AIP Applied Physics Letters

Bias-enhanced nucleation of diamond on silicon dioxide

M. D. Irwin, C. G. Pantano, P. Gluche, and E. Kohn

Citation: Applied Physics Letters **71**, 716 (1997); doi: 10.1063/1.119839
View online: http://dx.doi.org/10.1063/1.119839
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/71/5?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Microwave plasma enhanced chemical vapor deposition of nanocrystalline diamond films by bias-enhanced nucleation and bias-enhanced growth
J. Appl. Phys. **115**, 024308 (2014); 10.1063/1.4861417

Ultrananocrystalline diamond nano-pillars synthesized by microwave plasma bias-enhanced nucleation and bias-enhanced growth in hydrogen-diluted methane
J. Appl. Phys. **112**, 124307 (2012); 10.1063/1.4769861

Systematic studies of the nucleation and growth of ultrananocrystalline diamond films on silicon substrates coated with a tungsten layer
J. Appl. Phys. **111**, 124328 (2012); 10.1063/1.4729798

Growth, microstructure, and field-emission properties of synthesized diamond film on adamantane-coated silicon substrate by microwave plasma chemical vapor deposition
J. Appl. Phys. **107**, 103305 (2010); 10.1063/1.3427436

Role of cyclic process in the initial stage of diamond deposition during bias enhanced nucleation
J. Appl. Phys. **91**, 9752 (2002); 10.1063/1.1480116

Confidently measure down to 0.01 fA and up to 10 PΩ
Keysight B2980A Series Picoammeters/Electrometers
View video demo›
KEYSIGHT TECHNOLOGIES

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.236.82.7 On: Fri, 19 Dec 2014 11:52:56

Bias-enhanced nucleation of diamond on silicon dioxide

M. D. Irwin[a] and C. G. Pantano
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

P. Gluche and E. Kohn
Department of Electron Devices and Circuits, University of Ulm, Ulm/Donau D-89069, Germany

(Received 6 March 1997; accepted for publication 20 May 1997)

Characterization of amorphous SiO_2 surfaces after biasing pretreatments, which induce nucleation of diamond, has been carried out using x-ray photoelectron spectroscopy and Raman spectroscopy. A mixture of silicon carbide, silicon oxycarbide, and diamond are formed upon exposure of biased SiO_2 surfaces to a CH_4+H_2 plasma used for diamond deposition. It is concluded that nucleation of diamond on amorphous SiO_2 surfaces is promoted by formation of a SiC surface layer. Textured diamond films have been fabricated on bulk SiO_2 substrates using biasing pretreatments to induce diamond nucleation. © *1997 American Institute of Physics.* [S0003-6951(97)03829-1]

In order to grow diamond thin films via microwave plasma chemical vapor deposition, the substrate surface must be pretreated to promote diamond nucleation. The nucleation pretreatment is critical since high nucleation densities are required in order to obtain thin, smooth, textured diamond films. Bias-enhanced nucleation (BEN) generates nucleation densities which are orders of magnitude higher than conventional means such as diamond abrasion. Nucleation densities as high as $10^{10}/\mathrm{cm}^2$ have been achieved on Si and SiC.[1] Although BEN has been shown to be effective on substrate materials consisting of carbide-forming metals or metal carbides[1–4] such as Ti, W, Ta, Nb, and Hf as well as Si and SiC, nucleation and growth of diamond on oxides such as silicate glasses remains relatively unexplored. It was shown in a recent study[5] that biasing pretreatments promote nucleation of diamond on SiO_2 substrates. In this letter the results of surface characterization of bias-pretreated SiO_2 using x-ray photoemission spectroscopy (XPS) and Raman spectroscopy are reported. It is suggested that formation of SiC on the substrate surface during BEN facilitates diamond nucleation. Also, it is confirmed that relatively high diamond nucleation densities can be achieved on fused SiO_2 by BEN.

Deposition experiments were performed in two different ASTeX™ microwave plasma chemical vapor deposition systems (MPCVDs) both of which were modified in order to enable *in situ* biasing of the substrates. The initial biasing experiments were carried out in a quartz-tube chemical vapor deposition (CVD) reactor as shown in Fig. 1. The experiments were then reproduced in a larger MPCVD resonant chamber system which has been described elsewhere.[6] Substrates of high purity fused SiO_2 plates $1\,\mathrm{mm}\times1.5\,\mathrm{cm}\times1.5\,\mathrm{cm}$ were used. Each plate was cleaned prior to deposition by sonification in acetone, methanol, and 2-propanol for 5 min. intervals, respectively, and then rinsed in de-ionized water. The deposition process consisted of an *in situ* biasing pretreatment to promote diamond nucleation followed by a growth step in which no bias was applied to the sample. The nucleation and growth steps were carried out using a source gas mixture of hydrogen and methane. After the biasing pretreatment, the process parameters were adjusted during the growth stage to obtain a textured diamond surface.[7] Typical system parameters used during the biasing pretreatments and subsequent growth steps are summarized in Table I.

The biasing pretreatments produced nucleation densities approaching 1×10^8 nuclei/cm^2. A scanning electron microscope (SEM) micrograph of crystallites produced during the biasing pretreatments is shown in Fig. 2(a). The ''ball-like'' morphology was typical for crystallites produced during biasing pretreatment of SiO_2. After the pretreatment, the processing conditions were changed (see Table I) such that the continuous film of the ball-like crystallites produced by biasing was grown out and a textured diamond film [Fig. 2(b)] was formed. Raman spectra taken from a textured diamond film and a continuous film of ball-like crystallites on a bias-pretreated surface are shown in Fig. 3. The characteristic

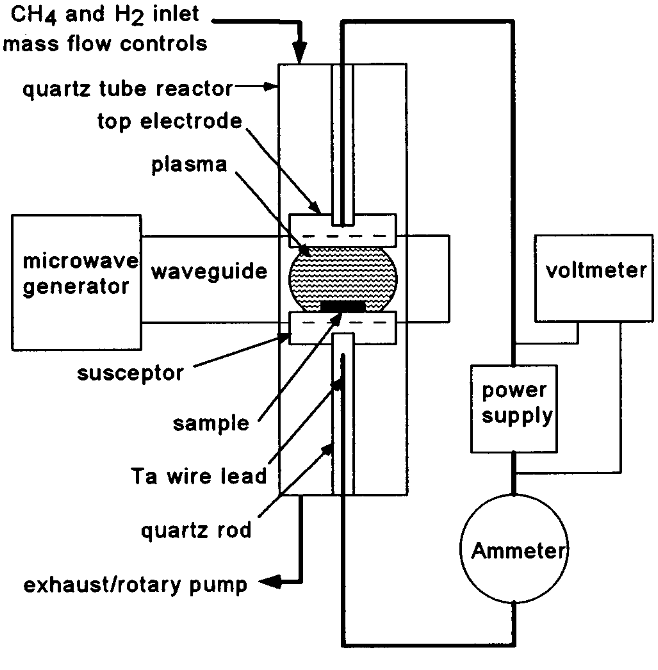

FIG. 1. Schematic of the quartz tube MPCVD reactor used for biasing experiments.

---

[a] Electronic mail: mdi2@psu.edu

TABLE I. Typical process parameters used for biasing pretreatments and growth of diamond films on amorphous SiO_2 substrates.

Parameter	Bias pretreatment	Growth
Bias voltage	190–210 V	none
Bias current	8–10 mA[a]	none
CH_4/H_2	2.5%–5%	1.5%
Pressure	17 Torr	30 Torr
Microwave power	140 W,[b] 700 W[c]	700 W
Substrate temperature	~900–1000 °C	680 °C
Time	30–120 min	variable[d]

[a] Biasing current changes as a function of pretreatment time.

[b] Quartz-tube MPCVD system.

[c] Resonant-chamber MPCVD system.

[d] The time required to grow out textured films depends on the deposition rate.

peak at 1332 cm^{-1} indicates that the crystallites formed during biasing pretreatments consisted of diamond.

A cross-sectional view of a textured diamond film grown on SiO_2 via BEN is shown in Fig. 2(b). Pyramidal features indicative of a (111) surface texture are observed. Ball-like diamond crystallites are seen in cross-section at the diamond SiO_2 interface as well as columnar, diamond grains that have grown over this layer of crystallites. The interface between the diamond film and the underlying SiO_2 substrate is intact indicating that the diamond adheres well to the surface; however, in some cases the SiO_2 fractured below the interface causing spallation of the film. This could be due to thermal stresses which develop due to mismatch in the coefficients of thermal expansion of diamond and SiO_2 at high temperatures (surface temperatures of ~900–1000 °C during biasing pretreatments). The substrates were also relatively thick, 1 mm, allowing for a significant thermal gradient to develop. It may be possible to avoid spallation of the film by reducing processing temperatures and using thinner substrates.

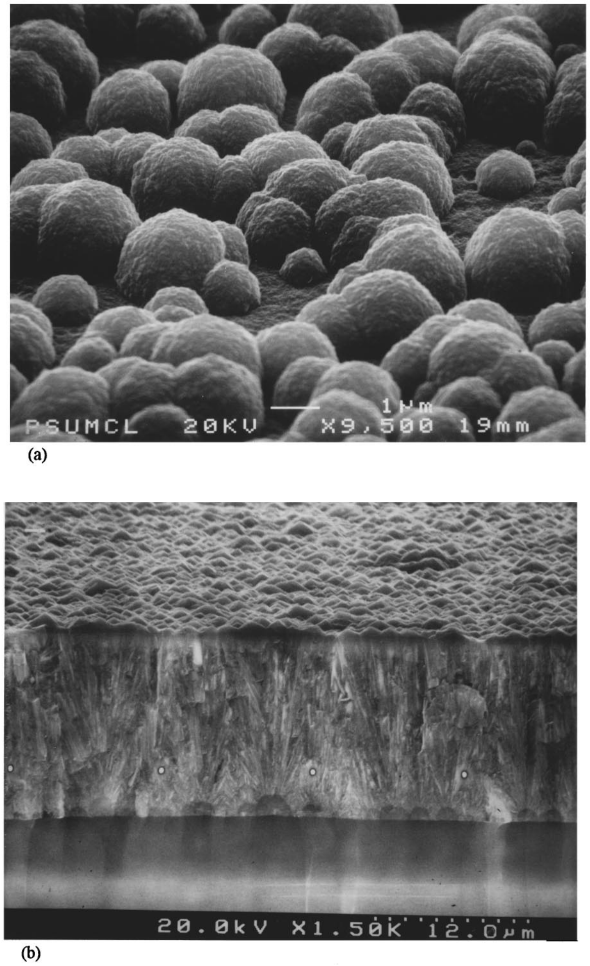

FIG. 2. (a) SEM micrograph showing ball-like diamond crystallites formed during biasing in the resonant chamber MPCVD reactor. (b) SEM micrograph showing a cross-sectional view of a diamond film grown on SiO_2. The diamond/SiO_2 interface as well as a (111) textured diamond surface can be seen.

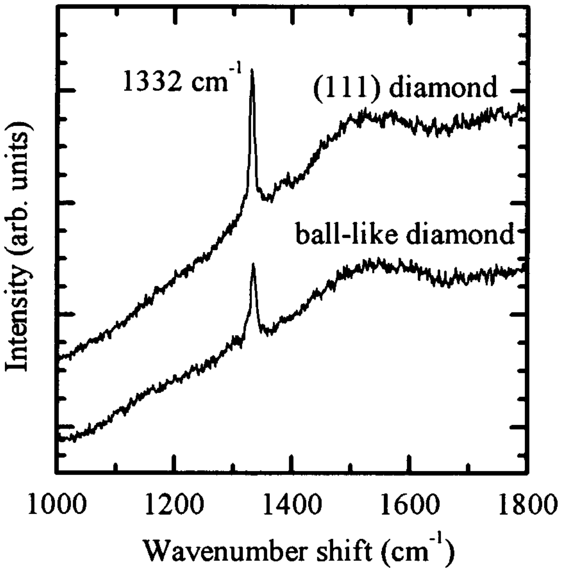

FIG. 3. Raman spectra taken from (111) textured diamond film and a continuous film of ball-like diamond crystallites formed during a biasing pretreatment.

Analysis of bias-pretreated surfaces using XPS indicated that a mixture of SiC, silicon oxycarbide, and a carbon phase (diamond and/or amorphous carbon) are formed during the biasing pretreatment. XPS silicon $2p$ and carbon $1s$ spectra taken from a sample which was subjected to a 30 min bias pretreatment are shown in Fig. 4. The Si $2p$ and C $1s$ peaks lying at 100.1 and 282.6 eV, respectively, in Figs. 4(a) and 4(b) clearly indicate that SiC has been formed on the substrate surface. The peak appearing at 103.7 eV in Fig. 4(a) is due to the Si $2p$ signal from the underlying SiO_2 substrate. The central peak seen in Fig. 4(a) at 102 eV could be attributed to the existence of a solution of oxycarbide compounds formed at the SiC/SiO_2 interface, all with binding energies lying between those of SiC and SiO_2 (rather than to a single compound with a discrete stoichiometry). The intermediate peak observed in the C $1s$ spectrum at 283.8 eV is also consistent with the presence of silicon oxycarbide compounds. The C $1s$ peak at 284.6 eV is primarily attributed to formation of diamond (as is confirmed by Raman, Fig. 3); however, other carbonaceous species such as amorphous carbon and/or graphite may also contribute to this signal. The data indicate that a silicon oxycarbide phase is formed upon exposure of the biased SiO_2 surface to the CH_4+H_2 plasma possibly via an O for C exchange reaction. As this reaction progresses a SiC layer is formed leaving an oxycarbide phase at the interface between the SiC layer and the SiO_2 substrate.

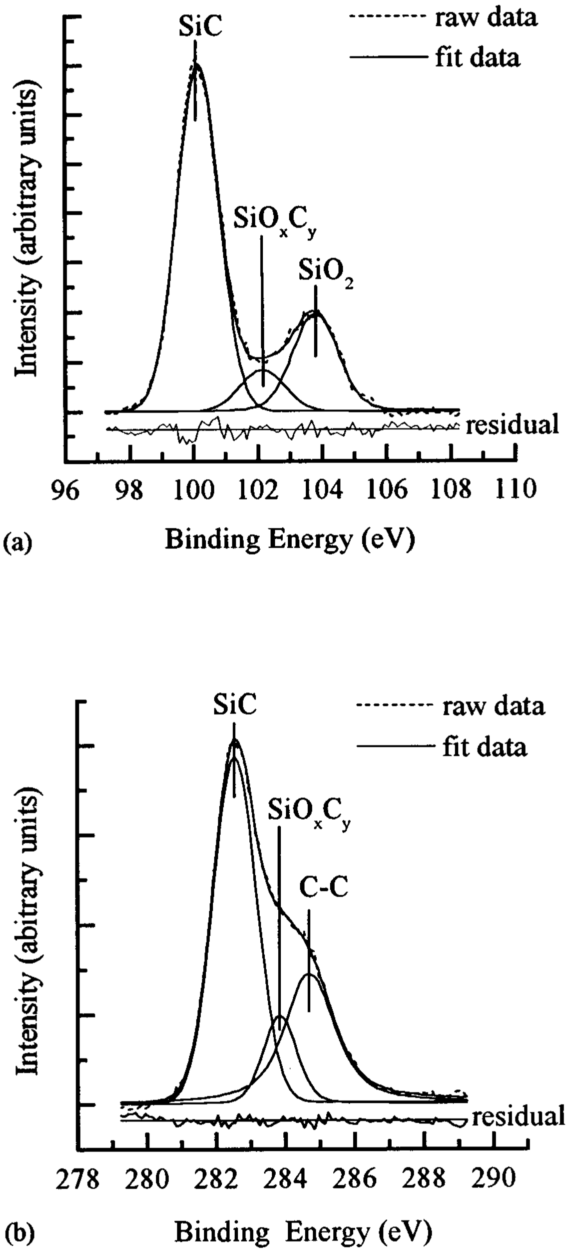

FIG. 4. (a) Silicon $2p$ and (b) carbon $1s$ x-ray photoelectron spectra taken after a 30 min bias pretreatment.

Diamond may subsequently nucleate on the silicon carbide or other carbonaceous species present on this surface layer.

It is generally accepted that one primary effect of the applied bias is to increase the flux of positively charged radicals such as C^+ and CH^+ to the substrate surface.[8–10] These radicals may react with, or attach to, the substrate surface at energetically favorable sites and form diamond nuclei. Although heterogeneous nucleation of diamond on a solid surface from the gas phase is not well understood it has been demonstrated that diamond readily nucleates on biased β-SiC.[11,12] A surface layer which consists of a mixture of amorphous SiC and microcrystalline SiC is seen to form on Si during biasing.[1,13] These SiC microcrystallites could serve as nucleation sites for diamond. Similarly, crystallites in the SiC surface layer formed on SiO_2 surfaces during biasing might act as diamond nucleation sites. A difference in crystallinity or morphology of the SiC overlayers could explain the lower diamond nucleation densities induced by BEN observed in this study on SiO_2($\sim 10^8/cm^2$) compared to those commonly reported for nucleation on Si ($10^{11}/cm^2$).[1] The crystallinity of the SiC surface layer formed on an amorphous SiO_2 surface would be expected to be lower than that of the SiC layer formed on single-crystal Si surfaces. Thus it may be possible to increase the nucleation density of diamond produced on SiO_2 via BEN by optimizing process conditions to increase the crystallinity of the carbide surface layer formed.

Bias-enhanced nucleation has been demonstrated to be a viable *in situ* process for deposition of diamond on SiO_2; however, more work is required to develop this technique for production of thinner, smoother diamond films that could be of use in fabrication of microelectronic devices or optical coatings. An investigation is currently underway in which bias-pretreated SiO_2 surfaces will be more thoroughly characterized and process conditions used during the pretreatment will be optimized in order to increase the density of nuclei produced by biasing.

[1] B. R. Stoner, G.-H. M. Ma, S. D. Wolter, and J. T. Glass, Phys. Rev. B **45**, 11067 (1992).
[2] P. Reinke, P. Kania, and P. Oelhafen, Thin Solid Films **270**, 124 (1995).
[3] S. D. Wolter, M. T. McClure, J. T. Glass, and B. R. Stoner, Appl. Phys. Lett. **66**, 2810 (1995).
[4] S. D. Wolter and J. T. Glass, J. Appl. Phys. **77**, 5199 (1995).
[5] J.-S. Lee, K.-S. Liu, and I.-N. Lin, J. Appl. Phys. **81**, 486 (1997).
[6] S. D. Wolter, T. H. Borst, A. Vescan, and E. Kohn, Appl. Phys. Lett. **68**, 3558 (1996).
[7] C. Wild, P. Koidl, W. Müller-Sebert, H. Walcher, R. Kohl, N. Herres, R. Locher, R. Samlenski, and R. Brenn, Diam. Relat. Mater. **2**, 158 (1993).
[8] S. Yugo, T. Kimura, and T. Kanai, Diam. Relat. Mater. **2**, 328 (1992).
[9] S. P. McGinnis, M. A. Kelly, and S. B. Hagström, Appl. Phys. Lett. **66**, 3117 (1995).
[10] J. Gerber, S. Sattel, K. Jung, H. Ehrhardt, and J. Robertson, Diam. Relat. Mater. **4**, 559 (1995).
[11] B. R. Stoner, G. H. Ma, S. D. Wolter, W. Zhu, Y.-C. Wang, R. F. Davis, and J. T. Glass, Diam. Relat. Mater. **2**, 142 (1993).
[12] R. Kohl, C. Wild, N. Herres, P. Koidl, B. R. Stoner, and J. T. Glass, Appl. Phys. Lett. **63**, 1792 (1993).
[13] J. Gerber, S. Sattel, H. Ehrhardt, J. Robertson, P. Wurzinger, and P. Pongratz, J. Appl. Phys. **79**, 4388 (1996).