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Fabrication of smooth diamond films on SiO₂ by the addition of nitrogen to the gas feed in hot-filament chemical vapor deposition

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Diamond films of small roughness have been deposited onto thermally oxidized Si substrates by a process of anisotropic crystalline growth induced by nitrogen in a hot-filament chemical vapor deposition reactor. Ethanol (C₂H₅OH), diluted in hydrogen and nitrogen, was used as the source of carbon. At high concentrations, nitrogen tends to suppress the diamond growth in the <100> direction, which allows the growth of square mesoscopic-like crystals ("plates") of large area in the directions parallel to the surface of the substrate. These plates stack upon each other, forming a thick diamond coating of uniform thickness. Analysis of the films made by micro-Raman spectroscopy and atomic force microscopy revealed that it is possible to obtain diamond coatings of high quality with a roughness comparable to that of the SiO₂ at the diamond/SiO₂ interface, and of nanometric roughness on the surface of the plates. A model to explain the morphology of the plates based on the microscopic mechanisms that involve the possible passivation of the (100) plane and an increase of vacancies by nitrogen is also discussed. © 2001 American Vacuum Society.
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I. INTRODUCTION

The success of diamond synthesis by chemical vapor deposition (CVD) has opened the possibility for diamond to become an important material in the production of electronic devices.¹⁻⁴ A consequence of this is an increase of interest in the production of diamond films with properties suited to the needs of the electronics industry. For example, for applications in integrated devices such as diodes, transistors, capacitors, and others, doped crystalline diamond films of very low surface roughness are necessary.⁵⁻⁷

The synthesis of CVD diamond is usually made by the dissociation of a gaseous carbon source highly diluted in hydrogen. Hydrogen acts as an efficient catalyst for hybridization of the existing free bonds of the already-deposited carbon atoms on the substrate so that the arriving carbon atoms may easily form C-C *sp*³ bonds.^{3,4} However, this process often produces a film of columnar structure with grain facets ending in (111) planes, which results in a film of very high roughness.

The addition of other gases to the CVD feed may modify the kinetics of the crystallization process at the atomic level, and contribute to the modification of the final surface roughness of the diamond film. Nitrogen, in particular, is a suitable gas for these studies since it is known that its presence in the CVD feed may induce the (100) faceting of the diamond grains.^{8,9} Nitrogen also forms several stable structures within the structure of diamond, such as point defects, aggregates and planar defects.^{10,11} However, few studies have been undertaken of diamond synthesis with high concentrations of

nitrogen,^{9,12} and none of them examined the detailed morphology of the films.

In this article, we study the morphology of diamond films deposited onto oxidized Si substrates in a hot-filament CVD reactor fed with the mixture C₂H₅OH+H₂+N₂ with 15–20% vol. of N₂. This work showed that square plates of nanometric roughness may be obtained on the top surface of the diamond films. Analysis of the films made by scanning elec-

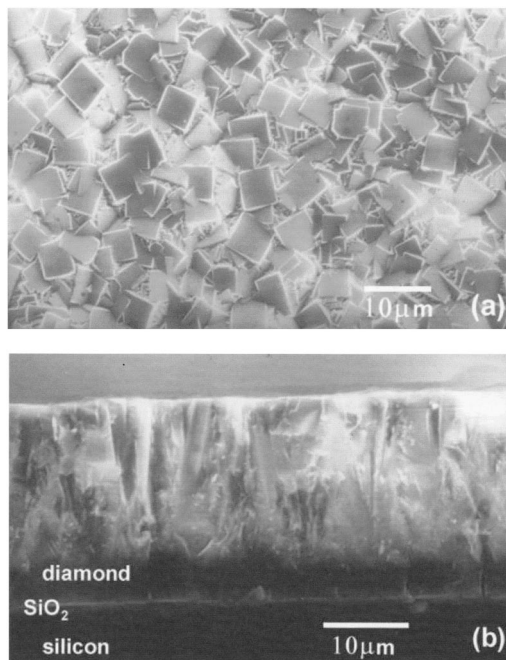


Fig. 1. Typical SEM images: (a) top-view and (b) cross-sectional fracture of a diamond film as-deposited on SiO₂ at a nitrogen concentration of 20% vol.

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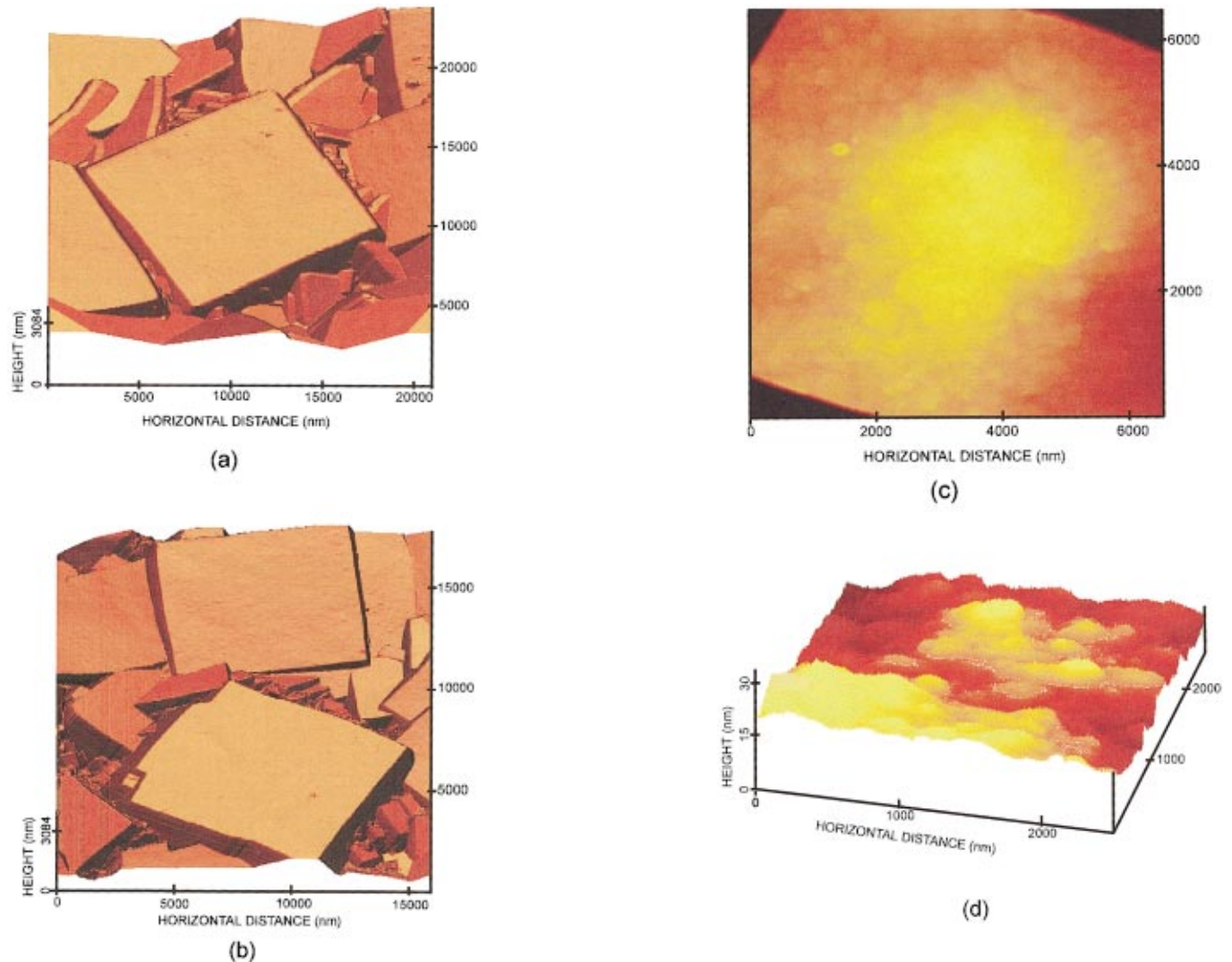


FIG. 2. Typical AFM images at different magnifications of an as-deposited diamond film on SiO₂ at a nitrogen concentration of 20% vol., showing the three-dimensional morphology of its surface (a), (b); details of the surface of the “plates” (c), and a three-dimensional image of its nanometric roughness (d).

tron microscopy (SEM), atomic force microscopy (AFM), and micro-Raman spectroscopy are discussed.

II. EXPERIMENTAL DETAILS

Diamond films were deposited from mixtures of ethyl alcohol (C₂H₅OH) diluted in hydrogen (99.5% vol.) in a hot filament chemical vapor deposition (HFCVD) system.¹³ The system consisted of a spiral tungsten filament of 238 μm diameter and of length 5 cm, mounted in a cylindrical quartz chamber evacuated by a rotary vane pump. Typically the power supplied to the filament was 160 W. Deposition temperatures, as measured by a thermocouple on the underside of the substrate, were in the range of 1120–1170 K. Gases (99.9% pure) were fed to the system via precision mass flow controllers. Nitrogen was added to the mixture in proportions of 15–20% vol. A total flow rate of around 120 standard cubic centimeters per minute (sccm) and a total pressure of about 20 Torr were maintained throughout. Deposition times of 6 h were used.

Thermally dry-oxidized silicon wafers with an oxide thickness of at least 200 nm were used as substrates. Prior to deposition, the oxidized wafers were dipped in a colloidal mixture of diamond dust (0.25 μm in diameter) dispersed by ultrasonic vibration in *n*-hexane. This “seeding” was the usual procedure used to increase the nucleation density of diamond films.¹⁴

The surface morphology was examined by scanning electron microscopy and atomic force microscopy using a JSM-5900 LV SEM and a Nanoscope II AFM, respectively. Raman spectroscopy was recorded at ambient temperature using a Renishaw microprobe system, equipped with a microscope whose focal spot diameter was about 2 μm from an Ar⁺ laser (6 mW power) at λ = 514.5 nm.

III. RESULTS AND DISCUSSION

Figure 1(a) shows a typical SEM top-view image of an as-deposited diamond film produced at a nitrogen concentration of 20% vol. Note that the surface is covered with well-

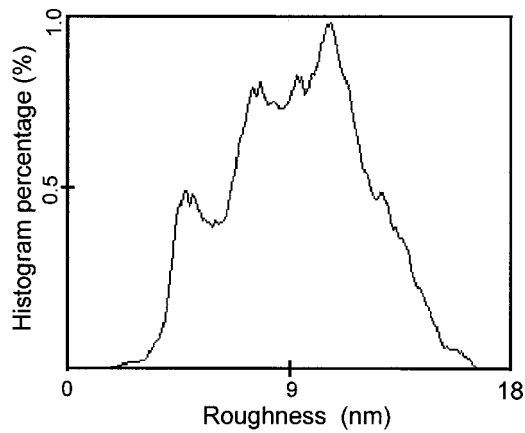


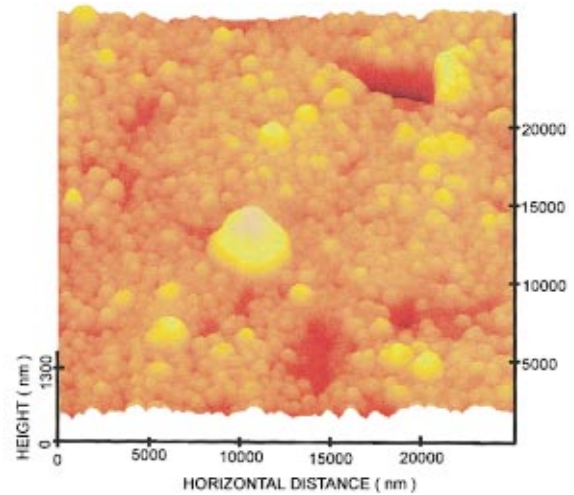
FIG. 3. Typical roughness distribution histogram of the diamond "plates" shown in the images of Fig. 2.

faceted structures of rectangular shape and relatively uniform size (squares of about $6 \mu\text{m}$). Strong charging effects in the SEM (due to the SiO_2 insulating layer beneath the film and the high electrical resistivity of the film itself) were observed. Figure 1(b) shows a typical SEM image obtained from a cross-sectional fracture of this sample. The dark area, in the lower part of this figure, corresponds to the SiO_2/Si substrate. One may see that the diamond/ SiO_2 interface and the top surface of the film are quite planar. The thickness of the diamond film is quite uniform and a growth rate of around $6 \mu\text{m h}^{-1}$ was estimated.

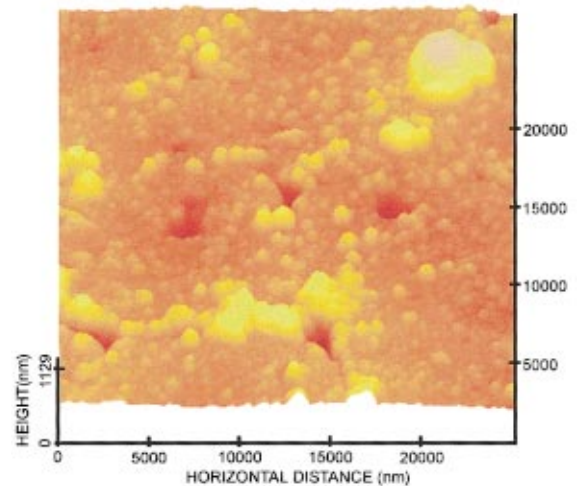
Details of the surface features were revealed by AFM. Figures 2(a) and 2(b) show typical AFM images taken on different areas of the sample. One may observe that the flat structures are practically mesoscopic, appearing as crystalline sheets randomly stacked on a plane surface. The apparent thickness of such "plates" is around $1.6 \pm 0.2 \mu\text{m}$, as determined statistically from the AFM images.

Figure 2(c) shows a magnified image of the surface, corresponding to the area of the plate shown in the lower part of Fig. 2(b). Some surface aggregates may be observed, but without any identifiable crystalline forms. Further magnification of this area [see Fig. 2(d)] shows that this surface has a very small roughness, characterized by a non-Gaussian height distribution histogram, centered around 11 nm and with a maximum height of 17 nm (see Fig. 3).

To analyze the roughness of the diamond/ SiO_2 interface it was necessary to detach the diamond film from the substrate. This procedure was performed using a sharp knife pressed on the lateral diamond/ SiO_2 boundary. Figures 4(a) and 4(b) show the topography of the SiO_2 [Fig. 4(a)] and that of the surface of the diamond [Fig. 4(b)] that was in contact with this SiO_2 surface. The nanometric vertical resolution of the AFM images allows the measurement of the submicron roughness of both surfaces. Some higher peaks (lighter-colored areas) are also observed in the images, but apparently they are due to the residues remaining from the forced separation of the diamond film from the SiO_2 surface. Excluding these peaks, the height histogram of these surfaces (see Fig. 5) indicates that they have similar roughnesses, be-



(a)



(b)

FIG. 4. AFM images of the diamond/ SiO_2 interface showing the topographic measurements of (a) the top surface of the SiO_2 layer and (b) of the bottom surface of the diamond film.

tween 250 and 380 nm. This suggests that the diamond growth at the first nucleation stages practically matched the topography of the SiO_2 surface. We also found [see Fig. 4(b)] that the diamond surface has areas of greater smoothness separated by rougher areas. Apparently, the rougher areas are related to the grain boundaries of the diamond film. Figures 6(a) and 6(b) show higher resolution images of the diamond surface corresponding to the upper and low-left areas shown in Fig. 4(b). Figure 6(a) probably corresponds to the bottom of a diamond grain or an area of nanometric nucleation, while the image shown in Fig. 6(b) corresponds to an area of grain boundaries or of poor nucleation. Comparing the corresponding roughness height histograms of such areas (see Fig. 7) we conclude that the area of grain boundaries, whose histogram is centered at about 380 nm, is the main contributor to the increase in the roughness statis-

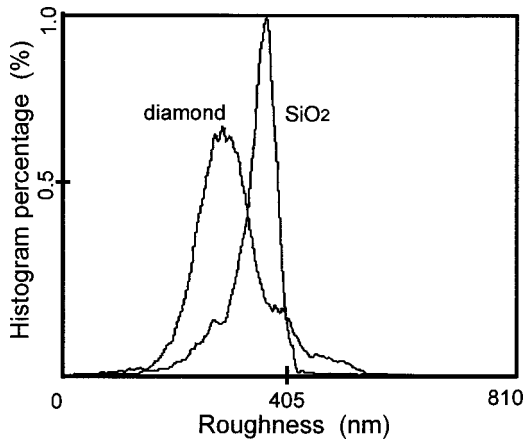


FIG. 5. Comparison of the roughness distribution histograms of the top surface of the SiO₂ layer and of the bottom surface of the diamond film.

tics when a larger area of the bottom of the diamond film is considered (see Fig. 5).

Typical Raman spectra of four samples are shown in Fig. 8. We verified that the peak at 1332 cm⁻¹, characteristic of the C-C *sp*³ bonds, is very prominent in the spectra of all the samples prepared with 15–20% vol. of nitrogen in the chamber feed. There are no large differences observed as the

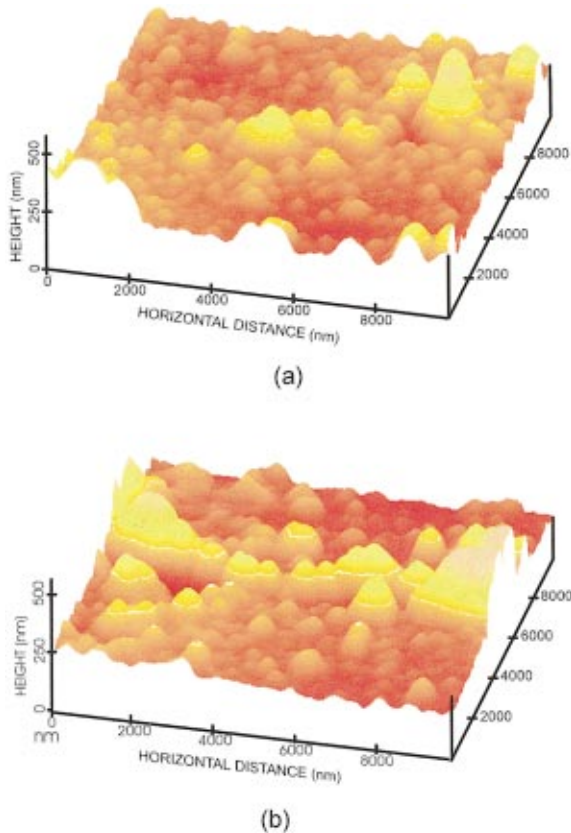


FIG. 6. AFM images of the bottom surface of the diamond film, made with higher magnification on the left-hand corners of the area shown in Fig. 4(b). Details of (a) an area of good nanometric nucleation (or the bottom of a diamond grain) and of (b) an area of poor nucleation (or grain boundaries), may be observed.

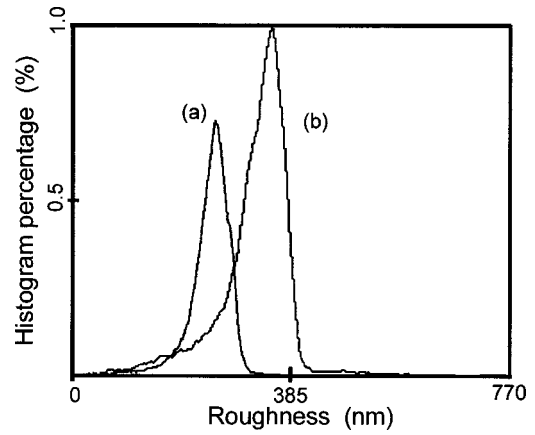


FIG. 7. Comparison of the roughness distribution histograms taken at different areas of the bottom surface of the diamond film. The histograms (a) and (b) correspond to height measurements made in the areas shown in Figs. 6(a) and 6(b), respectively.

nitrogen concentration is changed. The samples also present small broad peaks around 1450–1650 cm⁻¹, corresponding to graphite, amorphous carbon, or carbon nitrides.

We know that nitrogen atoms are directly related to the formation of several types of point defects and aggregates in diamond structures, including the formation of (100) planar defects, known as “platelets.”^{15–17} The “platelets” observed in natural crystals supposedly originate from the alignment of a very large number of type B defects, which are formed by aggregates of four to eight nitrogen atoms around a vacancy.⁹ The platelets can be observed by transmission electron microscopy, but little is known about their atomic structure. The existent models suppose that the plate-

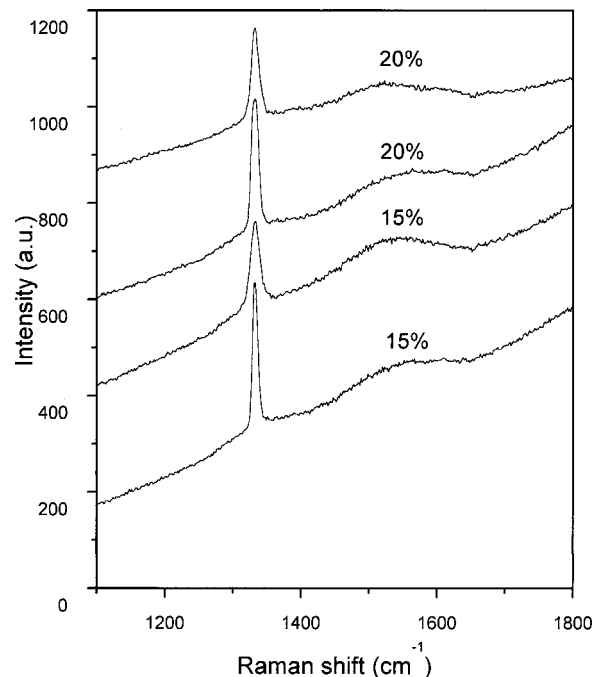


FIG. 8. Typical Raman spectra of four samples of as-deposited diamond films at nitrogen concentrations of 15 and 20% vol., as indicated.

let structure has one or two (100) planes inside the diamond crystal where the carbon atoms were replaced by nitrogen atoms.^{15–17}

This model of atomic structure has helped to explain the morphologies observed in this work. Hydrogen plays a fundamental role in diamond growth since it induces the carbon sp^3 hybridization in the growing film. The substitution of hydrogen by nitrogen in the covering of the surface of an already deposited carbon film may induce a passivating action on this surface since the C–N bonds are very strong and stable. Thus, the addition of nitrogen may inhibit diamond growth in the vertical direction, relative to an already-deposited surface. If this surface is a (100) plane the diamond growth may continue but with a lower rate, forming steps of ‘platelet-like’ structure. On the lateral surface of this structure the growth mechanisms may be different since there is probably an increase in the concentration of vacancies due to the distortions of the diamond structure provoked by the incorporation of substitutional nitrogen in the (100) surface. Since vacancies have a strong catalyzing action for the deposition of carbon in the diamond form, the lateral growth rate of the diamond should increase. Thus, the simultaneous inhibition of the vertical growth rate and stimulation of the horizontal growth rate may explain the interesting planar morphologies observed in these samples.

IV. CONCLUSIONS

We demonstrated that it is possible to deposit smooth diamonds films on SiO_2 -covered Si substrates using the hot-filament CVD process with the addition of nitrogen (15–20% vol.) to the gaseous mixture of $\text{C}_2\text{H}_5\text{OH} + \text{H}_2 + \text{N}_2$. Well-faceted structures of rectangular shape (lateral size $\sim 6 \mu\text{m}$) and low roughness ($\sim 11 \text{ nm}$) have been obtained on the top surface of the diamond films. Also, the diamond/ SiO_2 interface is relatively planar, showing roughness histograms with heights centered between 250 and 380 nm. Raman spectroscopy indicated that the films are of good quality diamond, but with a large number of defects, probably associated with distortions of the diamond structure provoked by

the substitutional nitrogen. The large amount of nitrogen introduced in the CVD process apparently caused changes in the diamond atomic structure, with the creation of planar defects similar to the platelets that occur in the natural diamonds rich in nitrogen. The nitrogen coverage of the diamond growth surface probably decreases the rate of vertical growth. In contrast, the presence of substitutional nitrogen in the diamond surface may provoke the appearance of lateral vacancies in the diamond structure which has the catalytic effect on the lateral rate of diamond growth. We conclude that the combination of these two different growth rates may explain the interesting morphology observed in these nitrogenated films.

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- ¹J. C. Angus and C. C. Hayman, *Science* **241**, 913 (1988).
- ²W. A. Yarborough and R. Messier, *Science* **241**, 688 (1990).
- ³B. V. Derjaguin and D. Fedoseev, *Izd. (Nauka, Moscow, 1977)*, Chap. 4.
- ⁴K. Tankala and T. DebRoy, *J. Appl. Phys.* **72**, 712 (1992).
- ⁵K. Okano, S. Koizumi, S. R. P. Silva, and G. A. J. Amaratunga, *Nature (London)* **381**, 140 (1996).
- ⁶X. Z. Liao, R. J. Zhang, C. S. Lee, S. Tong Lee, and Y. W. Lam, *Diamond Relat. Mater.* **6**, 521 (1997).
- ⁷S. G. dos Santos Filho, C. M. Hasenack, M. C. V. Lopes, and V. Baranauskas, *Semicond. Sci. Technol.* **10**, 990 (1995).
- ⁸S. Jin and T. D. Moustakas, *Appl. Phys. Lett.* **65**, 403 (1994).
- ⁹R. Locher, C. Wild, N. Herres, D. Behr, and P. Koidl, *Appl. Phys. Lett.* **65**, 759 (1996).
- ¹⁰J. E. Walker, *Rep. Prog. Phys.* **42**, 42 (1979).
- ¹¹T. Evans and P. Rainey, *Proc. R. Soc. London, Ser. A* **344**, 111 (1975).
- ¹²V. Baranauskas, B. B. Li, A. Peterlevitz, M. C. Tosin, and S. F. Durrant, *J. Appl. Phys.* **85**, 7455 (1999).
- ¹³V. Baranauskas, A. Peled, V. J. Trava-Airoldi, C. A. S. Lima, I. Doi, and E. J. Corat, *Appl. Surf. Sci.* **79/80**, 129 (1994).
- ¹⁴R. C. M. Barros, E. J. Corat, N. G. Ferreira, T. M. Souza, V. J. Trava-Airoldi, N. F. Leite, and K. Iha, *Diamond Relat. Mater.* **5**, 1323 (1996).
- ¹⁵A. R. Lang, *Proc. Phys. Soc.* **84**, 871 (1964).
- ¹⁶N. Sumida and A. R. Lang, *Proc. R. Soc. London, Ser. A* **419**, 235 (1988).
- ¹⁷P. R. Bridon and R. Jones, *Physica B* **185**, 179 (1993).