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Nucleation Studies of Pulsed Bias Enhanced CVD of Diamond on Biomaterials

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The effects of bias voltage, bias time, frequency, and duty cycle on the nucleation of diamond were investigated. Pulsed duty cycles were 0.4 μs, and the frequency varied between 0 and 100 kHz. The substrates were pretreated by a direct current (dc) bias using 3 vol.% CH_4 in Ar/H_2 plasma. Growth and surface roughness were controlled using pulsed frequencies, with mean R_a values of 20 nm. Films were characterized in terms of orientation and surface roughness using transmission electron microscopy and atomic force microscopy. Bias-enhanced nucleation is shown to profoundly increase the nucleation densities by promoting ion bombardment of the substrate surface, thus creating nucleation sites for subsequent growth on substrates such as titanium alloys and steel. This technology promotes smooth diamond facets without abrasive surface damage. Controlling the surface roughness and morphology is of critical importance for many new biomedical and electronic devices.

Keywords bias-enhanced nucleation (BEN), biocompatibility, chemical vapor deposition (CVD), diamond growth and characterization, nanocrystalline

1. Introduction

Chemical vapor deposited diamond has an individual combination of mechanical, biomedical, and optical properties (Ref 1) that make it a highly desirable material for a wide range of applications. However, polycrystalline diamond films deposited by chemical vapor deposition (CVD) methods generally have a high surface roughness, particularly for biomedical and optical applications (Ref 2). Therefore, there is a need to find ways in which the surface roughness can be reduced while retaining the excellent tribological properties of diamond. Several methods have been reported on decreasing the surface roughness, including surface pretreatments based on abrasion (Ref 3), but these methods damage the surface and cannot be readily controlled. An attractive alternative is substrate biasing, whereby a negative direct current (dc) voltage is applied directly to the substrate, causing ion bombardment of the surface. This creates nucleation sites for subsequent diamond deposition (Ref 4-7).

In this paper, a modified method of biasing the substrate has been introduced using a time-modulated bias treatment. In this method, the bias voltage is oscillated between 300 and 0 V over a duty cycle of 50% with the frequency varied between 0 and 100 kHz. Diamond films have then been grown using a hot-filament CVD system (Ref 8). The surface morphology, film structure, and the nucleation densities were investigated. Further confirmation of the nature of the films was done using Raman spectroscopy.

2. Experimental Procedures

Experiments were performed in a HFCVD system previously described elsewhere (Ref 9, 10). A water-cooled, electrically grounded, stainless steel chamber equipped with calibrated mass flow controllers to regulate the gas flow was utilized. The system allowed independent dc bias voltages to be applied between the substrate and the filament. A Mo substrate holder (25 mm^2) was coated with a diamond film (Ref 11). The filament was precarburized to avoid Ta contamination. No additional substrate heating was used.

The substrate was Ti_6Al_4V (5 mm^2), typically biomedical grade. Growth was carried out using a two-stage deposition process: (a) a negative bias of −300 V was applied to the substrate for varying duration of time between 0 and 30 min, and (b) the bias voltage was turned off and standard deposition conditions were resumed for a further 4 to 10 h.

For the biasing stage of the growth process, the CH_4 concentration was increased to 3 vol.% and the substrate was biased negatively (−300 V), establishing a purple glow discharge (Fig. 1) typical of Ar/H_2 plasmas. The emission current increased steadily and then remained constant at 200 mA, as the plasma dispersed across the diamond-coated substrate holder.

The biasing conditions were optimized from a series of experiments to maximize the nucleation density of diamond crystals on Ti_6Al_4V substrates. The duty cycle of the pulsed bias was 50%, with an on time of 0.4 μs and an off time of 0.4 μs. All other deposition parameters are outlined in Table 1. The surface morphology, growth rate, and quality of the diamond films were investigated after steps (a) and (b) of the growth cycle, using a JEOL scanning electron microscope (SEM, model JSM 5600LV, JEOL, Tokyo, Japan) and Raman spectroscopy (Kaiser HoloProbe, Kaiser Optical Systems, Inc., Ann Arbor, MI) with a 532 nm Nd:YAG laser as the excitation source.

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Fig. 1 Photographic image of plasma during BEN

Table 1 HFCVD parameters used throughout nucleation and diamond growth

Setup		Deposition parameters
Substrate	Ti_6Al_4V	5 mm^2
Filament	Tantalum	0.50 mm (d)
Temperature	(Filament)	1650-1800 °C
Temperature	(Substrate)	650-850 °C
Bias temperature		650 °C
Pulsed bias duration	0.4 μs^{-1}	15 min
Bias voltage		300 V
Reactive gases	Methane	1 vol.%
		3 vol.% during BEN
	Hydrogen	1-100 vol.%
	Argon	0-98%

3. Results and Discussion

Figure 2 shows SEM images of samples grown on Ti_6Al_4V: (a) no bias nucleation stage; (b) 15 min biased using 20 kHz; and (c) after 30 min bias followed by a standard 4 h growth using conditions outlined in Table 1.

Figure 2(a) shows a SEM image of diamond films deposited for 4 h without biasing. The average crystallite sizes were between 3 and 5 μm, showing a mixed morphology typically of CVD diamond with the films having {110} and {111} orientations. The film thickness was measured to be 3.5 ± 0.5 μm. The Raman spectrum of the same sample shows a sharp peak at 1336/cm, which is characteristic of the sp^3 bonding of diamond. A broad absorption band is also observed at 1528/cm, indicating the presence of a small amount of graphitic or amorphous carbon in the film. Figure 2(b) shows a SEM image of diamond films grown for 4 h, after pulsed biasing using 20 kHz for 15 min. The crystallite sizes have dramatically reduced in size to 0.5 μm, and the film is continuous and exhibits "ballas type" diamond typical of NCD. A SEM image of diamond deposited for 4 h using 100 kHz pulsed biasing is shown in Fig. 2(c). The films exhibit voids, and the average diamond crystallite size is 0.1 μm. Figure 3 shows a bar chart of mean

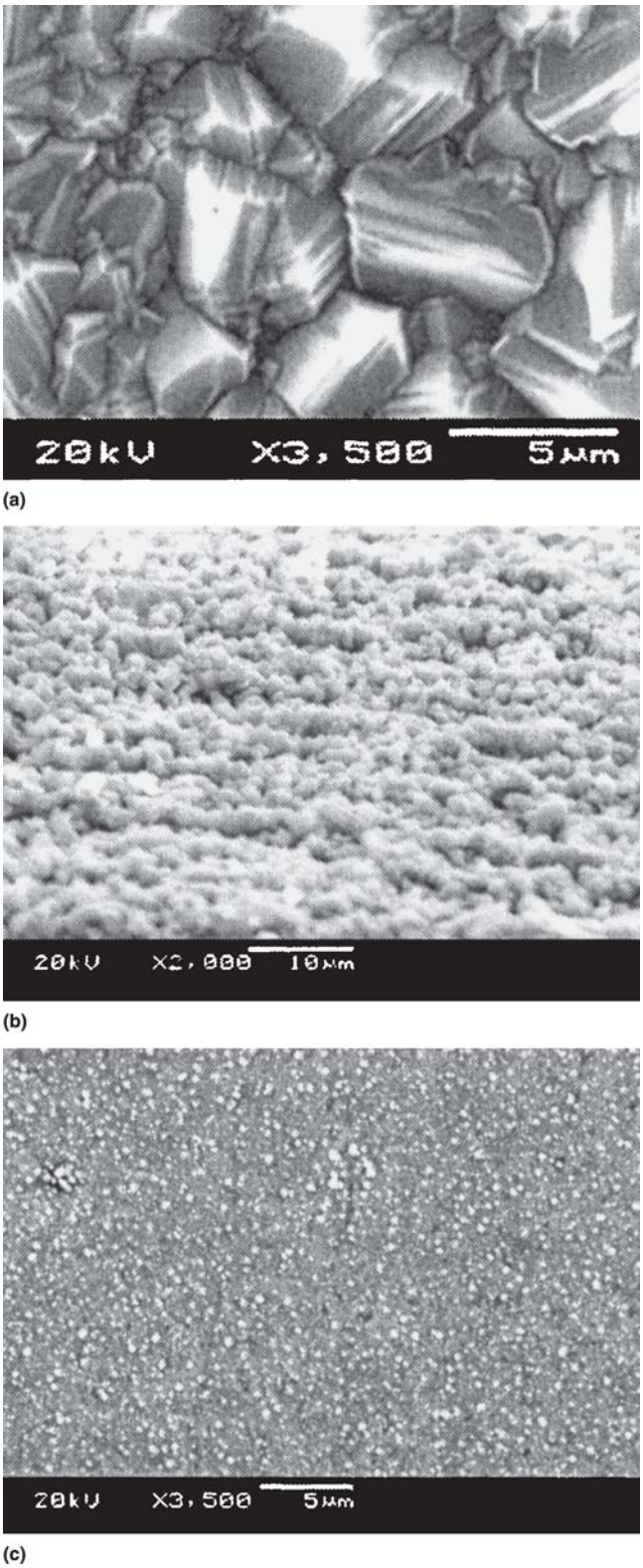

Fig. 2 SEM images of diamond on Ti_6Al_4V deposited for 4 h after (a) no bias pretreatment, (b) 15 min of pulsed BEN using 20 kHz, and (c) 15 min of pulsed BEN using 100 kHz

diamond crystallite sizes after various bias-pretreatment procedures. A sharp decrease in crystallite size with increased frequency is observed.

Figure 4 shows a Raman spectrum of diamond deposited for 4 h after 15 min of pulsed biasing at –300 V. The peak at

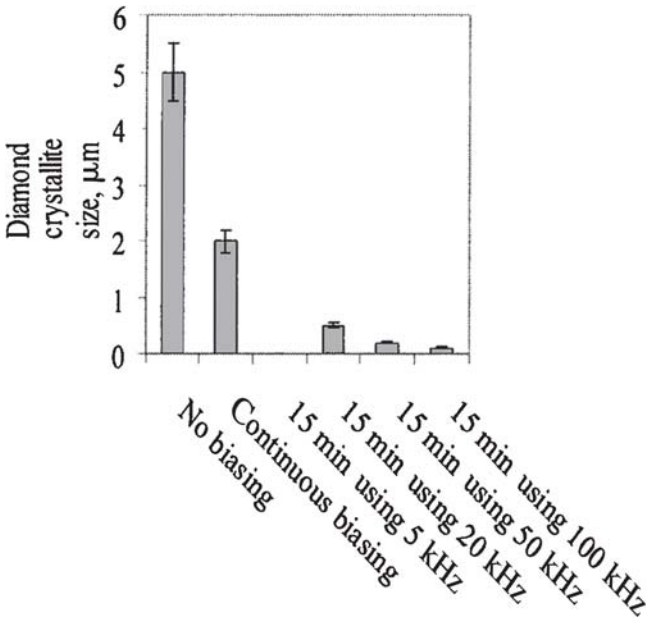

Fig. 3 Bar chart representing average diamond crystallite size after 4 h of deposition using the various bias procedures

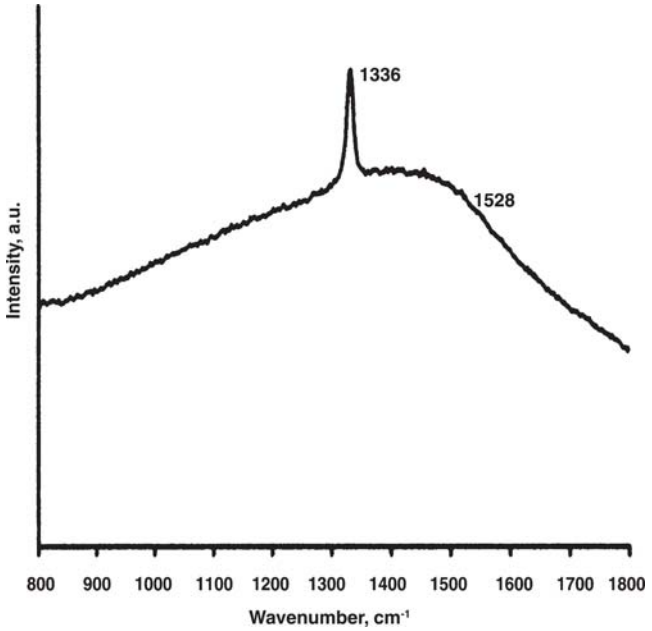

Fig. 4 Raman spectra of diamond films deposited using 15 min of BEN (−300 V) pulsed bias (20 kHz) on Ti_6Al_4V

1336/cm is indicative of diamond, shifted slightly (−7 GPa) due to compressive stress (Ref 12), on Ti_6Al_4V.

Overall, the biasing results are indicative of growth of amorphous carbon on the nanocrystalline diamond during the plasma exposure rather than damage of the diamond through an etching process. It has been reported that hydrogen plasma etching of CVD diamond is a slow process (Ref 13, 14) and the crystalline film morphology is retained. However, in this experiment, the diamond surface is completely changed after relatively short plasma exposure times and the increasing nonuniformity of the amorphous structures with bias time is commensurate with the growth of a carbon layer. It is apparent that the crystallite size and roughness of the diamond films is critically dependent on the morphology and uniformity of the underlying amorphous layer.

4. Conclusions

The nucleation density can be considerably increased using HFCVD with a pulsed bias-enhanced process step, leading to a decrease in the crystal size of diamond films. Exposure of the substrate to 3 vol.% CH_4 in Ar/H_2 plasma rapidly produces an amorphous carbon film. The crystal grain density and roughness of the final diamond film are dependent on the morphology and uniformity of the underlying amorphous layer. To obtain uniform and smooth diamond films with a high crystallite density, a bias exposure time of 30 min is required. Good-quality nanocrystalline films have been deposited using pulsed bias pretreatment with control of the crystallite size and orientation compared with standard HFCVD processes.

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