University of Pennsylvania
ScholarlyCommons

Departmental Papers (MEAM)

Department of Mechanical Engineering & Applied Mechanics

4-2-2008

Synthesis and characterization of smooth ultrananocrystalline diamond films via low pressure bias-enhanced nucleation and growth

Y. C. Chen
National Tsing-Hua University

X. Y. Zhong
Argonne National Laboratory

A. R. Konicek
University of Wisconsin

D. S. Grierson
University of Wisconsin

N. H. Tai
National Tsing-Hua University

See next page for additional authors

Reprinted from *Applied Physics Letters*, Volume 92, Article 133113, March 2008, 3 pages.
Publisher URL: http://dx.doi.org/10.1063/1.2838303

This paper is posted at ScholarlyCommons. http://repository.upenn.edu/meam_papers/146
For more information, please contact repository@pobox.upenn.edu.

Synthesis and characterization of smooth ultrananocrystalline diamond films via low pressure bias-enhanced nucleation and growth

Abstract
This letter describes the fundamental process underlying the synthesis of ultrananocrystalline diamond (UNCD) films, using a new low-pressure, heat-assisted bias-enhanced nucleation (BEN)/bias enhanced growth (BEG) technique, involving H2/CH4 gas chemistry. This growth process yields UNCD films similar to those produced by the Ar-rich/CH4 chemistries, with pure diamond nanograins (3–5 nm), but smoother surfaces (~6 nm rms) and higher growth rate (~1 μm/h). Synchrotron-based x-Ray absorption spectroscopy, atomic force microscopy, and transmission electron microscopy studies on the BEN-BEG UNCD films provided information critical to understanding the nucleation and growth mechanisms, and growth condition-nanostructure-property relationships.

Keywords
atomic force microscopy, diamond, heat treatment, nanostructured materials, nanotechnology, nucleation, transition electron microscopy, XANES

Comments
Reprinted from *Applied Physics Letters*, Volume 92, Article 133113, March 2008, 3 pages.
Publisher URL: http://dx.doi.org/10.1063/1.2838303

Author(s)
Y. C. Chen, X. Y. Zhong, A. R. Konicek, D. S. Grierson, N. H. Tai, I. N. Lin, Bernd Kabius, Jon M. Hiller, A. V. Sumant, Robert W. Carpick, and Orlando Auciello

This journal article is available at ScholarlyCommons: http://repository.upenn.edu/meam_papers/146

Synthesis and characterization of smooth ultrananocrystalline diamond films via low pressure bias-enhanced nucleation and growth

Y. C. Chen,[1,2] X. Y. Zhong,[6] A. R. Konicek,[3] D. S. Grierson,[4] N. H. Tai,[1] I. N. Lin,[5] B. Kabius,[6] J. M. Hiller,[6] A. V. Sumant,[7] R. W. Carpick,[8] and O. Auciello[2,7,a)]
[1]*Department of Materials Science and Engineering, National Tsing-Hua University, Hsin-Chu 300, Taiwan*
[2]*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[3]*Department of Physics, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA*
[4]*Department of Engineering Physics, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA*
[5]*Department of Physics, Tamkang University, Tamsui 251, Taiwan*
[6]*Center for Electron Microscopy, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[7]*Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[8]*Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA*

(Received 26 November 2007; accepted 4 January 2008; published online 2 April 2008)

This letter describes the fundamental process underlying the synthesis of ultrananocrystalline diamond (UNCD) films, using a new low-pressure, heat-assisted bias-enhanced nucleation (BEN)/bias enhanced growth (BEG) technique, involving H_2/CH_4 gas chemistry. This growth process yields UNCD films similar to those produced by the Ar-rich/CH_4 chemistries, with pure diamond nanograins (3–5 nm), but smoother surfaces (~6 nm rms) and higher growth rate (~1 μm/h). Synchrotron-based x-Ray absorption spectroscopy, atomic force microscopy, and transmission electron microscopy studies on the BEN-BEG UNCD films provided information critical to understanding the nucleation and growth mechanisms, and growth condition-nanostructure-property relationships. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2838303]

Ultrananocrystalline diamond (UNCD) films developed at Argonne National Laboratory[1] are outstanding material candidates for the fabrication of multifunctional devices, such as for microelectromechanical/nanoelectromechanical systems (MEMS/NEMS),[2,3] requiring high Young's modulus, low friction coefficient, and high resistance to wear, requiring low threshold voltage for electron emission,[4] and biomedical devices,[5] requiring bioinertness and/or biocompatibility. Improving the performance of UNCD films for MEMS/NEMS devices requires either the optimization of the synthesis process using the original Ar-rich growth chemistry developed to synthesize UNCD films, or developing new processes that yield stress-free UNCD films with stronger adhesion to the substrate, higher growth rate, and smoother surfaces. The surface roughness and growth rate of UNCD films grown using Ar-rich (99%)/CH_4 (1%) chemistries are typically 7–15 nm root-mean-square (rms) and ~0.3–0.4 μm/h, respectively, depending on the pregrowth diamond seeding and growth parameters.[2,6] The film adhesion, surface roughness, and growth rate of UNCD films are controlled by nucleation and growth processes.[6–8] The bias-enhanced nucleation (BEN) process investigated by several groups has several advantages over mechanical polishing or ultrasonic seeding processes, namely, (a) better efficiency,[9] (b) stronger adhesion to substrates,[8–11] and (c) an integrated fully dry nucleation/growth process using plasma processing only. Prior work[8] demonstrated that the BEN process enhances UNCD film adhesion to substrates, although UNCD films were grown using an Ar/CH_4 chemistry without bias, on BEN layers produced by 70 mbar H_2/CH_4 plasma chemistry. Other prior work involved BEN plus bias enhanced growth (BEG) processes, using H_2/CH_4 chemistries for growing nanocrystalline diamond (NCD) (30–100 nm grains) films, resulted in formation of diamond clusters, relatively high surface roughness, high compressive stress, delamination of the film, and high content of nondiamond phase.[11,12] By contrast, we describe here a process to grow UNCD films identical to those produced by the Ar/CH_4 chemistry, but using relatively low pressure (25 mbar) H_2/CH_4 gas chemistry and an integrated BEN-BEG process that yields films with low stress, ultrasmooth surfaces, high growth rates, and uniform grain size (3–5 nm) throughout the whole film area, making them potential candidate materials for the fabrication of UNCD-based MEMS/NEMS devices.

The low pressure BEN-BEG process described here involves the following steps: (1) etching of the Si (100) substrate for 10 min in a pure hydrogen plasma under bias to remove the native SiO_2 layer from the surface; (2) *in situ* BEN-BEG, using a H_2 (93%)/CH_4 (7%) plasma produced by 2.2 kW microwave power at 25 mbar pressure and applying −350 V bias on a substrate heated to 850 °C in a 2.45 GHz 6 in. IPLAS CYRANNUS microwave plasma chemical vapor deposition system. The UNCD thin films were characterized by several complementary techniques, as discussed below.

X-ray absorption near edge structure (XANES) spectroscopy analysis revealed the atomic bonding characteristics of the UNCD films. Compared with visible Raman, XANES unambiguously distinguishes between the sp^2 and sp^3-hybridized bonds in carbon-based materials. Figure 1 shows the C (1*s*) XANES spectra for the top surface of the BEN-BEG UNCD films grown at 850 °C for 10–45 min. The XANES spectra show characteristic diamond features, namely, a peak at 289.3 eV (diamond C 1*s* electron core

[a)]Author to whom correspondence should be addressed. Electronic mail: auciello.@anl.gov

 © 2008 American Institute of Physics
Downloaded 29 Apr 2008 to 130.91.116.168. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

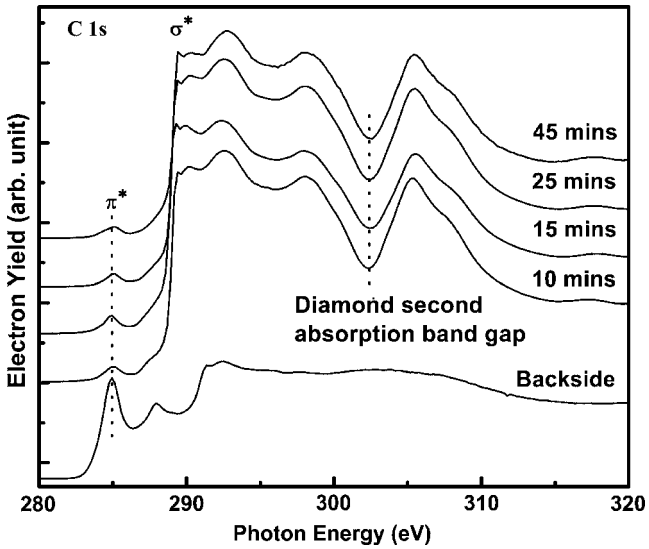

FIG. 1. XANES spectra on the top surface of UNCD films with different growth times and the back side surface of the UNCD film at the UNCD/Si interface.

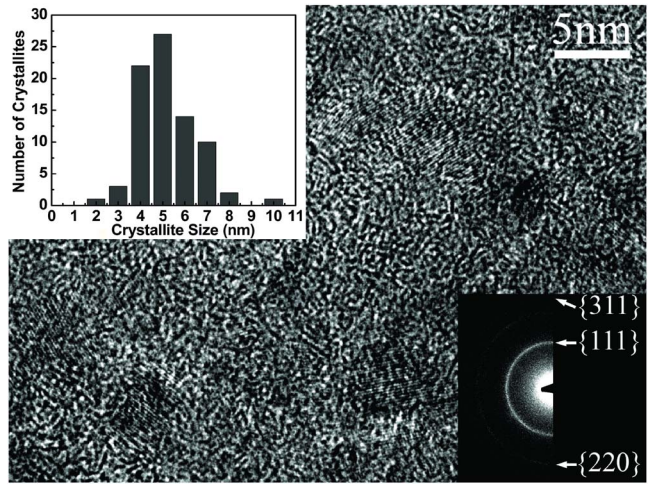

FIG. 2. (Color online) The HRTEM image of BEN-BEG UNCD film. The bottom right inset shows SAED pattern that can be indexed as polycrystalline diamond. The top left inset shows the corresponding size distributions of UNCD grains.

excitation), a dip around 302 eV (second absorption band gap of diamond),[13] and a small peak at 285 eV corresponding to the C═C ($1s \rightarrow \pi^*$) transition for sp^2-bonded carbon, which is substantially located along grain boundaries of UNCD films as revealed in prior experiments,[14] and in agreement with computer simulations.[15] The nature of the "back side" surface of the BEN-BEG UNCD films at the UNCD/Si interface was investigated by etching away the Si substrate, using a mixture of nitric and hydrofluoric acid, as described previously.[6] The XANES spectrum of the UNCD back side shows peaks at ~285 eV [C═C ($1s \rightarrow \pi^*$)] and ~287.5 eV, [C—H ($1s \rightarrow \sigma^*$)] transition caused by C—H bonding produced during Si etching with a mixture of nitric and hydrofluoric acids to lift-off the UNCD film. The larger C═C ($1s \rightarrow \pi^*$) peak for the back side of UNCD films, compared to the top surface, indicates a higher sp^2-bonded carbon content at the UNCD/Si interface, suggesting that the nucleation process, for the growth conditions used here, results in the formation of a nondiamond carbon layer with possible nanodiamond inclusions (cross-sectional TEM studies below), as shown also by prior work.[9]

Figure 2 shows a high-resolution transmission electron microscopy (HRTEM) image of a BEN-BEG UNCD film. The corresponding selected area electron diffraction (SAED) pattern shows diffraction rings corresponding to the {111}, {220}, and {311} planes of diamond (bottom right inset of Fig. 2). The histogram from the HRTEM images (80 grains) shows an average grain size of 5.6 nm with standard deviation around 1.3 nm (top left inset of Fig. 2). The XANES and TEM analyses show that BEN-BEG UNCD films exhibit identical carbon bonding characteristics and grain size distribution (3–5 nm) as for UNCD films grown with the Ar-rich/CH_4 chemistries without bias.

Bias current density (J_e) versus time curves acquired under constant bias, during UNCD film nucleation and growth, provided information to understand nucleation and growth kinetics. One such curve, shown in Fig. 3(a), shows an abrupt increase of J_e after an incubation period of about 5 min and saturation at ~4.5 mA/cm^2 at 15 min after the onset of the BEN process. Prior literature[4] suggests that electron emission arises mainly from the grain boundaries of the film, due to carriers originating from the formation of the sp^2-bonded carbon. Therefore, the abrupt increase and subsequent saturation of J_e can be attributed to the rapid growth of diamond nuclei and subsequent full coverage of the substrate surface by the diamond grains, respectively. The correlation between bias current evolution and film surface roughness may help to identify the BEN-BEG conditions that produce the smoothest surface, to minimize friction and wear in devices involving moving parts with contacting surfaces.[16] The surface roughness of a 1 μm thick BEN-BEG UNCD film was ~10 nm rms over a ~10 μm^2 area after J_e reached steady state [Fig. 3(a)], then reduced to ~6 nm rms after 60 min, as revealed by atomic force microscopy (AFM) [inset of Fig. 3(d)]. The corresponding scanning electron microscopy (SEM) images of UNCD surfaces at different growth times are shown in Figs. 3(b)–3(d).

Further investigation of the UNCD/Si interface was performed using cross-sectional HRTEM. The formation of zigzag regions on the Si surface with peak-to-valley roughness (R_{pv}) ~ 15 nm can be attributed to ion bombardment during the 10 min of hydrogen plasma etching [Figs. 4(a) and 4(b)]. The same zigzag morphology was observed previously on a silicon surface[17] during a diamond BEN process. However,

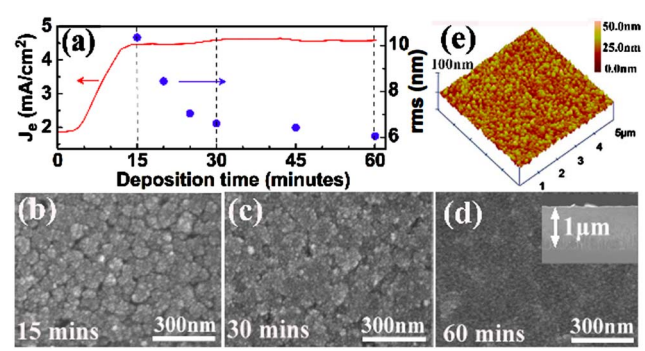

FIG. 3. (Color online) (a) Current density and surface roughness vs time curves corresponding to the BEN-BEG UNCD films. SEM images of UNCD films grown for (b) 15, (c) 30, and (d) 60 min. (e) Three-dimensional AFM image for UNCD film grown for 60 min resulting in ~1 μm thick film [inset of (d)].

Downloaded 29 Apr 2008 to 130.91.116.168. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

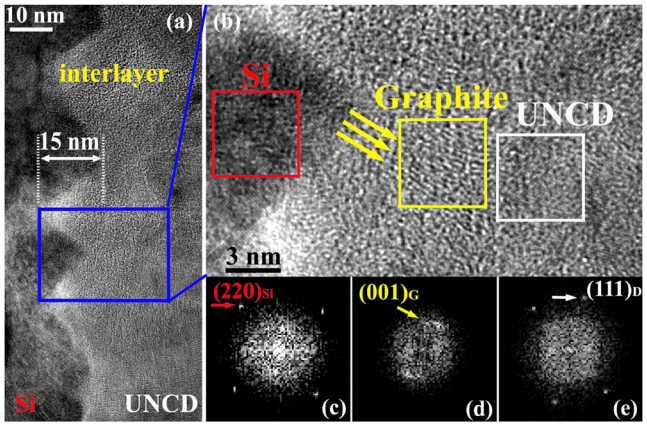

FIG. 4. (Color online) (a) Low magnification and (b) enlarged HRTEM cross-sectional image of the UNCD/Si (100) interface. The corresponding diffractograms are from the (c) Si substrate, (d) graphite interlayer, and (e) UNCD grain.

no detailed explanation was given regarding its origin. We believe that ion bombardment results in preferential etching of the Si surface along the (100) crystallographic direction, which etches faster than the (111) direction, resulting in the triangular Si interface profile defined by the (111) planes.[18] Such interfacial morphology of Si may contribute to the enhanced film-substrate adhesion. Using the lattice fringes from the Si substrate as internal calibration [Fig. 4(c)], the diffraction pattern from the interlayer between the Si substrate and the UNCD layer could be indexed as the graphite (001) plane and diamond oriented along the $[01\bar{1}]$ zone axis, respectively [Figs. 4(d) and 4(e)]. Diffractograms from the graphite and the diamond regions indicate that the (001) crystallographic plane of the graphite area is approximately parallel with the (111) crystallographic plane of the diamond grain, suggesting that cubic UNCD diamond nuclei formed on a hexagonal graphite interlayer. These results are consistent with a model[19] that suggested that diamond nucleation can occur on graphite planes by hydrogenation of the $\{1\bar{1}00\}$ prism planes. Also, no formation of a SiC phase was detected at the diamond/Si interface in prior work.[10] However, the absence of a SiC phase in TEM studies is not conclusive, since nanoscale SiC regions may statistically be missed when preparing cross-sectional TEM samples. Therefore, this issue should be considered as unresolved and open for further study.

Optical emission spectroscopy (OES) analysis was performed to reveal the species present in the plasma during film growth, to determine nucleation and growth mechanisms. The CH_4/H_2 plasma emission spectrum (not shown) obtained under applied bias, showed two sharp peaks corresponding to H_α and H_β emissions, a CH peak from the breakup of CH_x, and a C_2 peak from the breaking of C_2H_x species. The OES analysis complemented the XANES, AFM, and TEM studies to help map the steps involved in the BEN-BEG UNCD nucleation-growth mechanism. The proposed mechanism includes several concurrent processes: (1) silicon etching and formation of silicon facets by ion bombardment of accelerated H^+ during the initial hydrogen plasma exposure. (2) Subsurface implantation, temperature-induced diffusion, and reaction of carbon atoms with Si atoms to form a graphite interlayer, resulting from the impact on Si of energetic carbon ions, produced by substrate bias-induced acceleration of ions from the plasma. (3) Nanodiamond growth and renucleation resulting from impact of energetic C ions from the plasma and ion-induced dissociation of C_2 and/or CH_x species landing on the surface, (4) Ion bombardment of incipient diamond grains producing sputtering of carbon atoms, which can be subplanted in the surface of the substrate and growing film contributing to UNCD grain renucleation, as well as enhanced film adhesion.

In summary, a low-pressure heat-assisted BEN-BEG process has been developed to grow UNCD films with nanoscale surface roughness, high growth rate, uniform nanosized crystalline diamond grains, and very low content of sp^2-bonded carbon atoms. A mechanism is proposed to explain the relationship between the growth conditions, structures, and properties of the films.

The authors acknowledge the support of the U.S. Department of Energy, BES-Materials Sciences, both for work in the Materials Science Division and the new Center for Nanoscale Materials under Contract No. DE-AC02-06CH11357. R.W.C. acknowledges support from the Air Force Office of Scientific Research under Contract No. FA9550-05-1-0204. XANES measurements were conducted at the Synchrotron Radiation Center at the University of Wisconsin-Madison (NSF Grant No. DMR-0537588).

[1] D. M. Gruen, Annu. Rev. Mater. Sci. **29**, 211 (1999).
[2] O. Auciello, J. Birrell, J. A. Carlisle, J. E. Gerbi, X. Xiao, B. Peng, and H. D. Espinosa, J. Phys.: Condens. Matter **16**, R539 (2004).
[3] S. Srinivasan, J. Hiller, B. Kabius, and O. Auciello, Appl. Phys. Lett. **90**, 134101 (2007).
[4] J. M. Garguilo, F. A. M. Koeck, R. J. Nemanich, X. C. Xiao, J. A. Carlisle, and O. Auciello, Phys. Rev. B **72**, 165404 (2005).
[5] X. Xiao, J. Wang, J. A. Carlisle, B. Mech, R. Greenberg, R. Freda, M. S. Humayun, J. Weiland, and O. Auciello, J. Biomedical Materials **770**, 273 (2006).
[6] A. V. Sumant, D. S. Grierson, J. E. Gerbi, J. A. Carlisle, O. Auciello, and R. W. Carpick, Phys. Rev. B **76**, 235429 (2007).
[7] N. N. Naguib, J. W. Elam, J. Birrell, J. Wang, D. S. Grierson, B. Kabius, J. M. Hiller, A. V. Sumant, R. W. Carpick, O. Auciello, and J. A. Carlisle, Chem. Phys. Lett. **430**, 345 (2006).
[8] Y. C. Lee, S. J. Lin, C. Y. Lin, M. C. Yip, W. Fang, and I. N. Lin, Diamond Relat. Mater. **15**, 2046 (2006).
[9] J. Gerber, S. Sattel, H. Ehrhardt, J. Robertson, P. Wurzinger, and P. Pongratz, J. Appl. Phys. **79**, 4388 (1996).
[10] B. R. Stoner, G.-H. Ma, S. D. Wolter, and J. T. Glass, Phys. Rev. B **45**, 11067 (1992).
[11] Y. Lifshitz, X. M. Meng, S. T. Lee, R. Akhveldiany, and A. Hoffman, Phys. Rev. Lett. **93**, 056101 (2004).
[12] Y. C. Lee, S. J. Lin, C. T. Chia, H. F. Cheng, and I. N. Lin, Diamond Relat. Mater. **14**, 296 (2005).
[13] A. Laikhtman, I. Gouzman, A. Hoffman, G. Comtet, L. Hellner, and G. Dujardin, J. Appl. Phys. **86**, 4192 (1999).
[14] J. Birrell, J. A. Carlisle, O. Auciello, D. M. Gruen, and J. M. Gibson, Appl. Phys. Lett. **81**, 2235 (2002).
[15] P. Keblinski, D. Wolf, F. Cleri, S. R. Phillpot, and H. Gleiter, MRS Bull. **23**, 36 (1998).
[16] D. G. Bhat, D. G. Johnson, A. P. Malshe, H. Naseem, W. D. Brown, L. W. Schaper, and C. H. Shen, Diamond Relat. Mater. **4**, 921 (1995).
[17] S. T. Lee, H. Y. Peng, X. T. Zhou, N. Wang, C. S. Lee, I. Bello, and Y. Lifshitz, Science **287**, 104 (2000).
[18] *Ion Bombardment Modification of Surfaces: Fundamentals and Applications*, edited by O. Auciello and R. Kelly (Elsevier, New York, 1984).
[19] W. R. L. Lambrecht, C. H. Lee, B. Segall, J. C. Angus, Z. Li, and M. Sunkara, Nature (London) **364**, 607 (1993).

Downloaded 29 Apr 2008 to 130.91.116.168. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp