2001

Boron-Doped Homoepitaxial Diamond (100) Film Investigated by Scanning Tunneling Microscopy

Bing Xiao
Old Dominion University, bxiao001@gsa.odu.edu

Weihai Fu
Old Dominion University

Sacharia Albin
Old Dominion University, salbin@odu.edu

Jason Moulton
Old Dominion University

John Cooper
Old Dominion University, jcooper@odu.edu

Original Publication Citation

Xiao, B., Fu, W., Albin, S., Moulton, J., & Cooper, J. (2001). *Boron-doped homoepitaxial (100) diamond film investigated by scanning tunneling microscopy.* Paper presented at the Sixth Applied Diamond Conference/Second Frontier Carbon Technology Joint Conference (ADC/FCT 2001), Auburn, AL, August 6-10, 2001.

Proceedings of the Sixth Applied Diamond Conference/Second
Frontier Carbon Technology Joint Conference (ADC/FCT 2001)
Y. Tzeng, K. Miyoshi, M. Yoshikawa, M. Murakawa, Y. Koga,
K. Kobashi, G.A.J. Amaratunga (Editors)

BORON-DOPED HOMOEPITAXIAL DIAMOND (100) FILM INVESTIGATED BY SCANNING TUNNELING MICROSCOPY

Bing Xiao, Weihai Fu, and Sacharia Albin*
Microelectronics Laboratory
Department of Electrical and Computer Engineering
Old Dominion University, Norfolk, VA 23529, USA

Jason Moulton, and John Cooper
Department of Chemistry and Biochemistry
Old Dominion University, Norfolk, VA 23529, USA

ABSTRACT

Conducting epitaxial diamond films of high quality are essential for many diamond studies and diamond electronic device fabrication. We have grown boron-doped epitaxial diamond films on type IIa natural diamond (100) substrates by microwave plasma chemical vapor deposition. A gas mixture of H_2/CH_4 was used. Boron doping was done by placing solid sources of pure boron in the microwave plasma. Homoepitaxial films with atomic smoothness were achieved under the following growth conditions: substrate temperature 900 °C, gas pressure 40 Torr, and gas flow rates of H_2/CH_4 = 900/7.2 sccm. The growth rate was 0.87 µm/hr. Surfaces of the homoepitaxial films were studied by scanning tunneling microscopy (STM). STM images show smooth and continuous surface with ripple-like features on micrometer scale. On nanometer scale, alternating terraces of 2×1 and 1×2 dimerization were clearly observed.

Keywords: diamond thin film, homoepitaxy, scanning tunneling microscopy (STM).

INTRODUCTION

Boron-doped homoepitaxial films are commonly used for the study of various properties of diamond thin films, such as surface structures (refs. 1 to 3), electrical or electronic characteristics (refs. 4 to 6), and electrochemical behavior (refs. 7 and 8). In addition, such films are used in many diamond electronic devices (refs. 9 and 10). For epitaxial growth of diamond, microwave plasma chemical vapor deposition (MPCVD) has been widely used and studied (refs. 1 to 6, 9). A lot of work has been done on surface morphology and structures of polycrystalline (refs. 11 and 12) or single-crystalline (refs. 1 to 3, 13) CVD diamond thin films, which show strong dependence on growth conditions. In these studies, images from optical microscopy and scanning electron microscopy (SEM) are usually used to show surface morphology on micron or sub-micron scale, while scanning tunneling microscope (STM) and atomic force microscope (AFM) are used to observe the surface from micron level to atomic level.

In this study, STM was utilized to investigate the surface morphology of boron-doped homoepitaxial diamond (100) films on both micron and nanometer scale.

EXPERIMENTS

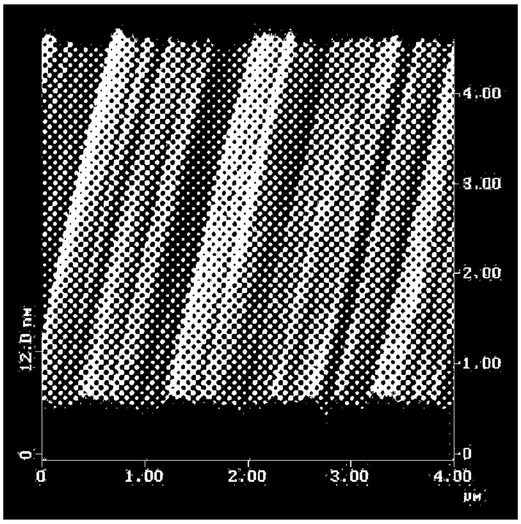
Type IIa (100)-oriented natural diamond substrates (3×3×0.25 mm^3) were used in this study. Diamond substrates were degreased in acetone and ethanol, then cleaned in a 1:1 solution of HNO_3 and HF, and in a 1:3 solution of HNO_3 and HCl. They were finally rinsed with deionized water and mounted in a shallow dip on a Si wafer which was used as the sample holder.

Diamond epitaxial growth was carried out in the 6-inch cylindrical chamber of a MPCVD system (ASTeX). Hydrogen and methane were used as reactant gases. The gas flow rates of H_2 and CH_4 were 900 and 7.2 sccm,

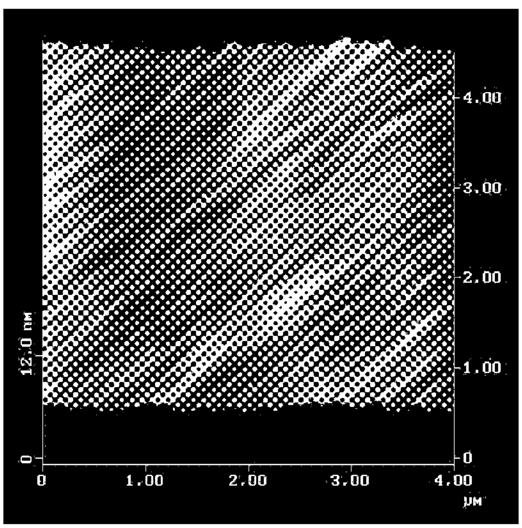
*Author to whom all correspondence should be addressed; email: salbin@odu.edu, fax: (757)683-3220, phone: (757)683-4967.

respectively. The diamond substrate mounted on the Si sample holder was placed on a graphite heater in the CVD chamber. The heater temperature was controllable during the whole CVD process. The gas pressure was maintained at 40 Torr during the diamond growth.

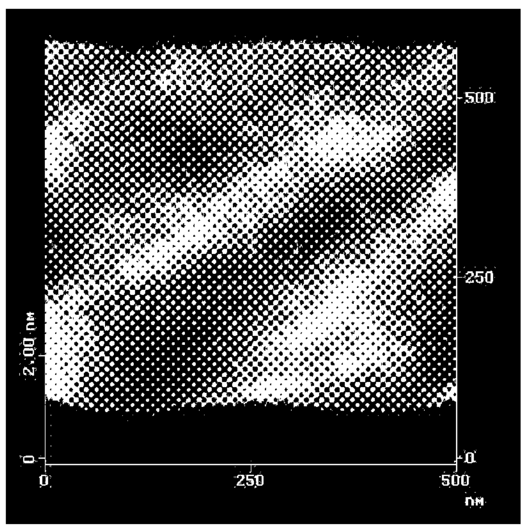
The CVD chamber was first pumped down to a base pressure below 10^{-4} Torr. Then diamond substrate was heated up in vacuum. When graphite heater reached 900 °C, hydrogen was introduced into the chamber and hydrogen plasma was ignited by a 2.45 GHz microwave input with a power of 1000 W. After the sample was treated in the hydrogen plasma for 5 min, CH_4 was introduced into the chamber to begin diamond growth. The growth time was 1 hr. Boron doping was done by placing four small pure boron pieces around the diamond substrate. Microwave power and CH_4 flow were turned off to stop diamond growth, and the sample was cooled down to 600 °C in H_2. At 600 °C, hydrogen plasma was started again to treat the diamond surface for another 5 min. Finally, the diamond sample was cooled down to room temperature in H_2 gas ambient.



(a)

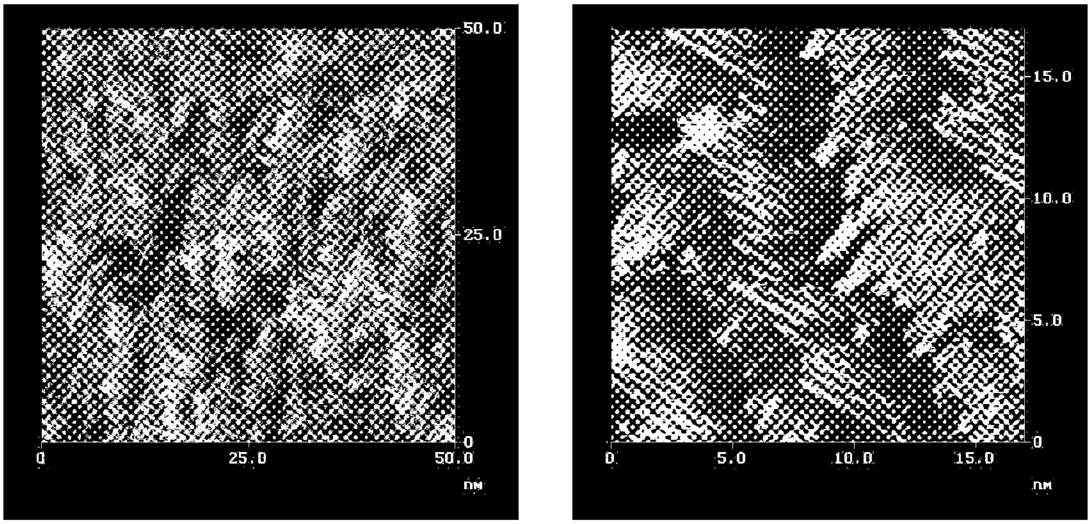


(b)



(c)

Figure 1. Height mode STM images of diamond (100) surfaces: (a) surface before CVD growth; (b) and (c) surface of the boron-doped homoepitaxial film.



(a) **(b)**

Figure 2. STM images of the homoepitaxial diamond (100) film showing 2×1 surface reconstruction. (a) A large-area height mode image shows alternating terraces of 2×1 and 1×2 dimerization. (b) Current mode image shows that individual dimers are resolved.

Diamond samples were investigated in air by a commercial STM system (NanoScope III). Mechanically cut Pt-Ir or ac-etched tungsten tips were used to probe the diamond surface. For scanning range on micrometer scale, height mode operation was applied while images with atomic resolution were obtained in both height mode and current mode.

RESULTS AND DISCUSSIONS

The homoepitaxial growth rate of 0.87 μm/hr was calculated from the sample weight increase after CVD deposition. After the sample was boiled in H_2SO_4 or HNO_3, the surface of the epitaxial film still had a relatively high conductivity of approximately ~10^{-1} Ω·cm. This result demonstrate that the electrical conduction was created by boron doping, not by the surface hydrogenation since the high-conductivity layer near the surface, induced by hydrogen incorporated in the surface region, can be removed by oxidation of the surface using strong acid solutions such as H_2SO_4 and HNO_3 (ref. 6).

Figure 1(b) and 1(c) are STM images showing the surface of the deposited diamond (100) film on micron and sub-micron scale. For comparison, Figure 1(a) shows the STM image of the polished diamond surface prior to epitaxial growth. The diamond substrate was treated in hydrogen plasma for 5 min to obtain surface conduction needed for STM imaging. As shown in Figure 1(a), the parallel-groove pattern is considered to be formed during the surface polish process (ref. 14), and the surface roughness is 0.583 nm_{rms} and 4.509 nm_{pp}. After homoepitaxial growth, the parallel-groove pattern is still visible but smaller groove depths make a smoother surface with a roughness of 0.384 nm_{rms} and 2.781 nm_{pp} (Figure 1(b)). In Figure 1(c), the long-range height variation is also due to the parallel-groove pattern and the surface appears consisting of nano-scale features which are believed to be the terraces formed during the diamond deposition (ref. 15). The surface roughness in this 500×500 nm^2 area is 0.096 nm_{rms} and 0.893 nm_{pp}. It is expected that the surface height variation could be further reduced with a longer annealing time in hydrogen plasma and a thicker film grown for longer time.

The atomic-resolution STM pictures are shown in Figure 2. Terraces with alternating 2×1 and 1×2 dimerization are clearly displayed and individual dimers are also resolved. This kind of surface structure, i.e. double-domain surface, is considered to be created by two-dimensional nucleation (ref. 15). The average terrace width is ~4 nm while adjacent terraces are separated by a single-layer step.

SUMMARY

Boron-doped homoepitaxial diamond (100) films have been grown on type IIa natural diamond substrates. The surface morphology was observed using STM. Compared with the diamond surface before CVD growth, the deposited surface is smoother with less surface height variation. Atomic-resolution STM images were obtained revealing the surface reconstruction of 2×1 dimerization.

ACKNOWLEDGMENT

This work is supported by a grant from National Science Foundation.

REFERENCES

1. Kuang, Y., Wang, Y., and Lee, N., et al.: Surface Structure of Homoepitaxial Diamond (001) Films, A Scanning Tunneling Microscopy Study. Appl. Phys. Lett., vol. 67, no. 25, Dec 1995, 3721.
2. Kawarada, H., Sasaki, H., and Sato, A.: Scanning-Tunneling-Microscope Observation of The Homo epitaxial Diamond (001) 2×1 Reconstruction Observed Under Atmospheric Pressure. Phys. Rev. B, vol. 52, no. 15, Oct 1995, 11351.
3. Takami, T., Kusunoki, I., and Nishitani-Gamo, M., et al.: Homoepitaxial Diamond (001) Thin Film Studied by Reflection High-Energy Electron Diffraction, Contact Atomic Force Microscopy, and Scanning Tunneling Microscopy. J. Vac. Sci. Technol. B, vol. 18, no. 3, May/Jun 2000, 1198.
4. Shiomi, H., Nakahata, H., and Imai, T., et al.: Electrical Characteristics of Metal Contacts to Boron-Doped Diamond Epitaxial Film. Jpn. J. Appl. Phys., vol. 28, no. 5, May 1989, 758.
5. Shiomi, H., Nishibayashi, Y., and Fujimori, N.: Characterization of Boron-Doped Diamond Epitaxial Films. Jpn. J. Appl. Phys., vol. 30, no. 7, Jul 1991, 1363.
6. Hayashi, K., Yamanaka, S., and Okushi, H., et al.: Study of The Effect of Hydrogen on Transport Properties in Chemical Vapor Deposited Diamond Films by Hall Measurements. Appl. Phys. Lett., vol. 68, no. 3, Jan 1996, 376.
7. Yanagisawa, M., Jiang, L., and Tryk, D.A., et al.: Surface Morphology and Electrochemical Properties of Highly Boron-Doped Homoepitaxial Diamond Films. Diamond Relat. Mater., vol. 8, no. 11, Nov 1999, 2059.
8. Swain, G.M., Anderson, A.B., and Angus, J.C.: Applications of Diamond Thin Films in Electrochemistry. MRS Bulletin, vol. 23, no. 9, Sept 1998, 56.
9. Shiomi, H., Nishibayashi, Y., and Fujimori, N.: High-Voltage Schottky Diodes on Boron-Doped Diamond Epitaxial Films. Jpn. J. Appl. Phys. Part 2, vol. 29, no. 12, Dec 1990, L 2163.
10. Ariki, T., Shikama, S., and Suzuki, S., et al.: Efficient Field Effect in Heavily Doped Thin-Film Diamond Metal-Insulator-Semiconductor Diode Employing $BaTiO_3$ Insulator Film. Jpn. J. Appl. Phys. Part 2, vol. 33, no. 6B, Jun 1994, L 888.
11. Zhou, D., Gruen, D.M., and Qin, L.C., et al.: Control of Diamond Film Microstructure by Ar Additions to CH_4/H_2 Microwave Plasmas. J. Appl. Phys., vol. 84, no. 4, Aug 1998, 1981.
12. Fitzgerald, A.G., Fan, Y., and John, P., et al.: Characterization of the Surface Morphology and Electronic Properties of Microwave Enhanced Chemical Vapor Deposited Diamond Films. J. Vac. Sci. Technol. B, vol. 18, no. 6, Nov/Dec 2000, 2714.
13. Shiomi, H., Tanabe, K., and Nishibayashi, Y., et al.: Epitaxial Growth of High Quality Diamond Film by The Microwave Plasma-Assisted Chemical-Vapor-Deposition Method. Jpn. J. Appl. Phys., vol. 29, no.1, Jan 1990, 34.
14. Spear, K.E., and Dismukes, J.: Synthetic Diamond: Emerging CVD Science and Technology. John Wiley & Sons, New York, NY, USA, 1994, 322.
15. Tsuno, T., Tomikawa, T., and Shikata, S.: Diamond (001) Single-Domain 2×1 Surface Grown by Chemical Vapor Deposition. Appl. Phys. Lett., vol. 64, no. 5, Jan 1994, 572.