International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:4, No:1, 2010

Effect of Surface Pretreatments on Nanocrystalline Diamond Deposited On Silicon Nitride Substrates

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***Abstract*—**The deposition of diamond films on a Si_3N_4 substrate is an attractive technique for industrial applications because of the excellent properties of diamond. Pretreatment of substrate is very important prior to diamond deposition to promote nucleation and adhesion between coating and substrate. Deposition of nanocrystalline diamonds films on silicon nitride substrate have been carried out by HF-CVD technique using mixture of methane and hydrogen gases. Different pretreatment of substrate including chemical etching consists of hot acid etching and basic etching and mechanical etching were used to study the quality of diamond formed on the substrate. The structure and morphology of diamond coating have been studied using X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) while diamond film quality has been characterized using Raman spectroscopy. AFM was used to investigate the effect of chemical etching and mechanical pretreatment on the surface roughness of the substrates and the resultant morphology of nanocrystalline diamond. It was found that diamond film deposited on as-received, basic etched and grinded substrate shows the morphology of cauliflower while blasted and acidic etched substrates produce smooth, continuous diamond film. However, the Raman investigation did not show any deviation in quality of diamond film for any pretreatment.

***Keywords*—**Nanocrystalline diamond, Chemical Vapor Deposition, Pretreatment, Silicon Nitride

I. Introduction

DIAMOND is a unique material because of its exceptional mechanical, thermal, optical and electronic properties. The fabrication of diamond by chemical vapor deposition (CVD) typically involves activation of a mixture of hydrogen and hydrocarbon gases. Silicon nitride (Si_3N_4) based ceramic tools are widely used as cutting tools because of their high hardness, high thermal conductivity and low thermal expansion coefficient. However, in some applications, silicon nitride surface can be damaged by particle impact or by oxidation. Thus, by coating the Si_3N_4 by a very hard, erosion resistant coating such as diamond film can reduce chemical wear of nitride ceramic and also protect the Si_3N_4 from failure [1, 2]. Si_3N_4 ceramic appears to be a favorable material to be diamond deposited considering its thermal expansion coefficient (2.9 X 10-6 < α < 3.6 X 10-6 K-1 for 20 < T < 1500°C) is closer to that of diamond [3]. Also, the absence of graphite catalyser such as Co and others binders make Si_3N_4 suitable material as substrate for diamond deposition [4]. Even though diamond deposition on Si_3N_4 is relatively simpler that other substrates material, there are adhesion issues that need to be addressed. Surface pretreatment is very important in promoting nucleation and enhancing diamond adhesion onto the substrates. The quality of diamond deposited on silicon nitride substrate, therefore, strongly dependent and correlated with diamond nucleation and growth, presence of defect and interfacial stresses [1].

In this paper, we have systematically investigated the effect of surface pretreatment on the morphology and quality of diamond film deposited. The identification and characterization of deposited diamond film was investigated using scanning electron microscope (SEM), X-ray diffraction (XRD) and Raman spectrometer

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II. Experimental

A. Preparation of substrates

The substrate used for the deposition of diamond film was silicon nitrides with dimension of 12mm x 12mm x 4mm. Prior to deposition, the substrates were cleaned ultrasonically in acetone for 10 minutes to remove any impurities such as dust and debris. Then, the substrates were subjected to various pretreatment as described in Table 1. Prior to deposition, the surface roughness of the substrates were measured using Mitutoyo SJ-301 profilometer before and after each pretreatment. All substrates were then seeded with diamond and SiC powder suspended in Tickopur solution.

Table 1 Substrates surface pretreatment

Sample No.	Treatment
1	As cut, rinsed acetone
2	Strong Acid etching,65% HNO_3 and 49% HF (1:1) , 50ºC,20 minutes
3	Basic Etching, 30% KOH, 60ºC, 20 minutes
4	Blast with SiC 180 for 30 sec

B. *Diamond deposition*

The diamond deposition was performed in a HFCVD reactor with pre-carburized tungsten filament (Φ=0.4 mm, length = 135 mm). The synthesis condition of the Hot Filament Chemical Vapor Deposition (HF CVD) machine used in this experiment is described in Table 2.

TABLE 1 HF CVD DEPOSITION PARAMETER

Parameter	
Pressure (mBar)	10.2
Methane concentration (vol%)	1
H_2 gas flow rate (sccm)	3000
CH_4 gas flow rate (sccm)	30
Filament temperature (°C)	2290±5
Deposition time (hr)	22

C. *Characterization of the deposited diamond film*

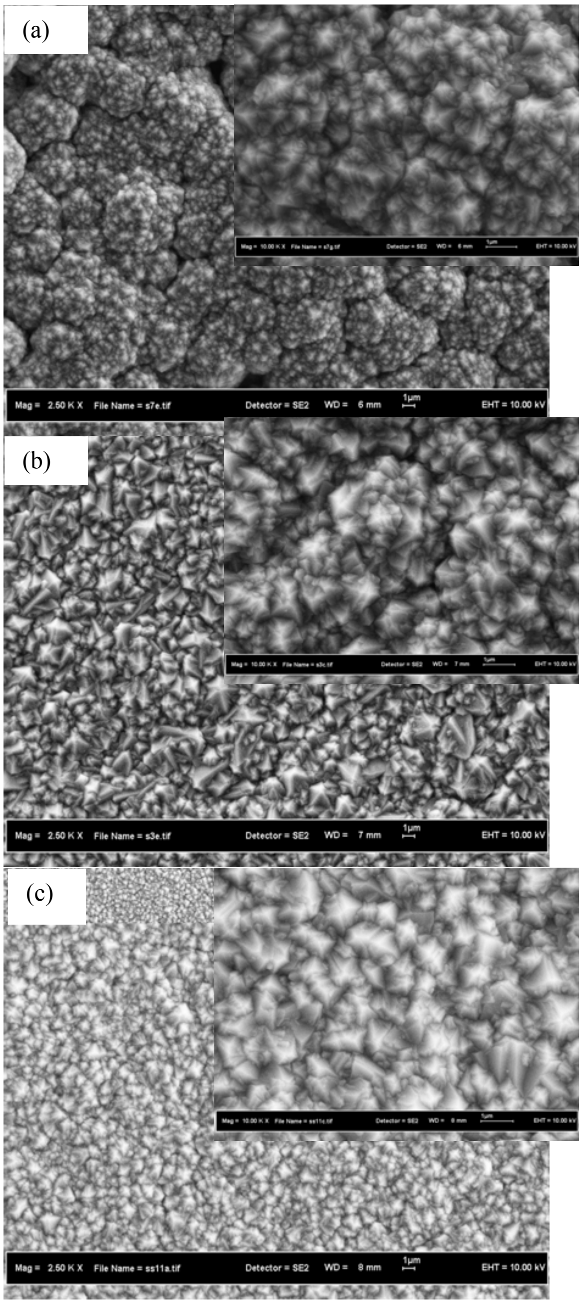
Surface topography and surface roughness of deposited film were characterized using Ambios Technology Universal SPM atomic force microscopy (AFM) The morphologies of the diamond films were examined using Scanning Electron Microscopy (Zeiss Supra 35VP) while phase analysis were done using X-Ray Diffractometer (Cu Kα radiation, Siemen Diffraktometer D5000). The diamond film quality was evaluated by Raman spectroscopy (Renishaw inVia Raman Microscope) at room temperature. The samples were excited by the 514.5 nm line of an Ar+ laser beam.

III. RESULTS AND DISCUSSION

A. *Effect of surface pretreatment on diamond morphologies*

Fig.1 shows the scanning electron microscope (SEM) micrographs of diamond films at 2500x magnification deposited on various pretreated substrates with their inset showing the films at 10k magnification. Fig. 1(a) exhibits the continuous diamond film with cauliflower or ball-like morphology which is usually associated with nanocrystalline diamond. Fig. 1(b) also shows cauliflower morphology with coarser grain. Fig. 1(c) and (d), on the other hand, shows smooth continuous microcrystalline diamond film with well-facetted pyramidal shape grain.

Diamond film with cauliflower morphology usually associated with deposition parameter such as gas pressure, substrates temperature or gas species concentration and composition [1]. However, since the deposition parameter in this experiment are fixed, thus the growth of cauliflower diamond in this experiment are caused by the secondary nucleation during diamond growth process [2]. Higher surface roughness of the substrates, on the other hand, influence the diamond growth by "trapping" more diamond seed, thus enhancing nucleation and growth of diamond film. Thus, smoother diamond films are observed as the surface roughness increased.



International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:4, No:1, 2010

(d)

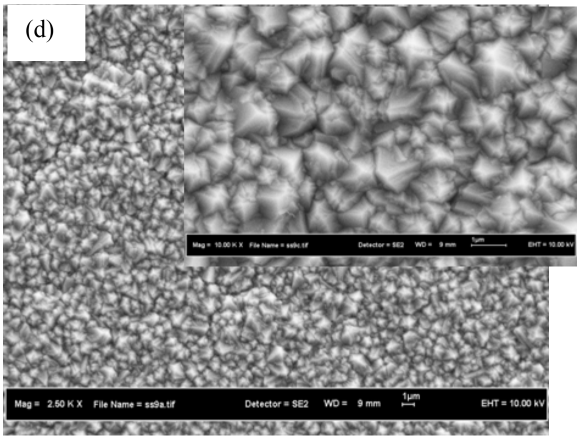


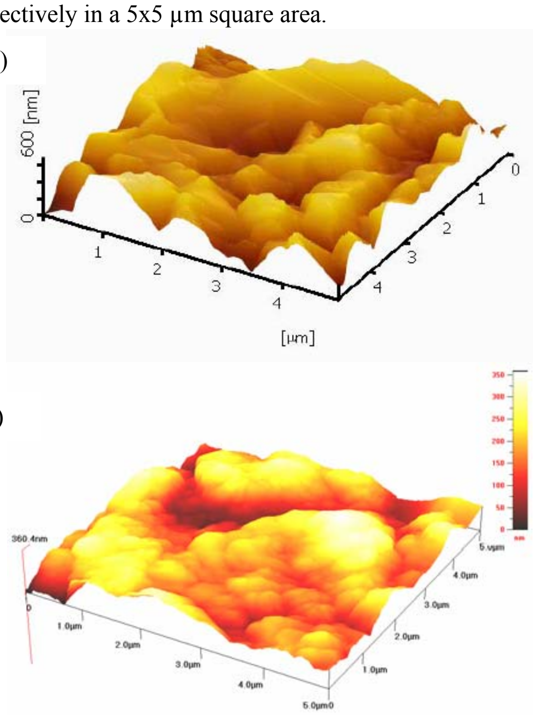
Fig. 1 SEM micrographs of diamond film grown for 22 hours with surface pretreatment of (a) as-received (b) acid etching, (c) basic etching and (d) sand blasting.

B. Atomic Force Microscopy analysis on the deposited diamond film

Atomic force microscopy (AFM) was used to study the effect of etching on surface topography and surface roughness. Fig. 2 (a) shows the 3D topography of diamond deposited on acid etched substrates while Fig 2(b) and (c) shows diamond deposited on basic etched and sand blasted substrates respectively in a 5x5 µm square area.

(a)

(b)



(c)

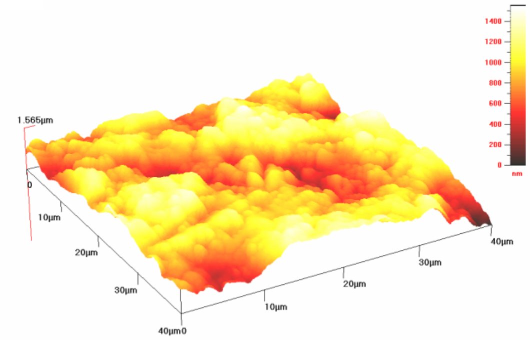


Fig. 2 AFM image analysis showing 3-dimensional view of substrates undergoes pretreatment of (a) acid etching, (b) basic etching and (c) sand blasting.

Fig. 2 shows the AFM image analysis of substrate pretreated under strong acid etching for 10 minutes. Although the chemical etching capable to expose the surface of the substrates, the slow etch rate was unable to etch entirely the bigger, rod-like particles thus leaving the larger particle protruding while the smaller grain being etched deeper. Chemical etching removed most of the intergranular phase in the Si_3N_4, thus leaving behind rod-like particle of β-Si_3N_4 [7]. Chemical etching is a nontraditional machining process in which material removal is carried out by using strong chemical solution, called “etchant”. This is simply the “accelerated and controlled corrosion” process [1] Acid etching using hydrofluoric acid (HF) and nitric acid (HNO_3) is an isotropic process in which the material is removed non-directionally from the surface substrates. Basic etching, on the other hand, is an anisotropic etching in which the etching rate is orientation dependant especially in silicon wafer [8].

Mechanical pretreatment introduces grooves and highly disordered surfaces that create high energy sites which are the preferred nucleation sites for diamond nucleation. It is because high surface energy minimized the interfacial energy by formation of diamond on sharp convex surfaces and presence of dangling bonds at sharp edge favored the chemisorptions of nucleating species [9]. This factor when coupled with low pressure CVD obviously increased the nucleation density in the mechanically pretreated substrates.

Surface roughness of deposited diamond films influence mechanical properties of the film in term of hardness and Young’s modulus value [10]. Since lower surface roughness indicates smaller crystallite, it also indicates increases in the grain boundaries thus resulting in the increase of amorphous carbon content [11]. This explains why diamond with cauliflower morphology has lower surface roughness compared to well faceted diamond. Various tribological studies on diamond film indicates that reduced surface roughness in beneficial in decrease in cutting resistance and friction coefficient [12-14].

C. Phase and diamond quality analysis using XRD and Raman spectroscopy

Fig. 3 (a) shows the comparison of XRD spectra between the samples. Because the thickness of diamond films produced was only around 7 µm, Si_3N_4 substrate peaks were more intense than those of diamonds. It is shown that diamond (1 1 1) and (2 2 0) diffractions could be identified at around 44.2º and 75.8º respectively, in addition to those of Si_3N_4 peaks in the substrate. This means that the films produced on the substrates consisted of diamond crystals. Furthermore, there was no evidence for the presence of graphitic or amorphous carbon. This gives further evidence that the deposited films were composed of diamond grains.

Raman analyses were done to evaluate the quality of diamond film. Fig. 3(b) shows the Raman spectra of the diamond films deposited on the Si_3N_4. The important feature is the diamond band at 1330 cm^{-1}. Compared to the value of 1332 cm^{-1} that is usually associated with diamond sp^3 bonding, observed negative shift in the Raman peak is associated with the low thickness of the deposited diamond film (~7µm) [3]. Other important feature that can be seen in the Raman spectra is soft peak at 1140 cm^{-1} and broad peak with maximum at 1480 cm^{-1} assigned to C–H chain structures as transpolyacetylene [trans-(CH)n] and widely accepted as typical spectra of nanocrystalline diamond [6,[4] .

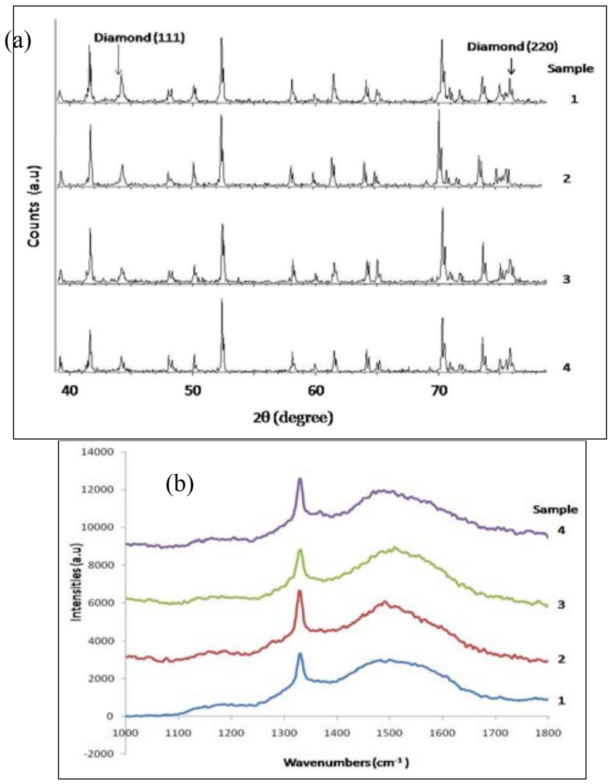


Fig. 3 XRD spectra and (b) Raman spectra of diamond film grown on substrates with various surface pretreatments

Table 3 shows the (111) to (110) ratio taken from XRD spectra of the diamond film produced at different pretreatment. High intensity of (111) peaks indicates higher crystallinity in (111) ratio and higher film thickness [5]. Table 3 also shows the comparison value of calculated β and FWHM of peak 1330 cm^{-1} based on Raman spectra in Fig. 4.Qualities of diamond film were calculated by taking into account the decomposition of Raman spectra into pure diamond (I_D) and non-diamond (I_N) components [6]. Thus, diamond qualities were characterized by a figure of merit, β, which is defined as:

$$\beta = \frac{I_D}{I_D + I_N}$$

where I_D, I_N are integrated intensities of diamond and non-diamond Raman bands, respectively.

TABLE II ANALYSIS OF DIAMOND QUALITY BASED IN XRD AND RAMAN PEAK

Sample	$I_{(110)}/I_{(110)}$	Surface roughness, Ra (nm)	Diamond Quality, β	FWHM of 1330 cm^{-1} peak
1	1.15384	60.76	0.5314	13.84
2	1.28294	67.72	0.5139	14.0133
3	1.01789	32.8	0.5080	13.7565
4	0.68571	95.68	0.5491	12.8545

From Table 3, blasted substrates produced slightly higher quality diamond film compared by treating by chemical means. Furthermore, higher surface roughness of the substrates related to the morphology of the substrates in which higher surface roughness will produce well-faceted diamond film while low surface roughness produces diamond film with cauliflower morphology. However, it can be seen that there are no significant dependencies or deviations for the various substrates pretreatment investigated. Thus, one conclusion can be drawn from these data which is the degree of crystallinity of diamond deposited on the substrates are not affected significantly by surface pretreatment. Instead, it can be attributed to the deposition parameter.

IV. CONCLUSIONS

This paper reports that diamond deposited on as-received and basic etched substrates show the morphology of cauliflower while blasted and acidic etched substrates produce smooth, continuous diamond film. High surface roughness of the substrates increases nucleation density sites thus facilitates well-facetted, continuous diamond film. However, XRD and Raman investigation shows blasted surface produced higher quality diamond film although there is no significant deviation in term of quality of the diamond films.

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