Direct observation of chemical vapor deposited diamond films by atomic force microscopy

V. Baranauskas, M. Fukui, C. R. Rodrigues, N. Parizotto, and V. J. TravaAiroldi

Citation: [Appl. Phys. Lett.](#) **60**, 1567 (1992); doi: 10.1063/1.107253

View online: <http://dx.doi.org/10.1063/1.107253>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v60/i13>

Published by the [American Institute of Physics](#).

Additional information on Appl. Phys. Lett.

Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT

The advertisement banner features a background of orange and yellow diagonal stripes. At the top, the "AIP Applied Physics Letters" logo is displayed in white. Below the logo, on the left, is a white envelope icon. To its right, the text "Accepting Submissions in Biophysics and Bio-Inspired Systems" is written in black. Further right, a white button with the text "Submit Today" in orange is shown. On the far right, the "AIP Publishing" logo is displayed in blue and yellow.

Direct observation of chemical vapor deposited diamond films by atomic force microscopy

V. Baranauskas, M. Fukui, C. R. Rodrigues, and N. Parizotto

Department of Semiconductors and Photonics, State University of Campinas, 13083 Campinas SP, Brazil

V. J. Trava-Airoldi

Institute for Space Research, Department of Mechanics, São José dos Campos SP, Brazil

(Received 4 November 1991; accepted for publication 23 January 1992)

Diamond polycrystals deposited by the hot-filament chemical vapor deposition method on silicon (100) substrates have been examined by atomic force microscopy (AFM) in air. Measurements of the diamond unit cell show periodic spacings between 0.34 to 0.37 nm in a very good agreement with the theoretical value of the bulk constant of natural diamond (0.356 nm). Hybridized sp^3 bonds can also be observed at the (111) surface.

Diamond thin films have been grown by different methods of low-pressure and low-temperature chemical vapor deposition (CVD) such as hot-filament assisted CVD,¹⁻³ plasma-assisted CVD,⁴⁻⁶ and combustion flames.⁷ The source gas is typically a mixture of hydrocarbons, such as methane, ethane, ethylene, and acetylene diluted in hydrogen.⁸ As the formation of diamond kinetically competes with the graphite phase, the understanding of the growth mechanism is of utmost importance for the synthesis of large crystalline grains or even single crystals. In this direction, the characterization of the surface of the CVD films has become a subject of intensive research. Raman spectroscopy,⁹ x-ray absorption fine structure and diffraction,¹⁰ scanning electron microscopy (SEM)¹¹ have been used. Recently, work by Busman *et al.*¹² has shown that the scanning tunneling microscopy (STM) could be used to present micrographs with better lateral and vertical resolution than those normally obtained by SEMs. In this letter, we present results demonstrating that by using the atomic force microscopy (AFM) we can achieve "atomic resolution" images of the diamond. To our best knowledge,¹³ these are the first atomic images of the as-grown diamond polycrystals.

All the samples for our AFM investigation were prepared by the hot-filament method using silicon (100) substrates of square geometry (1.0 cm × 1.0 cm) scratched with alumina powder (1 μ m grain size). The reaction gas was a mixture of pure CH_4 (0.7 vol %) and H_2 (99.0

vol %) doped with CF_4 (0.3% vol %) flowing at a rate of 75 sccm (total pressure 40 Torr) over the substrate kept at a temperature of 1093 K by the heating filament at 2473 K. The reaction time was 7 h. The as-grown samples were transferred to the AFM in the ambient atmosphere without any treatment of the surfaces to remove graphitic or other adsorbate films.

The AFM has a tip sensor mounted in a cantilever with an effective spring constant that moves accordingly to the forces acting on the tip. The information to produce the image is obtained from the measurement of the cantilever displacement by laser interferometry, during the scanning of the surface area by the tip. Figure 1 shows a typical AFM image of the CVD diamond taken in the central area of the substrate at micron level of amplification. We can clearly see features with an equilateral triangle shape with a size between 4 and 5 μ m, indicating a possible predominance of the (111) orientation in the structure. Some cubic features are also present in other images. As the AFM surface forces are active, the images in the edges and apex of the crystals appear more rounded than those observed by the SEM. The surface of the grains is not very flat but

FIG. 1. Atomic force micrographs of diamond CVD films on silicon taken at scan rate of 1 Hz.

FIG. 2. Grain details showing steps of arrow shape.

FIG. 3. (a) "Atomic resolution" AFM image of the (100) surface with radicals on the left and right regions. (b) Height measurement showing a periodic atomic structure of 0.35 nm period in excellent agreement with the bulk constant of natural diamond. (c) Height measurement at orthogonal direction relative to (b) showing carbon atoms at the bottom and atoms above them on the left and right regions.

exhibits some corrugations. The upper surface of the triangles is either slightly convex or concave. Figure 2 is an enlarged image centered on a typical triangle surface. Some surface steps of lamellar planes with arrow features are presented in this surface, which suggests a competitive mechanism of epitaxial growth in the $\langle 112 \rangle$ direction. The morphology of the film deposited along the direction of the filament shows similar characteristics of the previous figures, forming a continuous stripe about 8 mm wide. In the transversal direction, outside of the stripe, nucleation sites and diamondlike balls can be easily identified. In this region, it is clear that the surface growth of the balls predominates over the creation of new seed sites. Moreover, the formation of rings like a well-distorted honeycomb can be easily seen in low magnified images.

Several existing theoretical models for the details of the

FIG. 4. (a) Atomic resolution AFM image showing sp^3 bonds between carbon atoms. (b) Interatomic distance between postulated $[1/2,0,1/2]$, $[0,1/2,1/2]$ atoms showing a spacing of 0.25 nm in good agreement with the bulk diamond spacing.

surface and gas-phase chemical kinetics of diamond deposition predicts the presence of hydrogen, hybridized surface radicals, and acetylenic or ethylenic intermediate complexes on the growing surface,¹⁴ or the formation of a graphitic phase on the surface after growth. These surface chemical species or the atmospheric pollution do not allow, at first glance, the clear observation in air of the structure of diamond surface at the atomic level of amplification. In our experiment, we used the attractive force between the tip and the surface atoms to remove two or more atomic layers from the area of interest. Figure 3(a) shows a typical "window" opened on the (100) surface. The contrast of this image was enhanced by a two-dimensional Fourier transform to cut high spatial frequencies above 12.5 nm^{-1} . The atomic spacing in the $\langle 100 \rangle$ direction shows a periodic spacing of 0.35 nm^{-1} [see Fig. 3(b)], in a very good agreement with the theoretical value of the bulk constant of natural diamond (0.356 nm). Figure 3(c) shows the atomic profile in the $\langle 110 \rangle$ direction of the same image. We can see the carbon atoms at the bottom and one or two monolayers of atoms above them in the left and right regions. In all the samples, the Fourier transform in the cubic cell directions show frequency values between $1/0.34$ and $1/0.37 \text{ nm}^{-1}$. Figure 4(a) shows a beautiful image at the atomic level of amplification, corresponding to the (111) plane. The sp^3 -hybridized bonds appear very clearly, and by distance measurement we can easily identify the

postulated $[1/2,0,1/2]$ and $[0,1/2,1/2]$ atoms of the diamond cell. The interatomic distance between them of 0.25 nm [see Fig. 4(b)] is in excellent agreement with the theoretical value (0.252 nm). Typical scan parameters used in the AFM “atomic images” are: scan rate 14.20 Hz, force 0.019 nN, and scan size up to 3.0 nm.

In summary, we demonstrated the possibility of AFM investigation of poly-CVD diamond films with atomic resolution in air, without any prior surface cleaning. This tool for probing the surface structures will certainly help to clarify the influence of the vacancies and surface reconstruction in the growth processes.

The measurements were performed using the facilities (nanoscope II) of the Laboratório do Departamento de Semicondutores, Instrumentos Fotônica (DSIF) of the State University of Campinas. The work was supported in part by the Fundo de Apoio a Pesquisa e Ensino (FAEP), Instituto Nacional de Atividades Espaciais and Ministério da Marinha.

- ¹S. Matsumoto and V. Matsui, *J. Mater. Sci.* **18**, 1785 (1983).
- ²B. V. Deryagin, D. V. Fedoseev, N. D. Polyanskaya, and E. V. Statenkova, *Krystallografiya* **21**, 433 (1976).
- ³A. Sawabe and T. Inuzulev, *Thin Solid Films* **137**, 89 (1986).
- ⁴D. E. Mayer, R. O. Dillon, and J. A. Woollan, *J. Vac. Sci. Technol. A* **7**, 2325 (1989).
- ⁵M. Kamo, Y. Sato, S. Matsumoto, and N. Setaka, *J. Cryst. Growth* **62**, 642 (1983).
- ⁶S. Matsumoto, *J. Mater. Sci. Lett.* **4**, 600 (1985).
- ⁷M. A. Cappeli and P. H. Paul, *J. Appl. Phys.* **67**, 2596 (1990).
- ⁸K. Kobashi, K. Nishimura, Y. Kawate, and T. Horiuchi, *Phys. Rev. B* **38**, 3815 (1988).
- ⁹N. Wada and S. A. Solin, *Physica B and C* **105B**, 353 (1981).
- ¹⁰T. W. Capehart, T. A. Perry, C. B. Beetz, D. N. Belton, G. B. Fisher, C. E. Beall, B. N. Yates, and J. W. Taylor, *Appl. Phys. Lett.* **55**, 957 (1989).
- ¹¹S. Iijima, Y. Aikawa, and K. Baba, *J. Mater. Res.* **6**, 1441 (1991).
- ¹²H. G. Busmann, H. Sprang, J. V. Hertel, W. Zimmermann-Edling, and H. J. Güntherodt, *Appl. Phys. Lett.* **59**, 295 (1991).
- ¹³N. A. Burnham, R. J. Cotton, and H. M. Pollock, *J. Vac. Sci. Technol. A* **9**, 2548 (1991).
- ¹⁴M. Frenklach and H. Wang, *Phys. Rev. B* **43**, 1520 (1991).

Published without author corrections