

Diamond Nucleation by a Selective Etching Technique

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Microwave plasma-enhanced chemical vapor deposition of diamond films on silicon carbide and tungsten carbide (with 6% cobalt) surfaces using fluorocarbon gases has been demonstrated. The diamond films are characterized by scanning electron microscopy and Raman spectroscopy. The proposed nucleation and growth mechanism involves concurrent etching of the non-carbon component by atomic fluorine and deposition of diamond. Optical emission spectroscopy is used to corroborate this growth mechanism.

1. INTRODUCTION

A major impediment to the wide-scale utilization of diamond films is the need to abrade/seed the substrate with diamond in order to have sufficient nucleation density¹. The seeding step produces scratches and leaves sub-micron size diamond seeds on the substrate surface to serve as nucleation sites. Alternative methods have been developed to circumvent this seeding step. These include the implantation of carbon²⁻⁵, fullerene nucleation layers⁶, buffer layers⁷⁻⁹, or biased enhanced nucleation¹⁰⁻¹¹. Most of these techniques rely upon the deposition or placement of non-diamond carbon on the substrate to start the nucleation process.

In our research, we study the growth of diamond on carbide substrates and use the carbon already present in the substrate as the starting point for nucleation. The unique etching and growth chemistry of a $C_xF_y/H_2/O_2$ plasma is responsible for the diamond growth on carbide substrates, and this work builds upon the first reported work of the production of diamond films from CF_4 gas and microwave plasma on non-diamond substrates.¹²

2. EXPERIMENTAL

The samples were grown in a microwave plasma chemical vapor deposition system described

previously¹³. No independent substrate heating is used; the plasma heats the substrate to the required growth temperature. Table I lists the growth parameters.

Table 1
Diamond Growth Conditions

Substrate:	WC / 6% Co or reaction-bonded SiC
Surface Modification:	WC/6%Co: Chemical etch to remove Co and roughen WC particles SiC: No Modification
Feed Gases:	CF_4 , C_2F_6 , C_3F_8 , or C_4F_8 , all at 1/2% - 3%, 1% O_2 , Balance H_2
Total Flow Rate:	200 sccm
Pressure:	40 mBar
Microwave Power:	350-400W
Substrate Temperature:	900 C
Growth Time:	1-6 hrs.

The substrates consisted of silicon carbide and tungsten carbide in two different forms. The first form is loose powder (-325 mesh typically 10 microns in size) while the second form is solid compacts in the form of reaction-bonded silicon carbide (RBSC) or tungsten carbide - 6% Cobalt (WC/6%Co) in the form of a tool insert. For the RBSC, samples were sectioned from a bulk rod and polished with 600 grit SiC paper to remove any diamond contamination from the cutting wheel. The WC/6%Co tool insert received two wet chemical etchings. The first, a mixture of potassium ferricyanide, $(K_3Fe(CN)_6)$, sodium hydroxide, (NaOH), and water served to roughen the WC surfaces. The second etch, to remove near-surface cobalt, utilized a mixture of iron chloride, $FeCl_3$, and water.

Characterization included scanning electron microscopy (SEM) evaluation as well as Raman spectroscopy to determine the crystallinity of the films. Plasma emissions were observed and recorded using a EG&G PARC Model 1470A Process Monitor coupled to a 1024 element photo-diode array. Sampling times were typically 0.03 to 0.06 seconds looking down into the plasma. Initially a background scan is taken of the chamber with a growth plasma but no substrate. Next a WC/6% Co substrate is positioned in the plasma and another series of spectra is taken. Finally the background emission spectra is subtracted from the substrate emission spectra to yield a difference spectra.

3. RESULTS

Figure 1. is low and high magnification SEM micrographs of diamond growth with CF_4 for one hour on tungsten carbide powder, (a) & (b), and silicon carbide powder, (c) & (d). Nucleation of crystals occurs on all of the particles shown with individual particles approaching one micron in size. In the higher magnification micrographs, the highest nucleation density occurs along the edges of the particles. In an identical experiment using CH_4 instead of CF_4 , virtually no diamond crystals form on the various carbide powders.

The effect of the various fluorocarbon gases

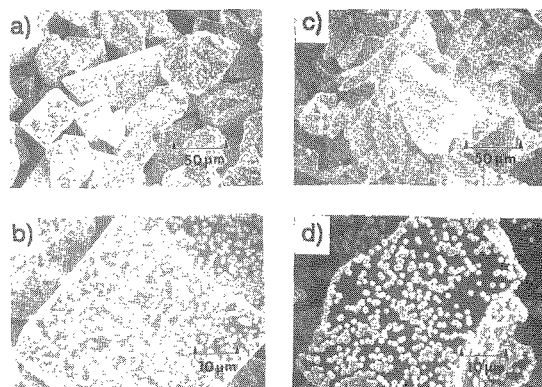


Figure 1. Micrographs of diamond nucleation on tungsten carbide (WC) powder (a) and (b) and on silicon carbide powder (c) and (d).

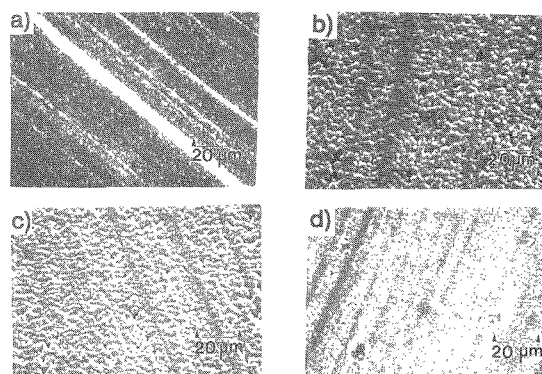


Figure 2. Growth of diamond on tungsten carbide - 6% cobalt using various fluorocarbon gases. (a) 1/2% CF_4 , (b) 1/2% C_2F_6 , (c) 1/2% C_3F_8 , and (d) 1/2% C_4F_8 .

is shown in Figure 2. All of the gases were used at the same percentages; however, each succeeding gas has an additional carbon atom. Consequently, there is up to four times as much carbon available to grow diamond. Not surprisingly, the nucleation density in (2d) is much higher than in (2a). These micrographs also indicate that a variety of fluorocarbon gases can be used to nucleate and grow diamond on WC/6%Co substrates. Similar results are seen for the RBSC case.

When growing on these carbides, the microstructure evolves from a circular texture to a (100) texture throughout the course of a six hour growth. Figure 3 is a micrograph of the surface morphology after a six hour deposition with the corresponding Raman spectra of the film. Only a single, sharp peak at 1332 cm^{-1} is found with little evidence of graphite co-deposition.

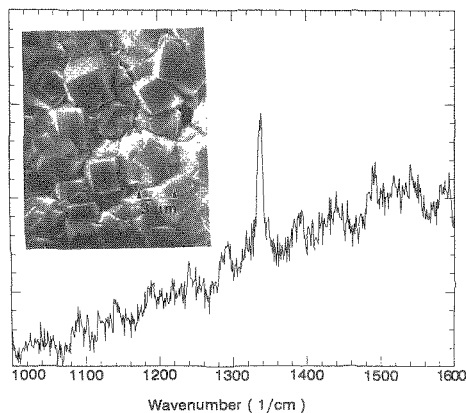


Figure 3. Raman spectroscopy of a diamond film grown on reaction-bonded silicon carbide. The inset is a photomicrograph of the diamond film showing the (100) texture.

To determine what species are present in the plasma, an optical emission study of the plasma was conducted with the results presented in Figure 4. This figure is the difference spectra described previously. Two peaks, at 400.9 nm and 413.7 nm, appear out of the background and are assigned to

elemental tungsten. The other peaks around 420 nm are from SiF_x emissions originating from the fused silica reaction tube. The elemental tungsten comes from the tungsten carbide substrate.

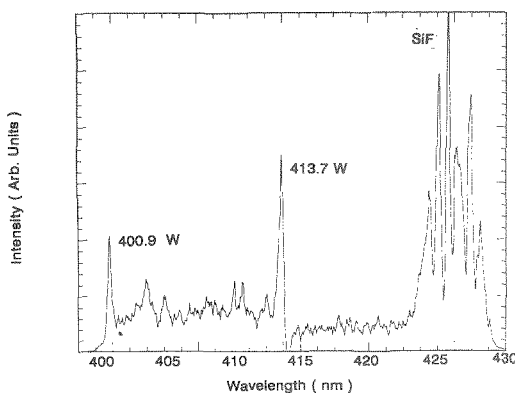


Figure 4. Optical emission spectra of a diamond growing discharge containing 1/2% CF_4 , 1% O_2 , balance H_2 with a tungsten carbide - 6% cobalt substrate.

4. DISCUSSION

Thermodynamic arguments suggest that the etching of SiC can occur quite readily by atomic fluorine, CF_4 and gaseous hydrogen fluoride. Table II lists the reactions of interest as well as their free energy changes at 1200 K (the approximate growth temperature) calculated from JANAF Thermochemical Tables¹⁴. Although not shown here, similar free energy changes are found for tungsten carbide reacting with the species listed above. Immediately obvious is that all of these reactions have negative free energy changes meaning that these reactions go to completion. In this case, completion means the production of volatile SiF_x species and the formation of a carbon-rich surface. Diamond nucleation can commence on this surface carbon with growth occurring through standard hydrogen abstraction and radical addition mechanisms proposed by other researchers.

Table 2
Thermodynamics of silicon abstraction

1)	$\text{SiC} + \text{CF}_4 \rightarrow \text{C-C} + \text{SiF}_4$
	$G_{\text{rxn}} = -629.8 \text{ kJ/mol}$
2)	$\text{SiC} + 4\text{F} \rightarrow \text{C} + \text{SiF}_4$
	$G_{\text{rxn}} = -1405.4 \text{ kJ/mol}$
3)	$\text{SiC} + 4\text{HF} \rightarrow \text{C} + \text{SiF}_4 + 2\text{H}_2$
	$G_{\text{rxn}} = -1099.7 \text{ kJ/mol}$

Proof for this mechanism lies in optical emission spectra presented earlier. The volatile fluorides produced at the substrate surface can be expected to be broken apart by the higher-energy electrons in the plasma leaving atomic fluorine, tungsten and silicon. The observation of atomic silicon is complicated because the reaction chamber is composed of fused silica making the separation of background and actual signal difficult. For elemental tungsten, these problems are not encountered, and upon subtracting the background, two large tungsten peaks are seen as shown in Figure 4. While it is possible that some of this tungsten may have been sputtered away by the plasma, the probability is small. The plasma is composed of 96% hydrogen, and at the pressures and energies used in this plasma, the hydrogen atoms and molecules do not possess enough energy or mass to remove the tungsten. The tungsten found in the plasma is from the reaction of atomic fluorine with the surface tungsten to form a volatile tungsten fluoride with the subsequent disintegration of the fluoride in the plasma to form atomic tungsten and fluorine.

Several works support this selective etching technique. Suguira et al.¹⁵ used mixtures of CF_4 and O_2 to reactive ion etch SiC thin films. When etching with this gas mixture, a carbon-rich surface layer was found to form on the SiC. Other researchers have seen the same type of behavior in their investigations of SiC etching. Palmour et al.¹⁶

examined the dry etching of SiC single crystal thin films and found the silicon peak corresponding to the LVV transition completely disappears indicating the presence of a carbon-rich surface. Even diatomic halogen gases such as chlorine¹⁷ can be used to preferentially remove the silicon from the silicon carbide matrix.

In this study only two different carbides were investigated; however, the technique should be applicable to several other carbide-forming elements. Elements such as molybdenum, niobium, and zirconium are known to form carbides that aid in the nucleation and growth of diamond thin films. Additionally, these carbides also form low-boiling point fluorides that are completely gaseous below the diamond growth temperature of 900 C. In summary, a technique has been developed to selectively remove the non-diamond component of a carbide and nucleate and grow diamond on the surface carbon left behind on the carbide. No diamond pre-treatment is necessary to produce the diamond films. The film morphology transforms from "cauliflower" to (100) as growth proceeds. This technique should be applicable to a variety of carbide surfaces.

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