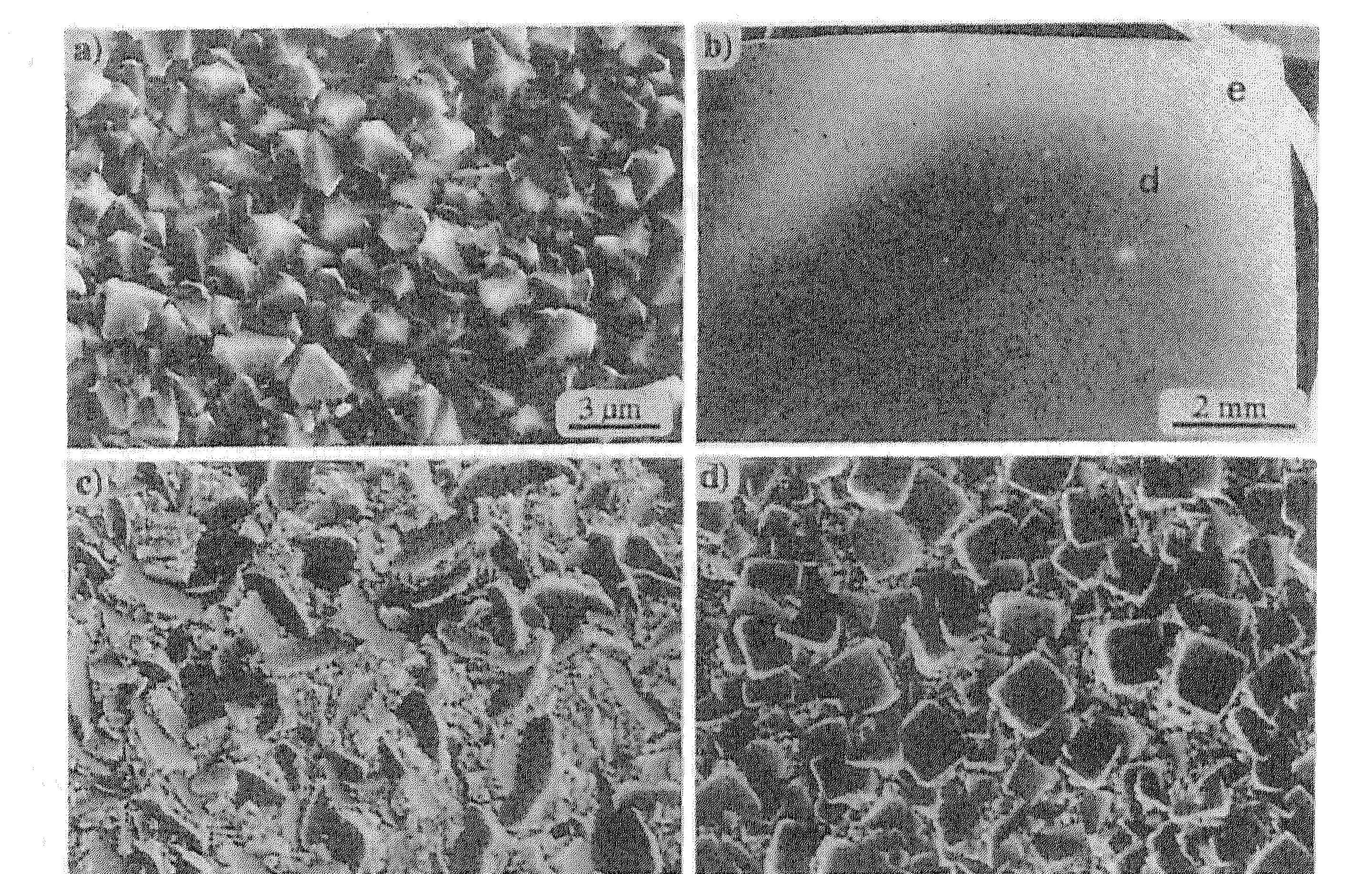
J. Appl. Phys. 79 (3), 1 February 1996

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TABLE I. Experimental conditions for HFCVD growth of diamond {100} textured films.

Filament temperature250Substrate temperature800Total gas flow100Total pressure in the reactor50Methane concentration1.5Ammonia concentration0-1Distance between filament and substrate6 mDeposition time3 hFilamentTag

2500 °C 800 °C 1000 scem 50 mbar 1.5 vol % 0-200 ppm 6 mm 3 h TaC



mond growth has a very important effect on the development

of a {100} fiber texture.

Although {100} textured growth has been obtained by quite different approaches, the influences of the biasenhanced nucleation, the nature of substrates, and the addition of a small amount of nitrogen during the growth on the {100} texture have not yet been expounded. Obviously further systematic and comprehensive studies are needed. In this article we present a study on the growth of fiber {100} textured diamond films as a result of the addition of a small amount of nitrogen in a hot-filament CVD (HFCVD) system. Furthermore, it is shown that our flame growth experiments support the HFCVD results.

The growth of diamond films was carried out in a conventional HFCVD reactor. The gases used were hydrogen and methane (4.5N). In the present study the hydrogen gas was purified by means of a palladium diffuser, resulting in a nitrogen impurity below ppm level. A mixture of ammonia (4000 ppm) in hydrogen was used as a nitrogen source. The growth conditions used in the experiments are given in Table I, unless specified otherwise. The substrates used were single-crystal Si {100} and polycrystalline molybdenum plates. Prior to the diamond growth, the substrates were thoroughly scratched with diamond powder and cleaned with isopropanol in an ultrasonic bath. In addition, two sets of type-IIa diamond substrates were used for homoepitaxial growth. Each set consisted of {111}, {110}, and {100} substrates oriented within 3° from the exact crystallographic plane as well as a {100} substrate with a misorientation of 7° toward $\{110\}$.

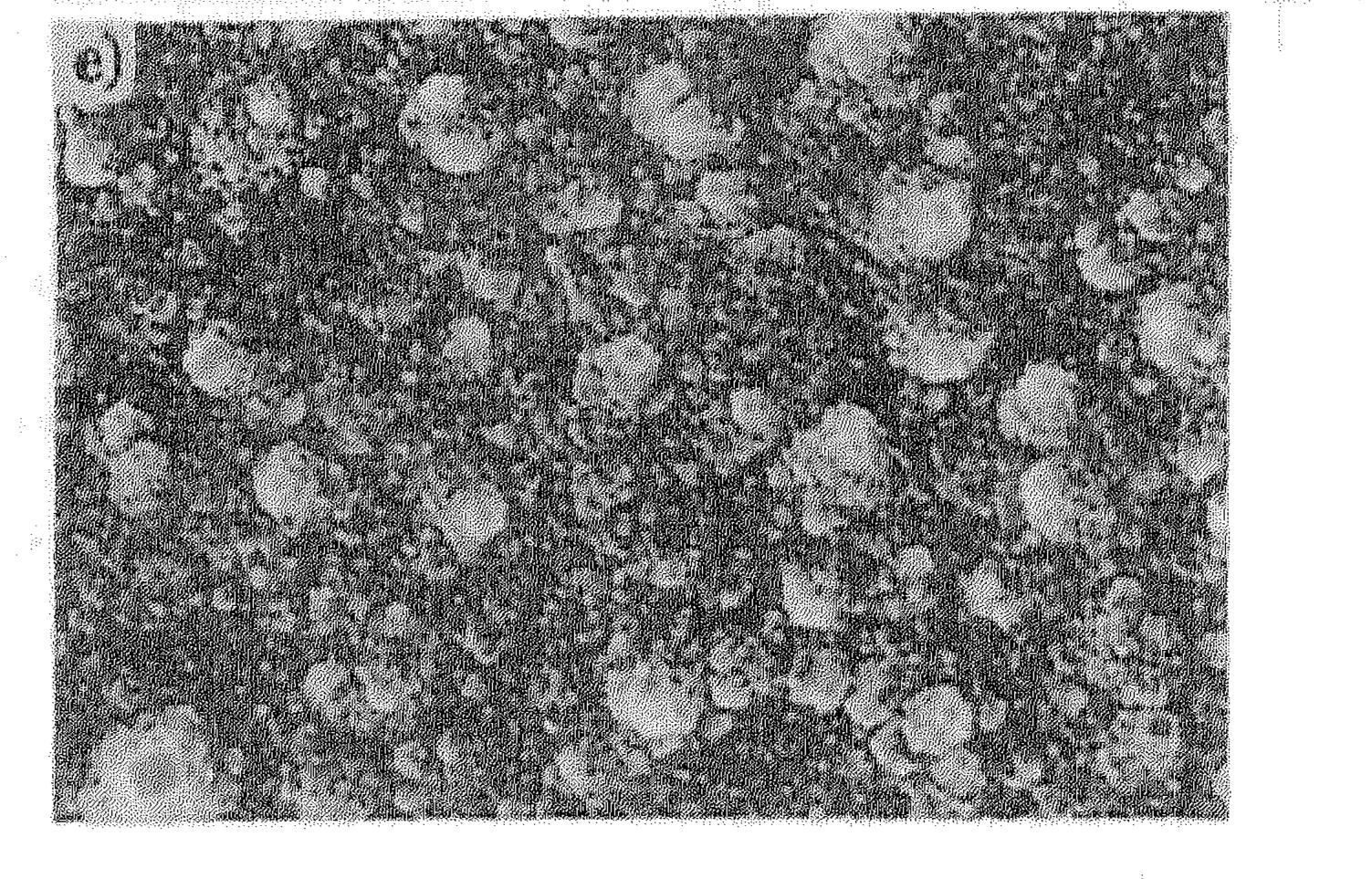


FIG. 1. SEM surface morphologies of polycrystalline diamond films deposited on single-crystal silicon substrates (a) without nitrogen addition and (b)–(e) with 100 ppm nitrogen in the gas phase. The details of the areas (c) with significantly tilted $\{100\}$ faces (d) large, highly oriented $\{100\}$ facets, and (e) nanocrystallites with only a few $\{100\}$ faces are obtained from regions of the same sample as indicated in overview (b).

studies were carried out in a commercially available 8200MK II system fitted to a microscope stage. Typically an

The setup for flame deposition has been detailed

electron beam of 13 keV and 450 mA was used. To prevent heating up by the electron beam the samples were mounted onto a copper sample holder by conductive carbon tape.

III. GROWTH OF {100} TEXTURED DIAMOND FILMS WITH THE ADDITION OF NITROGEN

If no nitrogen (hereinafter ammonia is referred to as nitrogen) is introduced into the system during the growth, homogeneous polycrystalline diamond films are always obtained on silicon substrates under the process conditions given in Table I. Such films consist of randomly oriented {100} and {111} facets as shown in Fig. 1(a). However, if during growth a small amount of nitrogen, ranging from 20 to 200 ppm, is introduced into the system the morphology of the polycrystalline diamond films changes significantly. In this case the morphology of the layer is nonuniform as shown in Fig. 1(b). The part of the film that was located directly underneath the filament reveals a surface which, apart from flat {100} facets, is rough [see Fig. 1(c)]. The average tilt angle of the {100} faces with respect to the substrate surface is rather large. This angle decreases for the parts of the film which were located further away from the filament and {100} fiber texture occurs as can be seen in Fig. 1(d). The lateral dimensions of the {100} facets decrease simultaneously with the tilt angle and at the outer regions of the samples the $\{100\}$ faces almost vanish [see Fig. 1(e)]. Localized {100} textured growth has been widely reported earlier for both microwave²¹ and flame grown CVD diamonds.^{17,18} This implies that the range of experimental

elsewhere.^{23,24} Oxygen (4.5N) and acetylene (2.6N) were used as source gases. Nitrogen in the gas phase originates from contamination of the acetylene (between 1000 and 2000 ppm) and from in-diffusion from the ambient. In the experiments molybdenum and natural type-IIa diamond plates were used as substrates.

The diamond films were characterized by means of a binocular microscope (BM), differential interference-contrast microscopy (DICM), scanning electron microscopy (SEM), cathodoluminescence topography (CL), and Raman spectroscopy. The Raman spectra were recorded with a Dilor XY multichannel spectrometer using the 514 nm line of an Ar^+ laser as an excitation source. Cold cathode luminescence

1358 J. Appl. Phys., Vol. 79, No. 3, 1 February 1996

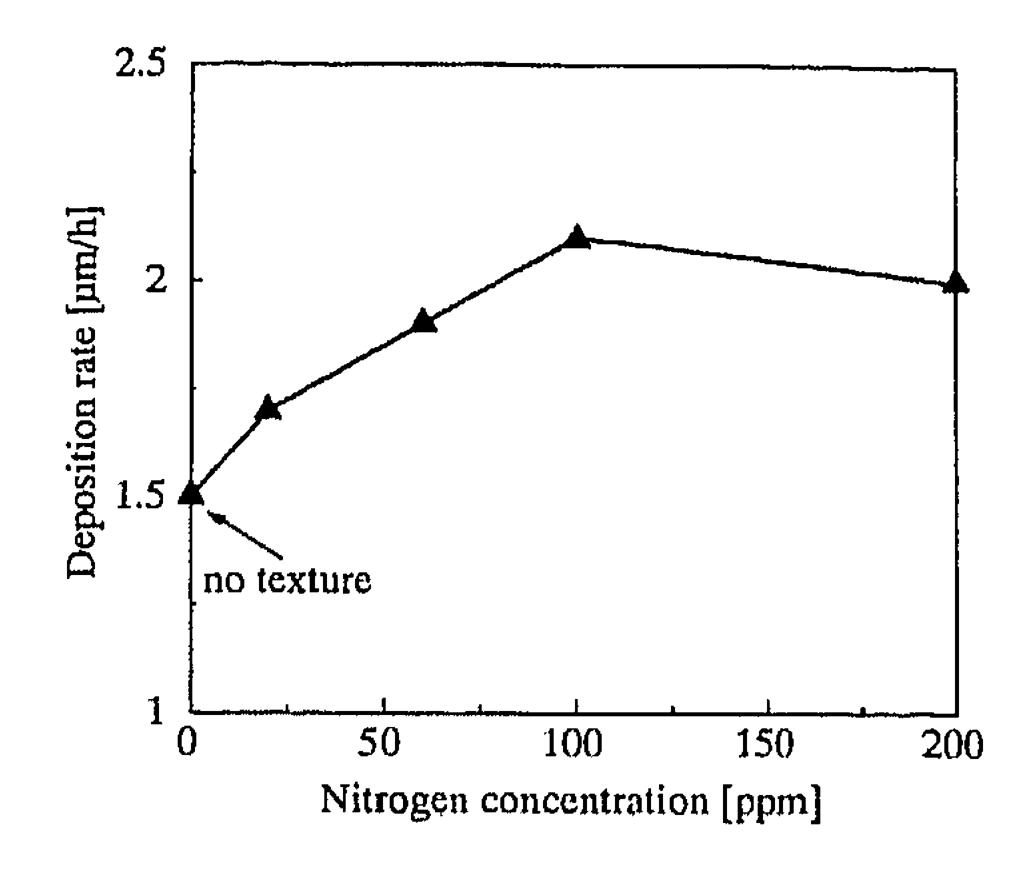
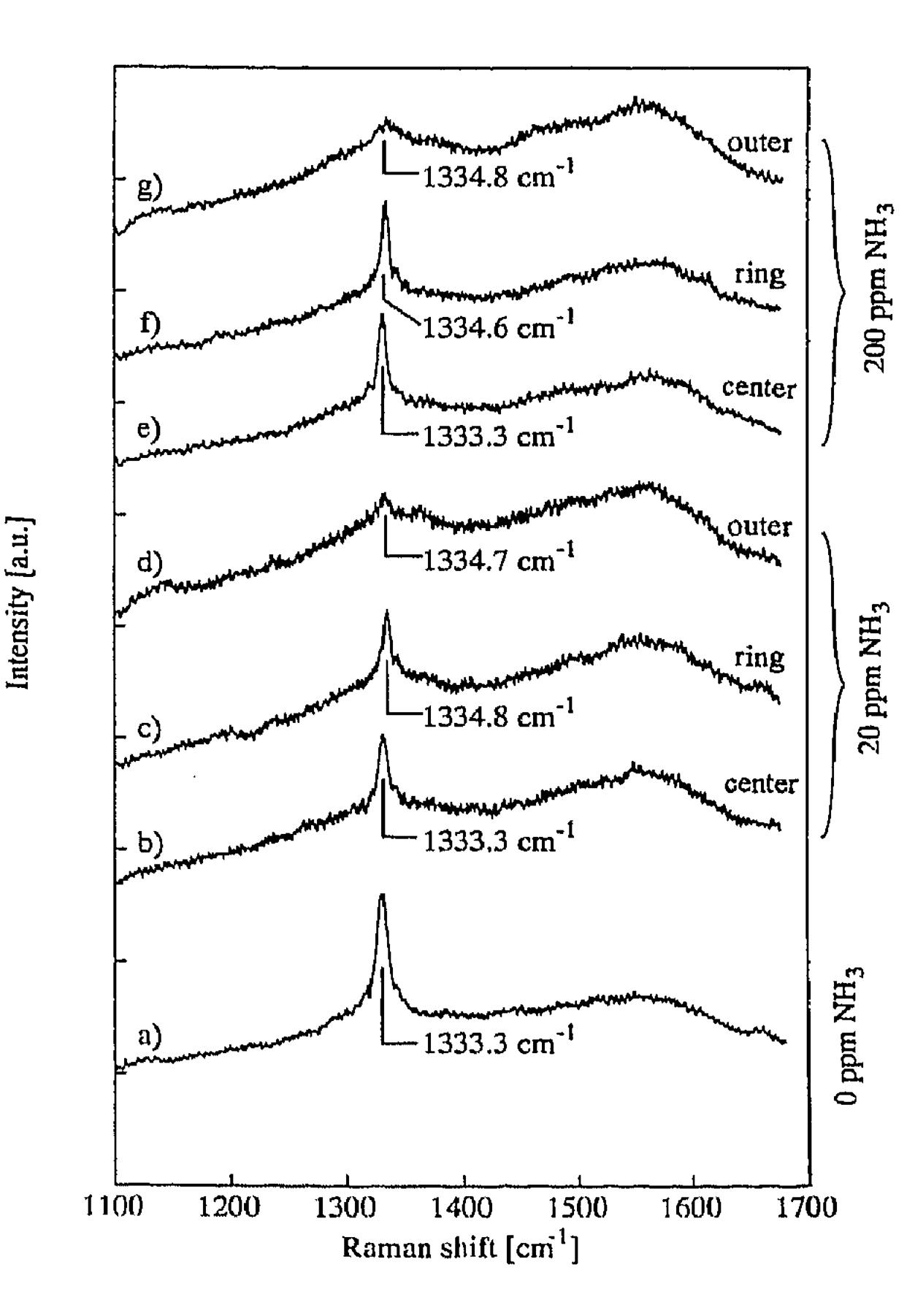


FIG. 2. The average growth rates of polycrystalline diamond films as measured by weight as a function of the nitrogen concentration in the gas phase,

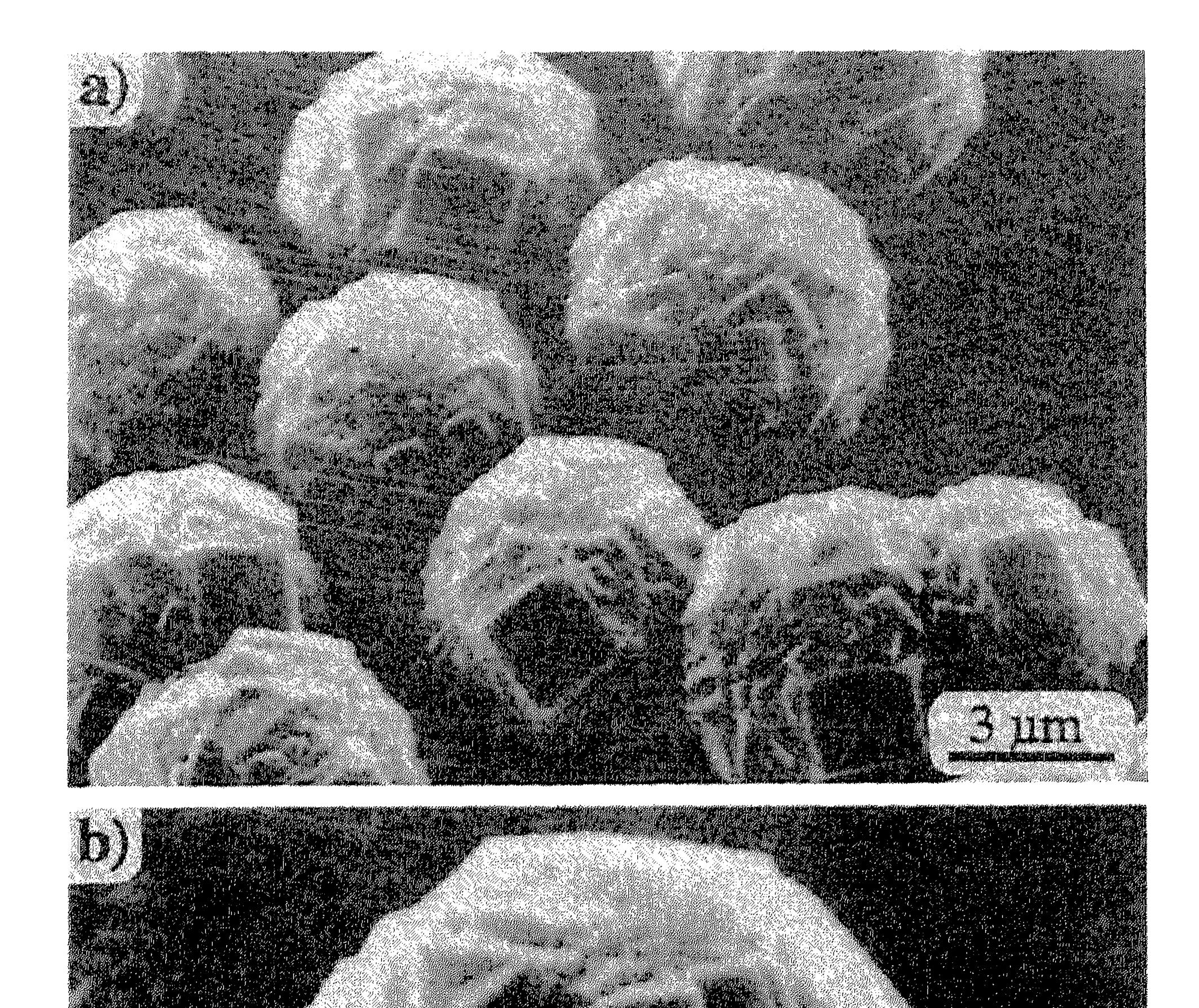


conditions to grow such $\{100\}$ textured films is very restricted. The relation between the observed large scale morphology of the samples and the position of the filament indicates that the occurrence of texture from a nitrogencontaining gas phase depends critically on the deposition temperature and/or the gas phase activation. Additional experiments confirmed that a small change of process conditions, such as the distance between the filament and substrates, may result in a total loss of texturing. The influence of the deposition temperature on the dimensions and the tilt angle of the $\{100\}$ facets as described above agrees well with the results reported by Wild *et al.*⁷

Figure 2 shows that the nominal growth rates of diamond films are enhanced by the addition of a small amount of nitrogen during growth. From the same figure it is clear that introduction of nitrogen concentrations above 60 ppm does not result in a significant further increase in growth rate. Similar results have been reported previously for both polycrystalline¹⁹ and single-crystal^{25,26} diamond growth. The increase of the diamond growth rate by the addition of nitrogen is discussed in detail in Sec. V. CL topographic examination of the nontextured diamond films grown without nitrogen addition shows that they emit a blue luminescence, known as "band A" in the literature.^{27–29} The films grown with nitrogen addition have an orange luminescence in the areas which reveal rather large {100} facets, whereas no significant luminescence is obtained from the areas in which the {100} facets are very small or completely disappeared. The orange luminescence of the 575 nm system, which originates from nitrogen-vacancy pairs,^{27,30,31} indicates that a certain amount of nitrogen has been incorporated into the diamond films during growth. The absence of luminescence from those parts of the films where almost no {100} facets are present suggests that so much nitrogen is incorporated or other defects have been formed that quenching of the signal occurs. The Raman spectra b, c, and d in Fig. 3 were obtained from different positions of a specimen grown with 20 ppm nitrogen added to the gas phase. The morphologies on these positions correspond to those shown in Figs. 1(c), 1(d) and 1(e), respectively. Spectra b and c reveal a clear diamond peak but spectrum d shows a broad band rather than a peak around 1335 cm⁻¹. All spectra exhibit a broad band between

FIG. 3. Raman spectra obtained from a polycrystalline diamond film grown without nitrogen (a) and from various positions on films grown with the addition of 20 ppm (b, c, and d) and 200 ppm (e, f, and g) of nitrogen.

1400 and 1600 cm⁻¹ introduced by nondiamond carbon phases, the concentration of which in this sample is significantly higher than for samples grown without nitrogen addition (see spectrum a). The increased presence of the nondiamond carbon phases is a result of the deterioration of the crystallites—especially the {111} faces—most probably by nitrogen-induced twinning which finally leads to the deposition of layers with an amorphous appearance (see Sec. IV). Spectra e, f, and g were obtained at equivalent positions as b, c, and d, respectively, on a sample that was grown with 200 ppm of nitrogen in the gas phase. From the fact that they are virtually identical to the corresponding spectra of the sample grown with 20 ppm nitrogen, it can be concluded that the increase of nitrogen concentration above 20 ppm does not lead to a significant further deterioration of the diamond crystallites in the different zones of the samples. From the above it is clear that the introduction of nitrogen concentrations as small as 20 ppm in the gas phase during diamond CVD introduces a considerable change in growth rate, crystallinity, morphology, and texture of the deposits. However, an increase of the nitrogen concentration above 100 ppm does not result in significant additional changes. As discussed in Sec. I, it has been argued that intermediate buffer layers, such as β -silicon carbide, may play an important role in diamond textured growth. In the following section, some experimental evidence is provided to show that the intermediate buffer layers are not the factor determining the fiber textured diamond growth.



diamond particles were grown, which in the outer regions of the sample are not single crystals as is clear from the large number and orientations of the square {100} facets [see Fig. 4(b)]. This feature, which has been reported in the literature as well,³² can be explained by multiple twinning of the {111} diamond faces during growth. Newly formed twins exhibit {111} as well as {100} faces; the cubic faces persist and eventually increase in size whereas the octahedral faces suffer from renewed twin formation. Figure 4(c) shows that in the central area of the samples, the particles have a shape which is expected for isolated diamond crystallites although it is clear that the "{111} facets" are already deteriorated by multiple twinning. The results agree well with our earlier work,³³ in which it was demonstrated that the {111} surfaces can incorporate much larger amounts of nitrogen than the {100} faces and suffer from an increased formation of twins. It is clear that the increased microtwin formation on {111} is related to the incorporation of nitrogen and thus results in the growth of larger planar {100} faces at the expense of {111} faces which are covered by microfacets. A high nucleation density is obviously necessary to grow a-continuoustextured diamond film, but it seems not to affect the formation of {100} facets and their progressive growth, as is demonstrated by the isolated crystallites on the mirror polished silicon substrate. The above experiments clearly demonstrate that the development of {100} facets by introducing the nitrogen is due to a change of the gas phase chemistry, which influences the surface kinetics at the diamond nuclei and to the twin formation on {111}, and is not related with the na-

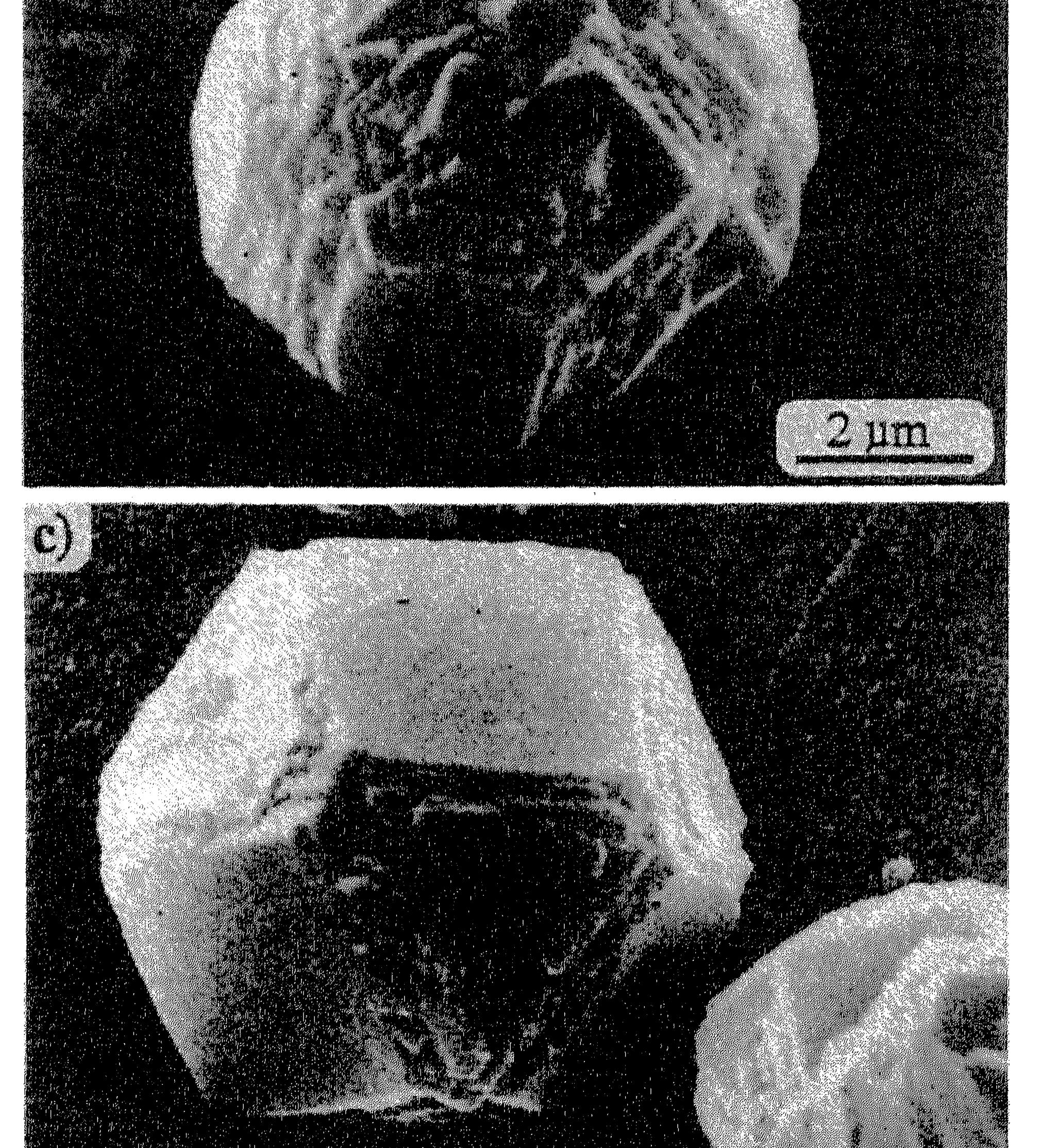


FIG. 4. SEM images of a cluster (a) and isolated (b) and (c) diamond particles with well-developed {100} facets deposited by HFCVD with 100 ppm nitrogen addition on a mirror polished single-crystal {100} silicon substrate. The multiple twinned diamond particle (b) is located at the outer region and the crystallite (c) with much less deteriorated {111} faces is situated near the center of the sample.

IV. INFLUENCE OF THE NATURE OF SUBSTRATES ON {100} FIBER TEXTURING

In a series of experiments diamond films were grown from a nitrogen-containing gas phase on various substrates other than scratched single-crystal silicon. These substrates were mirror polished single-crystal silicon, a polycrystalline diamond film in situ predeposited without nitrogen addition on silicon, and scratched molybdenum. All films have been grown under the same process conditions as given in Table I with 60-100 ppm nitrogen added into the system. For the last two substrates continuous polycrystalline diamond films were obtained, with localized {100} textured areas very similar to those shown in Figs. 1(b)-1(e) for films grown on scratched Si {100}. The CL and Raman characteristics are also comparable to those described in Sec. III, although the film grown on the polycrystalline diamond substrate shows a slightly better crystallinity. This may be attributed to the homoepitaxy on the already existing diamond particles. Figure 4(a) shows that on the mirror smooth polished silicon substrate the nucleation density was too low to grow a continuous diamond film. Instead only clusters of separated

ture of the substrates.

It is to be noted that the preferential formation of {100} facets by the addition of a small amount of nitrogen during the growth is different from the results of bias-enhanced nucleation which often leads to well-oriented nuclei and subsequent growth of epitaxially {100} textured diamond films.⁷ By the addition of nitrogen, growth of epitaxially textured diamond films is not expected due to the randomly oriented {100} facets formed by multiple twinning during growth. According to the literature it is known that, besides the nitrogen addition, there are several other factors which have a large influence on the formation of facets. These are

(i) methane concentration,³⁴
 (ii) substrate surface temperature,^{23,35} and
 (iii) addition of a small amount of oxygen.^{22,36,37}

It has been reported³⁸⁻⁴¹ that the concentration ratio of \cdot CH₃ to C₂H₂ growth species on the growth surface is strongly dependent on the substrate surface temperature, methane concentration, and oxygen concentration. By analyzing the terminating mode on {111} and {100} surfaces by electronenergy-loss spectroscopy, Sun and co-workers²² have concluded that a high concentration of C₂H₂ with respect to \cdot CH₃ results in the formation of {100} facets, whereas a relatively high concentration of \cdot CH₃ favors the formation of {111} facets. Although we have no direct experimental data on the concentration ratio of C₂H₂ to \cdot CH₃ growth species on the growing surface, it is possible that the addition of nitrogen enhances the concentration of \cdot CH₃ on the growth surTABLE II. Growth rates of homoepitaxial films grown on various surfaces with and without the addition of nitrogen.

Substrate orientation	Growth rate (µm/h) without nitrogen addition ^a	Growth rate (µm/h) with 100 ppm nitrogen addition
(111)	1.6	3.6
(110)	2.7	4.5
(100)	1.4	6.2
$(100) + 7^{\circ}$	1.5	8.0
α factor	1.5	3

^aDistance between filament and substrate: 10 mm.

face and thus increases the growth rate of the {100} facets. This speculation, however, needs further experiments to be

which grows via a mechanism of addition in rows of atoms. The $\{111\}$ and the (2×1) reconstructed $\{100\}$ faces are flat F faces, which grow slowly via a layer mechanism involving step flow.⁴⁴ Upon the introduction of a small amount of nitrogen (100 ppm) into the system during growth, the deposition rates of all surfaces are greatly enhanced. It is not clear to what extent this is caused by the nitrogen addition or is due to the smaller substrate-filament distance. However, from Table II it can be seen that the nitrogen has different influences on the various orientations: The exact and 7° misoriented {100} faces now have the highest growth rates as compared to the $\{111\}$ and $\{110\}$ surfaces. Accordingly the α factor has a value of 3 compared to 1.5 for the experiment without nitrogen in the gas phase. Following the van der Drift model for textured growth⁸ the enhanced growth rate along (100) well explains the occurrence of $\{100\}$ texture of the polycrystalline diamond films grown in the presence of nitrogen; however, the question remains why the growth rates of the {100} faces and maybe also that of the other faces are increased. The increase of the diamond growth rate by the addition of nitrogen was reported previously.^{20,25,26} Several possible explanations have been proposed. Bar-Yam and Moustakas⁴⁵ proposed a quasithermodynamic model on defect-induced stabilization of diamond. This model predicts that the incorporation of nitrogen donors charges the vacancies in the growing diamond surfaces and thus reverses the thermodynamic stability of diamond relative to graphite; therefore, the growth rate of diamond will be enhanced. This model has been used to explain the experiments in the literature²⁰ and in our previous articles;^{25,26} however, it does not explain the orientation dependence of the increase in growth rates. In fact, the {110} and {111} surfaces incorporate more nitrogen than the $\{100\}$ surface,^{33,46} thus, according to the defectinduced model, a larger enhancement of growth rate would be expected for {110} and {111} surfaces rather than for the $\{100\}$ surface. Of course, the addition of 20–200 ppm nitrogen slightly changes the gas phase chemistry, but a significant variation of the C_2H_2 and/or $\cdot CH_3$ concentrations is not to be expected. However, the presence of NH_r and possibly CNH_r radicals can significantly change the surface composition of adsorbed species, because, compared to the C-C bond the C—N bond is stronger,⁴⁷ and NH_x and CNH_y radicals have lower desorption rates. Therefore, upon adsorption of these species flat surfaces become closer to the "chemically roughening" transition⁴⁸ and consequently the growth rate increases. Due to selective adsorption of these species on surfaces with different orientations the presence of nitrogen can influence the α factor. In particular the nitrogen-related species may break part of the dimers on the (2×1) reconstructed {100} surface⁴⁹ and enhances the diamond growth rate of this face to a larger extent by the creation of additional kink sites at the growth steps. The surface morphology of the diamond films grown with and without nitrogen on {100} substrates with a misorientation of 7° toward $\langle 110 \rangle$ has been examined by means of DICM. In both cases exact {100} facets have developed on one side of the specimens. For the sample grown without nitrogen addition, the exact facet exhibits ran-

verified.

The above discussion indicates that the addition of nitrogen during the growth causes a change of gas phase chemistry and surface kinetics at the diamond crystallites, so that the formation of smooth $\{100\}$ surfaces appears more pronounced because the $\{111\}$ surfaces deteriorate due to multiple twinning. In addition, the growth rate of $\langle 100 \rangle$ with respect to $\langle 111 \rangle$ is increased, as is further elaborated in Sec. V. The type of substrate is not relevant.

According to the van der Drift competitive growth model⁸ the film texture is determined by the ratio of the growth rate along $\langle 100 \rangle$ and along $\langle 111 \rangle$. Wild *et al.*⁹ introduced a parameter α , which is defined as this ratio multiplied by a factor $\sqrt{3}$ and used it to describe experiments concerning oriented polycrystalline CVD diamond growth. The shapes of isolated crystallites can be used to determine the relative growth rates in the two crystallographic directions⁴² and thus the α factor. However, it is very difficult to determine the α factor directly from polycrystalline diamond films. In order to have an overall measure of α , homoepitaxial layers were deposited on {100} and {111} oriented type-IIa natural diamond substrates simultaneously.

V. HOMOEPITAXY AND GROWTH RATES OF DIFFERENT FACES

The growth rates obtained from a homoepitaxial growth experiment without nitrogen and one with 100 ppm nitrogen in the gas phase using natural diamond substrates with different orientations are summarized in Table II. The experiment with 100 ppm nitrogen was carried out under exactly the same process conditions as used for the polycrystalline deposition runs as discussed in Secs. III and IV (see Table I). Due to circumstances the epitaxial growth run without nitrogen addition was carried out with a substrate to filament distance of 10 mm instead of the 6 mm. Thus, the difference

between the absolute growth rates for both homoepitaxial experiments is, apart from the influence of nitrogen, partly due to the difference in distance between the filament and substrates.

In the case of homoepitaxial growth without nitrogen, the $\{110\}$ face grows fastest compared to the other faces (see Table II). This is simply because, according to the periodic bond chain (PBC) theory,⁴³ the $\{110\}$ face is a rough S face

J. Appl. Phys., Vol. 79, No. 3, 1 February 1996

Cao et al. 1361

films. As expected from the geometry front on molybdenum substrates reveal a Ń

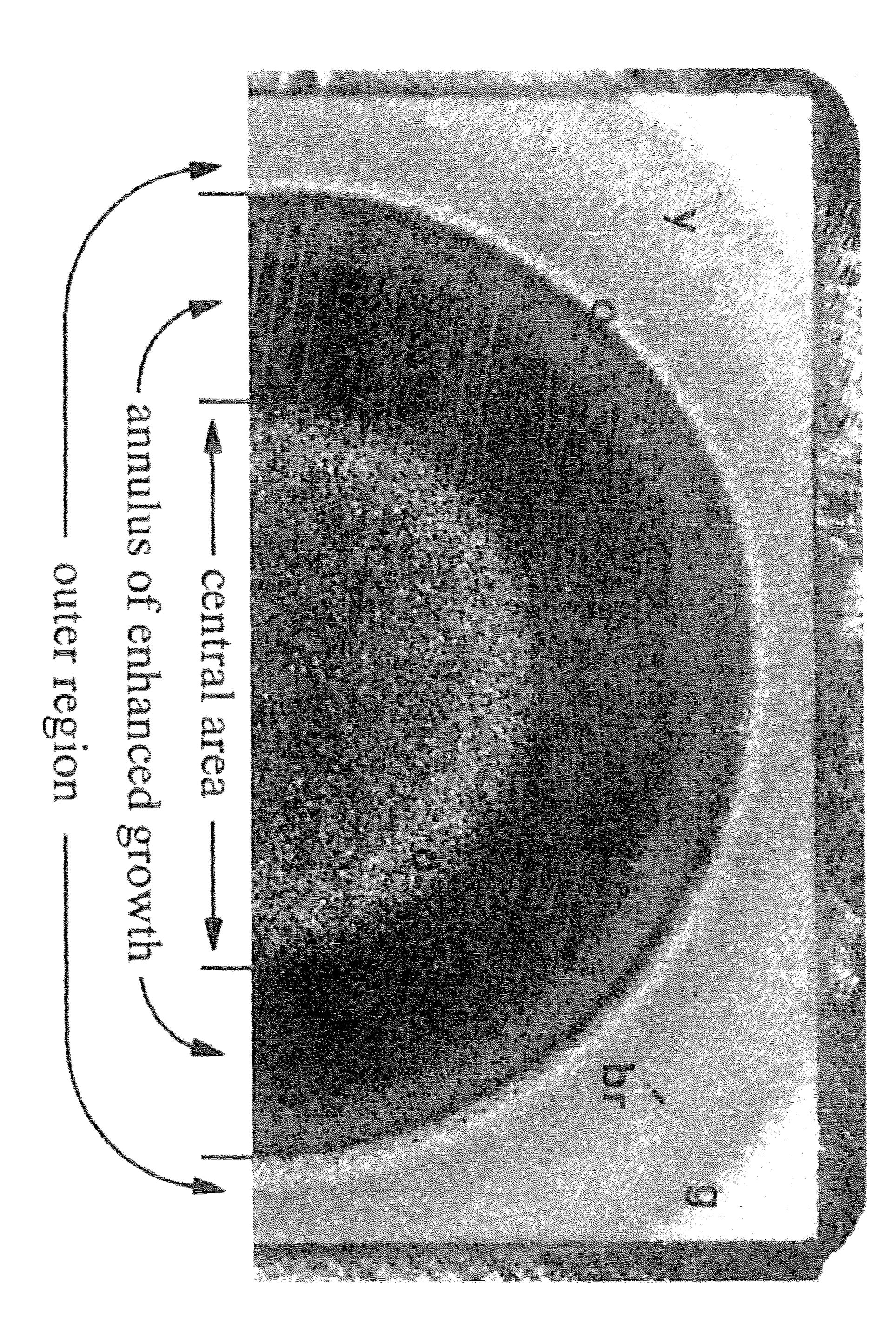
J W N N CONTINUCS S tion upon nitrogen addition. In a forthcoming article the sur-

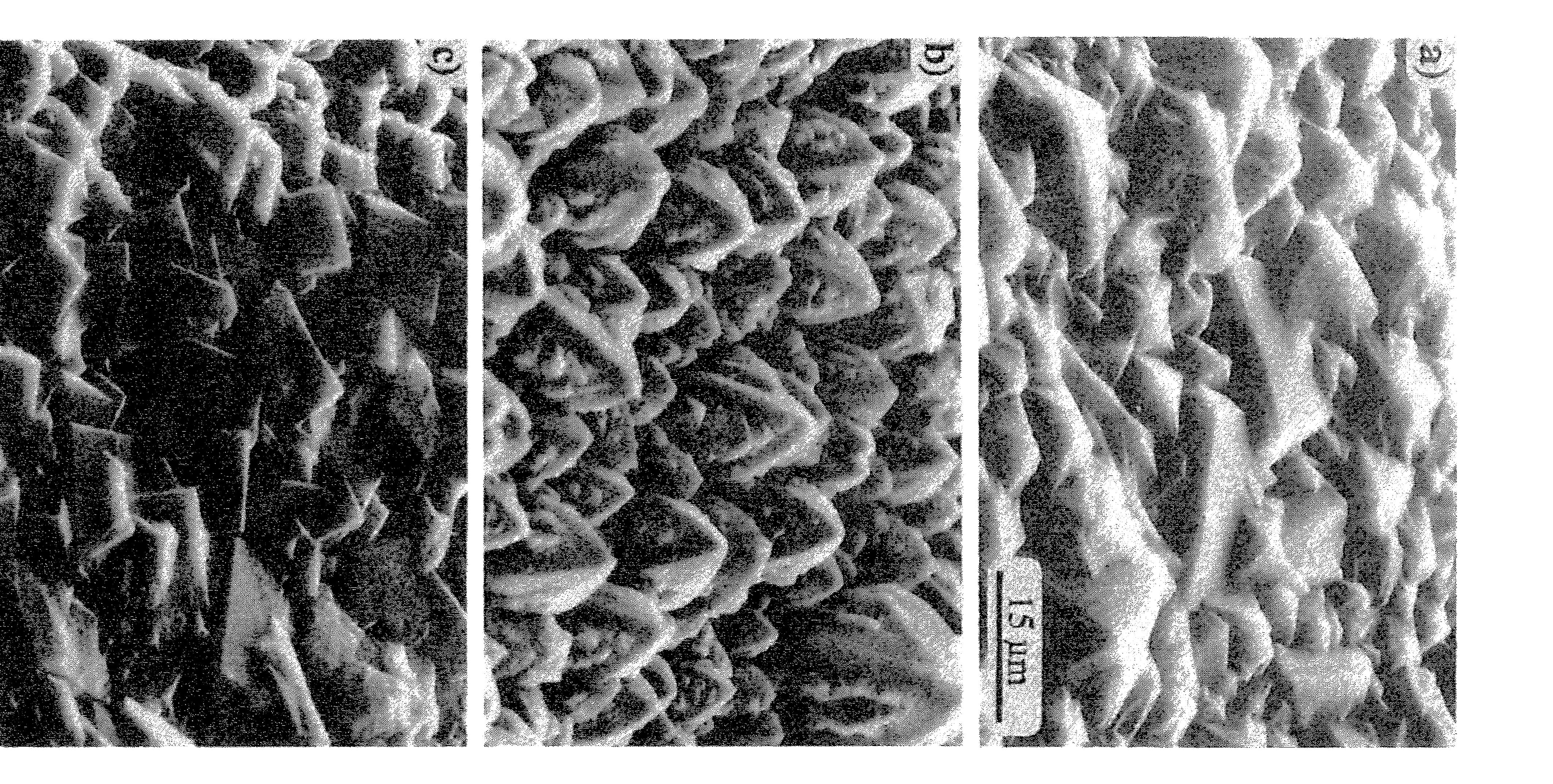
0 ness due to accumulation of lower steps to bunching patterns nitrogen addition; the strong temperature dependence of the adsorption and desorption processes may explain the varia-tion of the {100} tilt angle over the surface of the polycrys-talline diamond films. Furthermore the deterioration of the upon the introduction of nitrogen. These results indeed point orientation-dependent surface processes, such growth morphologies of layers on the {111} single-crystal strates, which show a significant increase in twin forma-sonewhat orange peel appearance. al optaxialy grown samples discussed

FIG. 6. SEM images showing the detailed monthology which is usually observed on polycrystalline diamond deposits obtained by the flane technique. The images a, b, and c, respectively, show the typical monthology of the center.^{17,23} Figure 6(a) shows that these crystallines induced growth.
the center.^{17,23} Figure 6(a) shows that these crystallues, which consist of (111) and (100) facets, are nondomly ordented. Especially if grown at high supersaturations, most of the crystallites are twinned and show secondary nucleation. The central area is surrounded by an annulus where high columnar crystallites surrounded by an annulus where high columnar crystallites surrounded by an annulus where high columnar crystallites surrounded by an annulus where high supersatived are twinned and show secondary nucleation. The central area is surrounded by an annulus where high columnar crystallites surrounded by an annulus where high samulus of enhanced growth and roughness the deposits have fig. 6(b)]. These crystallites frequently have (100) top facets annulus of enhanced growth and roughness the deposits have the same structure as the central region with a decreasing size of the crystallites going radially away from the centrat regions of the samples, in which crystallites form a continuous, highly (100) textured diamond layer [see Fig. 6(c)].
CL topography of these layers reveals a radially changing luminescent helavior which is strongly related to the morphology of the samples as described above (see Fig. 5 and Ref. 17). These CL observations can be ceptained by the

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fact that during deposition nitrogen (N_2) from the ambient diffuses into the acetylene feather. After decomposition by thermal dissociation or by reactions with other species, nitrogen is incorporated into the diamond lattice. In the gas phase above the outer boundary of the deposits nitrogen is only partly decomposed due to a relatively low flame temperature. This results in a relatively low concentration of nitrogen incorporated in the diamond layer. Consequently a green CL signal is obtained, which can be attributed to the simultaneous emission from the 575 nm system²⁷ and blue band-A luminescence.^{27–29} Toward the center of the acetylene feather, as the flame temperature rises, the decomposition of nitrogen increases and a large amount of nitrogen is incorporated into the diamond lattice. Thus one observes a shifting of the CL signal via yellow and brown toward a very pronounced orange-red emission of the 575 nm system in the small ring-shaped area with the {100} texture. Above the annulus the concentration of active nitrogen species in the gas phase reaches a maximum. Probably a large amount of active nitrogen introduces the dramatic change in the morphology of the deposited layer which, due to the limited amount of crystallites or quenching of the CL signal, emits no appreciable luminescence. The amount of nitrogen diffused further into the inner feather apparently decreases sharply, resulting in the "common" morphology of CVD diamond with the dominant blue band-A luminescence that is observed in the central area of the deposits. Between the annulus of enhanced growth and the blue luminescent central area a second orange luminescent ring is the transition region between the areas of too much nitrogen (quenching) and the area with very low nitrogen content. Although the nitrogen concentration in the gas phase above this central area is still well above 1000 ppm due to N_2 contamination of the acetylene

diameters between 2 and 3 mm by the flame technique.^{24,55,56} During deposition these substrates were located well within the homogeneous central part of the deposition area, which for these particular experiments was about 5 mm in diameter. The typical thickness of the layers grown (>50 mm) is significantly larger than for the single crystals grown by HFCVD.

For {100} and {111} single crystals grown by HFCVD without nitrogen addition the morphologies differ too much from that of flame-deposited single crystals to be explained by the higher layer thicknesses of the latter only.^{44,52} In contrast to this, especially the exact and near-exact {100} single crystals obtained by HFCVD with 100 ppm NH₃ in the gas phase have a surface appearance which is quite similar to that of the crystals grown by the flame technique, for which nitrogen concentrations in the gas phase exceed 1000 ppm. As already concluded from this study and previous work,¹⁹ this again indicates that nitrogen concentrations above 100 ppm in the gas phase generally do not result in additional changes in the diamond layers. It is clear now that, besides the growth rates, the active nitrogen species also affect the surface morphology of the {111} and {100} faces which grow by a layer mechanism. A detailed comparison of the surface morphologies of single crystals grown by the HFCVD and by the flame technique is beyond the scope of this article and will be elaborated elsewhere.⁵³

VII. CONCLUSIONS

The present study has demonstrated that the growth rate, morphology, crystallinity, and texture of CVD diamond films change considerably upon introduction of 20-100 ppm of ammonia into the gas phase; however, a further increase of nitrogen concentration does not result in additional changes of any significance. Partially {100} fiber textured diamond films were grown from a nitrogen-containing gas phase by HFCVD and the combustion flame technique. The addition of nitrogen during growth causes the growth of multiple twinned diamond crystallites and favors the formation of planar {100} faces at the expense of rough {111} faces, which are microfacetted due to microtwinning. The nature of the substrates used in the experiments has no appreciable influence on texturing. This {100} fiber texturing depends critically on the deposition temperature and/or the gas phase activation. Homoepitaxial growth on natural diamond substrates with different orientations clearly shows that without the addition of nitrogen the {100} surface has the slowest growth rate. However, the (100) direction grows fastest in comparison to the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions if 100 ppm nitrogen is introduced into the system during growth. The occurrence of the {100} texture on the polycrystalline deposits which were grown in the presence of small amounts of nitrogen under identical conditions can therefore be well explained by the evolution selection theory developed by van der Drift, which states that the fastest growth direction determines the texture. It is argued that the presence of NH_r and possibly CNH_r radicals can significantly change the surface composition of adsorbed species. Due to selective adsorption of these species on surfaces with different orientations the presence of

source gas, the nitrogen molecule with a triple bond (226 kcal/mol) is very stable and thus only a small fraction of nitrogen in the system will be activated and incorporated into the diamond lattice.

The above results clearly show that {100} silicon and/or SiC intermediate layers are not needed to obtain a {100} fiber textured diamond film, as was also found for the films grown by HFCVD. Furthermore, it is also demonstrated that the concentration range of nitrogen, which causes {100} textured growth is very narrow. For concentrations below this range the crystallites are randomly oriented and are bounded by both {111} and {100} facets. Above this range the growth of $\{111\}$ facets is almost totally obstructed^{20,25} due to the large amount of nitrogen-induced twinning and secondary nucleation, which finally leads to the deposition of amorphous material.¹⁷ The morphology of the annulus is consistent with the fastest growth rate in the (100) direction due to the change in growth mechanism by the adsorption of nitrogen as discussed in Sec. IV. In the same manner as observed for the {100} textured diamond films grown by hot-filament and flame CVD, the homoepitaxial films grown by the flame technique exhibit a lot of features that are similar to those on homoepitaxial layers grown by hot-filament CVD in the presence of nitrogen. Recently single-crystalline diamond layers were grown on top of cylindrical type-IIa natural diamond substrates with

Cao et al. 1363

J. Appl. Phys., Vol. 79, No. 3, 1 February 1996

nitrogen can influence the α factor. In particular these species may break part of the dimers on the (2×1) reconstructed {100} surface and enhance the diamond growth rate of this face to a larger extent than the {111} and {110} face, by the creation of additional kink sites at the steps. The observed increase of the surface roughness of the {100} face upon addition of nitrogen in the gas phase agrees well with the described mechanism.

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1364 J. Appl. Phys., Vol. 79, No. 3, 1 February 1996

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