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SEM studies on diamond films prepared by HF-CVD method

Nabeel A.Bakr^{1*}, Asaad A.Kamil¹, Abdulsamee F.Abdulaziz²

¹Department of Physics, College of Science, University of Diyala, Diyala, (IRAQ)

²Department of Physics, College of Education, University of Tikrit, Tikrit, (IRAQ)

E-mail : nabeelalibakr@yahoo.com

ABSTRACT

The structure and surface morphology of diamond films grown on (100) single crystal silicon substrates by HF-CVD technique using $H_2:CH_4$ (100:1 sccm) gas mixture are reported. The diamond films were characterized by scanning electron microscopy, x-ray diffraction and Raman spectroscopy. The influence of substrate pretreatment on the surface morphology and structure of the deposited diamond films have been explored. SEM micrographs of the deposited diamond film without any substrate pretreatment were found to consist of scattered diamond nuclei of about 5 μm or less in diameter having cubo-octahedral shapes which clearly exhibit (100) and (111) planes of diamond lattice which are not significantly clustered. As the pretreatment time increases to 20 minutes the diamond nuclei grow in number and clustering starts to dominate and the signals of secondary nucleation disappear. After 30 minutes pretreatment of the substrate the micrographs of the deposited films showed that the film was continuous and nicely faceted exhibiting predominant (111) surface morphology. A successful attempt has been made to incorporate boron in easy and simple way in the deposited diamond films. It was found that the presence of boron introduced cauli-flower type features to diamond crystallites on micron scale. © 2014 Trade Science Inc. - INDIA

KEYWORDS

HF-CVD;
Diamond films;
Substrate pretreatment;
Boron incorporation;
SEM micrographs.

INTRODUCTION

Diamond is a material with interesting and different combinations of physical and chemical properties. Its properties are so tremendous that it is considered to be a first rate solid in material science. It possesses extreme values of hardness, electrical resistance, molar density, thermal conductivity and sound velocity. It also shows very useful optical and dielectric properties and exceptional inertness towards acids, alkalis and radiation damage^[1]. As a result diamond has great applica-

tion potential on industrial scale. The recent advances in low pressure chemical deposition (CVD) methods have made possible to synthesize diamond in the form of thin film configuration on variety of substrate materials. This advance has been considered as a revolutionary and has attracted many applications ranging from cutting and grinding technologies to optics and to opto-electronic devices^[2].

The main step responsible for the progress in synthesize of diamond thin films occurred in 1970's when Russian scientists Derjaguin and Fedoseev introduced

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a concept of 'gas activation' in thermal pyrolysis of hydrocarbon to produce diamond phase at low pressures and temperature^[3]. In their experiments, they used excess amount of hydrogen along with hydrocarbon gas and this mixture was activated by a hot filament/arc-discharge to produce super-equilibrium concentration of atomic hydrogen. Later on, it was realized that using gas activation methods, diamond deposited without any graphitic phase can be reproducibly obtained on non-diamond substrates. Depending upon the way of achieving gas activation, different CVD methods are evolved during past few years. These methods are broadly categorized in two groups: i) Activation by high temperature, which includes hot filament type^[4] and arc discharge type^[5], and ii) Activation by electric or electromagnetic gas discharge which includes microwave^[6], RF type^[7] and DC/AC glow discharge type methods^[8]. Many techniques have also used combination of two or more methods to achieve diamond synthesis for better control on nucleation and growth of CVD – diamond^[9]. Most popular amongst different methods are HF-CVD and RF/Microwave CVD methods. Each technique has its own advantages and limitations. The RF/Microwave plasma CVD techniques gained more popularity because of its ability to produce uniform diamond films with larger growth rate^[10]. It was found that these methods suffer from problems due to contamination of diamond films because of sputtering material of chamber-wall material and heating of electrically conducting substrates due to direct coupling with microwave energy. The high power requirement (20-75 KW), makes these methods more costly and thus become economically not feasible for large area depositions^[11]. The method of HF-CVD, on the other hand, offers many advantages. The method is sufficiently straight forward and relatively easy for fabrication of various components. It does not require any highly complicated instrumentation, except mass flow controllers and thus offers comparatively much lower capital and operating costs without much technical difficulties. Its operation is very easy and can be used very effectively over wide range of process parameters like gas flow rates, gas pressures, substrate temperatures and deposition rates etc. without much modification in the basic configuration of system. Because all of these advantages, HF-CVD technique has gained importance in diamond research in a

very short period of time^[12,13]. Therefore we have adopted this technique for synthesizing diamond films.

EXPERIMENTAL

The schematic diagram of HF-CVD system used in this study is shown in Figure 1. It comprises essentially the following sub-units: i) The HF-CVD reactor which consists of a stainless steel vacuum chamber connected to turbo molecular pump through a throttle valve to accurately control the process pressure backed by a mechanical rotary pump. The reactor has many ports for connecting different gadgets, the electrodes to mount the filament, a glass window to measure the temperature of the filament using an optical pyrometer, ports for connecting pressure gauges to measure the chamber pressure and the process pressure. The substrate holder with internally mounted heater is located inside the reactor at a convenient distance from the filament. The reactor is designed to allow water cooling of the vacuum chamber as well as the substrate in controllable way. The reactor was baked for 4-5 hours at 200 °C at a pressure < 10⁻⁶ mbar prior to the deposition. This allows the system to get degassed to minimize the possibility of the contamination in the deposited films, ii) Filament assembly which consists of stainless steel mounting electrodes specially designed so that 6 tungsten filaments each 0.5 cm apart, 2 cm length and 0.5 mm diameter can be mounted in parallel at a time. The design also enables to vary the distance between the substrate and the filament, iii) Power supply unit which supplies electric power to the filament by employing a high current AC transformer through a dimmer. Using filament assembly and power supply unit, filaments can be heated in the range of 1400-2200 °C, iv) Substrate heater consists of a stainless steel cylinder with a high wattage coil inside it. It has screwed holes in it from the bottom, to hold the substrates in place. A calibrated k-type thermocouple is secured inside the heater to monitor the substrate temperature. The heater leads are connected to the power supply while the thermocouple is connected to the temperature controller. The heater was maintained at the desired substrate temperature by a thermocouple feed-back controller. The substrate heater is designed to allow the circulating of chilled water at a speed of 2400 L/h to cool the substrate if it goes higher

than the desired temperature during the deposition process, v) Pumping system and measurement gadgets which consists of turbo molecular pump and a mechanical rotary pump combination connected to the HF-reactor through a throttle valve allowing accurate control of the process pressure during the deposition. A pressure gauge is connected to the chamber to measure the base pressure ($< 10^{-6}$ mbar). A capacitance manometer gauge is connected to the chamber to measure the accurate process pressure. A simple nitrogen gas purging system is connected to the rotary pump to exhaust the hazardous gases to the atmosphere, vi) Gas handling system which consists of the mass flow controllers, gas lines, manual control valves, gas mixing cylinder and gas inlet valve. It is an important part of the system because it introduces all the gasses into the chamber in a controlled fashion. For safety reasons, bypass valves are also added to the main gas pipes to remove the hazardous gasses in case of any breakdown in the mass flow controllers.

The type of substrate used in this study was (100)

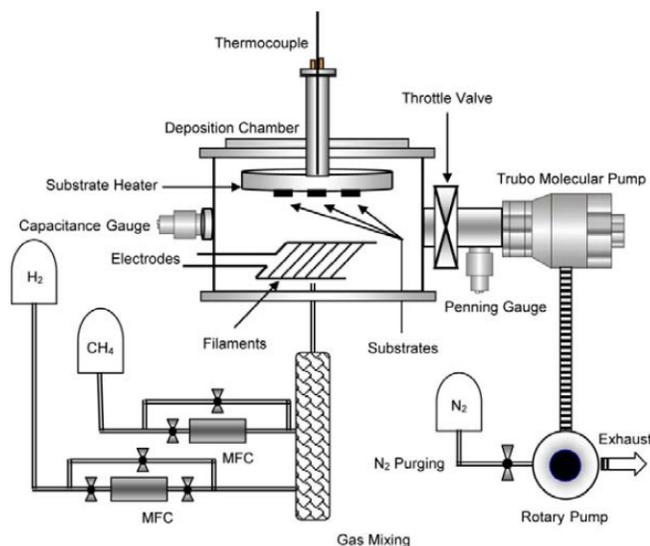


Figure 1 : Schematic diagram of HF-CVD used in the present study

single crystal silicon wafer which was well characterized earlier and expected not to add any complexity during diamond deposition as well as during characterization of the deposited diamond films. The area of the substrate used was 1 cm^2 while the filament area is adjusted to be 6 cm^2 .

To enhance the growth rate, pretreatment of substrates has been explored. In this context the chamber

was initially flushed with introduction of $\text{H}_2:\text{CH}_4$ (100:1 sccm) gas mixture at 50 Torr pressure. It was then pumped down to about 1 Torr with hydrogen flow switched off and simultaneously the substrate temperature was raised to $1000 \text{ }^\circ\text{C}$. The visual monitoring of substrate showed uniform blackening of sample surface within time period of 5 minutes. This pretreatment procedure was carried out using 10, 20 and 30 minutes before starting the diamond deposition according to the conditions depicted in TABLE 1.

The c-Si wafers were cleaned by a 1 minute dip in

TABLE 1 : Deposition conditions for growth of diamond films

Filament temperature	$2000 \pm 5 \text{ }^\circ\text{C}$
Deposition pressure	30 - 35 Torr
Substrate temperature	$900 \pm 5 \text{ }^\circ\text{C}$
H_2 flow rate	100 sccm
CH_4 flow rate	1 sccm
Filament to substrate distance	3 cm
Deposition time	3 Hours
Substrate pretreatment time	0, 10, 20 and 30 min

dilute HF (5 %) to remove the native oxide layer from the wafer surface^[14]. This cleaning method provides good adhesion of the films to the substrates. The substrates were loaded and the deposition chamber was evacuated to a base pressure less than 10^{-6} mbar. The chamber was baked for 2 hours at a temperature of $200 \text{ }^\circ\text{C}$ prior to each deposition to minimize the possibility of the contamination of the deposited films. Before any diamond deposition, it was found useful to carborize the filament. The carborization leads to formation of carbide layer on the filament surface. This pretreatment of the filament involves heating it over $500 \text{ }^\circ\text{C}$ for about 30 minutes at 1 Torr pressure of 1 sccm of methane gas flow rate.

Then the substrate was heated to the desired temperature by setting the temperature controller. The chamber then was purged by hydrogen before introducing pure CH_4 and H_2 gases inside the chamber and starting the deposition process. The deposition was carried out for the desired amount of time and the films were allowed to cool down to room temperature in vacuum. It is worthy to indicate that using the deposition parameters stated in the literature didn't produce the same structure of the resultant films. This has led to the conclu-

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sion that the deposition parameters are system dependent^[15].

An attempt has been made to incorporate boron in the deposited diamond films. This is achieved by using simple and easy way. The substrates prior to diamond deposition are scratched by using diamond grit (size $\sim 0.25 \mu\text{m}$) and are subsequently treated in suspension of boron powder (size $\sim 1.0 \mu\text{m}$) in methanol (concentration $\sim 0.1 \text{ M}$) using ultrasonic cleaner. The diamond depositions are then carried out using the same conditions shown in TABLE 1.

At least four specimens were synthesized under identical experimental conditions and characterized by various analytical techniques in order to check the reproducibility and repeatability of the results. The synthesized films were characterized by Low angle x-ray diffractometer (XRD) (D8, Advance, Bruker AXS model) with $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) as the incident radiation and the patterns were taken at a grazing angle of 1° . The scanning electron microscope (SEM) (model JEOL, JSM-6360A) observations were carried out with operating voltage of 20 kV and the emission current of 60 mA. The deposited diamond films were characterized by Raman spectrometer (Jobin-Yvon Horiba LABRAM800) using 5 mW $\text{Ar}^+/\text{He-Ne}$ laser (488 nm / 632.81 nm). It has back-scattering geometry for detection of Raman spectrum with resolution of 1 cm^{-1} .

RESULTS AND DISCUSSION

Figures 2a and 2b show the SEM micrographs of the deposited diamond film without any pretreatment of the substrate. It is clear that the film consists of scattered diamond nuclei of about $5 \mu\text{m}$ or less in diameter having cubo-octahedral shapes which clearly exhibit (100) and (111) planes of diamond lattice which are not significantly clustered. By 10 minutes pretreatment of the substrate these diamond nuclei have grown in number but not significantly in size, and clustering has started to take place over the film together with secondary nucleation as shown in Figure 2c. When the substrate pretreatment time has gone up to 20 minutes, clustering dominates the scene and the signals of secondary nucleation have disappeared, most likely due to shadowing effects from the now relatively bigger polycrystalline diamond chunks and it is clear that the film

was basically formed and needs just to grow in thickness and laterally to fill the voids left behind and the grains are approximately $10 \mu\text{m}$ in diameter as shown in Figure 2d.

The SEM micrographs at different magnifications of the deposited diamond films after 30 minutes pretreatment of the substrate are shown in Figure 3. These micrographs show that the film is continuous and nicely faceted exhibiting predominant (111) surface morphology. The apparently flat facets seen under SEM are actually found to consist of large number of twinning and stacking faults. Although the morphology is dominated by triangular symmetry, some crystals exhibiting fivefold or more complicated morphologies are also seen in the figure. These structures obviously occur because of defects which get incorporated during the growth process. In the defect free regions, the growth is still very slow and therefore very high quality. Similar results have been reported earlier^[16-18]. The thickness of this film was found to be about $4 \mu\text{m}$.

The low angle x-ray diffraction pattern of the deposited diamond film is shown in Figure 4. It exhibits two prominent peaks at $2\theta = 43.8^\circ$ and 75.2° corresponding to diffraction from $\langle 111 \rangle$ and $\langle 220 \rangle$ planes of diamond which matches the JCPDS card no. 06-0675. Since the substrate is $\langle 100 \rangle$ oriented single crystal silicon, it does not give any diffraction peak in low angle x-ray diffraction mode.

The Raman spectrum shown in Figure 5 for this film exhibited sharp peak at 1332.4 cm^{-1} indicating presence of diamond (sp^3) phase only^[19].

Figure 6 shows scanning electron micrographs of boronated diamond films. Because temperature involved during diamond deposition is sufficiently high, boron present on the substrate gets incorporated in CVD gas environment and also on the growing surface and affects nucleation and growth features of diamond. From the figure it can be clearly seen that boronated film is continuous with almost rounded grains. The diamond crystallites exhibit random growth due to high secondary nucleation leading to cauliflower structure. This is in contrast to crystallites observed in case of diamond deposits with same deposition conditions but without boron incorporation shown in Figure (3), and since both types of films are deposited in identical deposition conditions except presence of boron in the later case, the

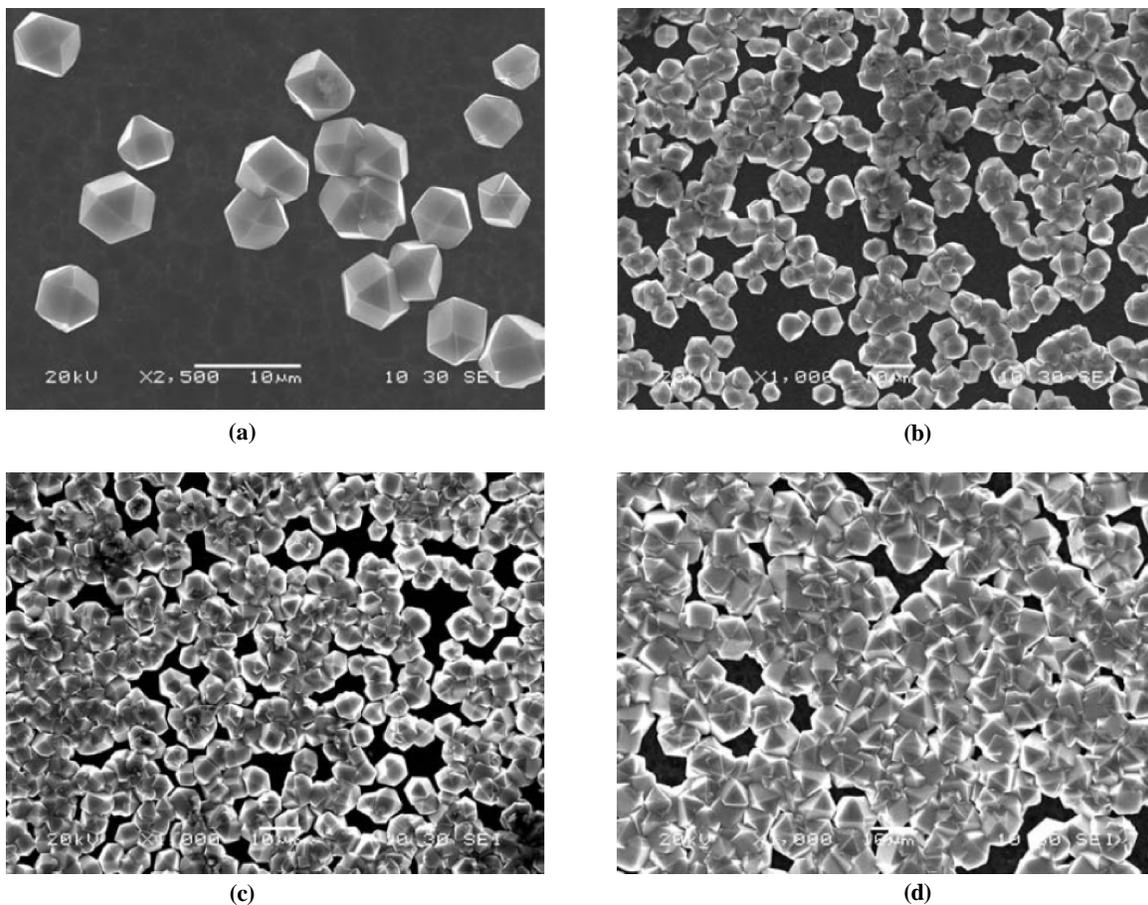


Figure 2 : SEM micrographs of diamond films, (a and b) without substrate pretreatment, (c) 10 minutes substrate pretreatment, (d) 20 minutes substrate pretreatment.

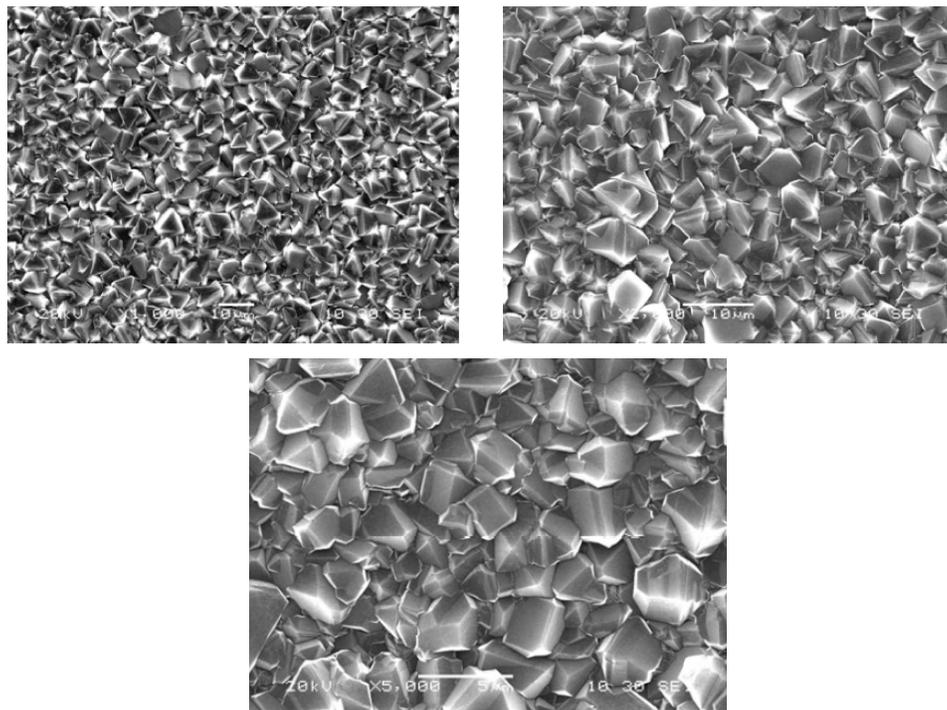


Figure 3 : SEM micrographs of diamond films after 30 minutes pretreatment of the substrate

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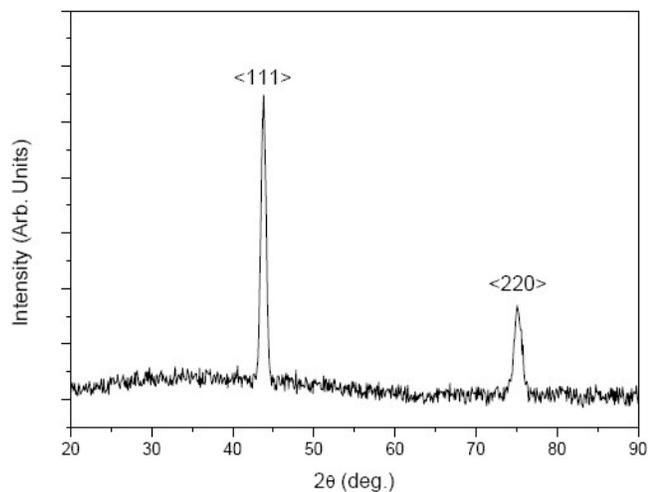


Figure 4 : Low angle x-ray diffraction pattern of the deposited diamond film after 30 minutes pretreatment of the substrate

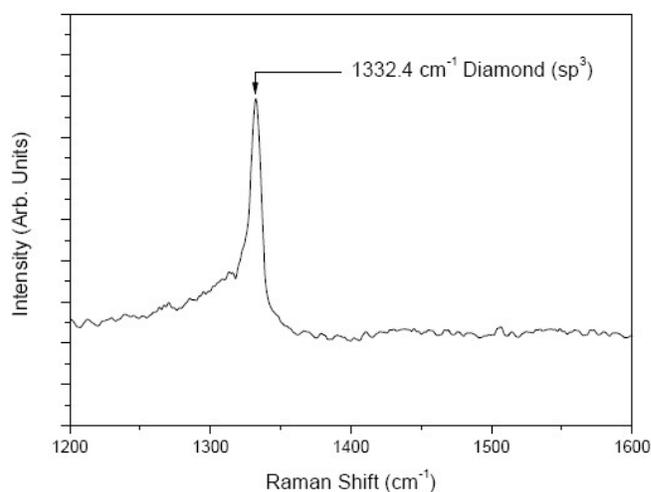


Figure 5 : Raman spectrum of diamond film after 30 minutes pretreatment of the substrate

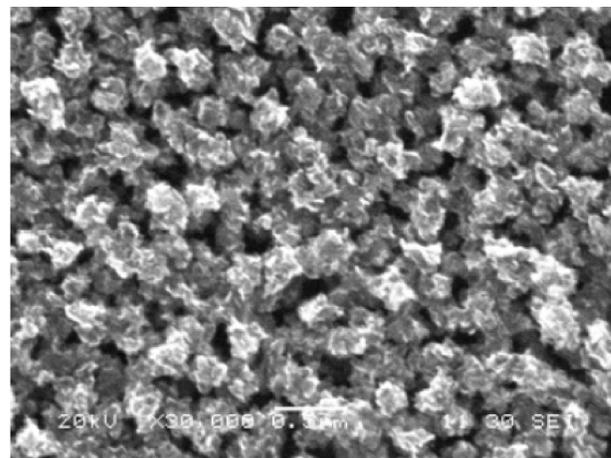
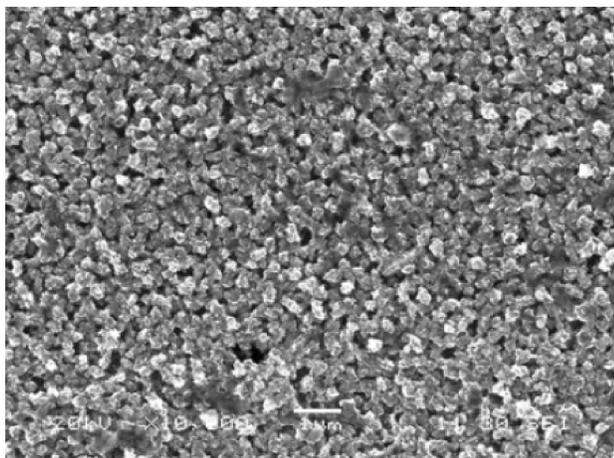


Figure 6 : SEM micrographs of boronated diamond films showing the cauliflower structure

variation in morphological features is expected to be due to presence of boron only. The presence of boron at the growing diamond surface could lead to secondary nucleation and modify the morphological features of resulting diamond films^[20,21]. The thickness of this film was found to be about 3.5 μm .

The low angle x-ray diffraction measurement is also carried out on the boronated diamond films and it is found that it exhibits significant diffraction peaks corresponding to $\langle 111 \rangle$ and $\langle 220 \rangle$ planes of diamond lattice as shown in Figure 7.

The Raman spectrum corresponds to the boronated diamond film is shown in Figure 8 which indicates peak corresponding to diamond (sp^3) phase at 1333.3 cm^{-1} and additionally wide peak near 1550.6 cm^{-1} due to non-diamond (sp^2) phase^[22] which can be attributed to higher amount of grain boundaries present in the

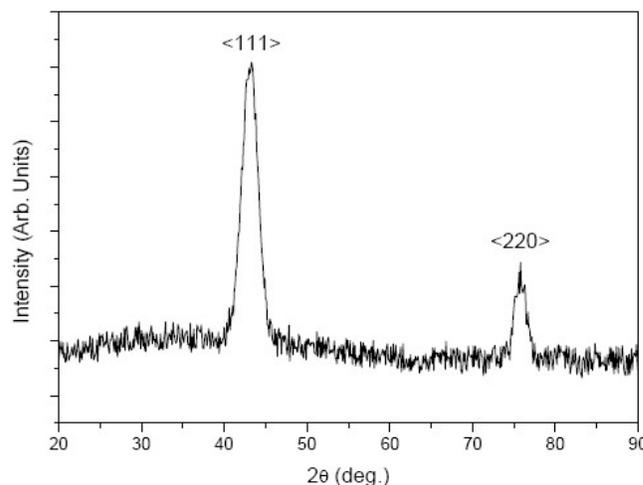


Figure 7 : Low angle x-ray diffraction pattern of the boronated diamond film

boronated diamond films as compared to that in the intrinsic diamond films.

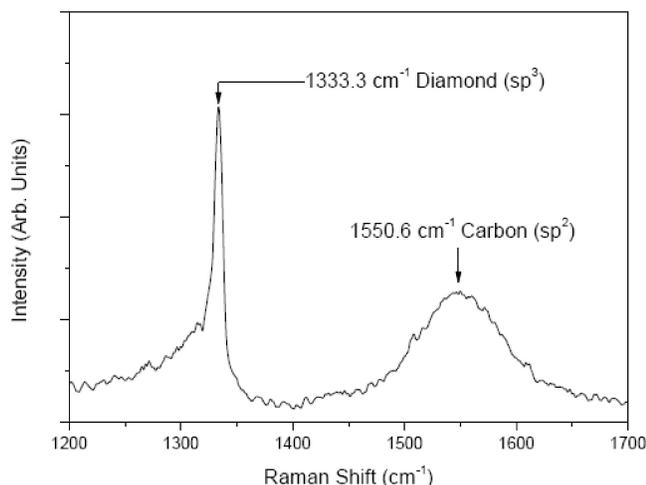


Figure 8 : Raman spectrum of boronated diamond film

CONCLUSIONS

Diamond films have been successfully deposited on (100) single crystal silicon substrates by HF-CVD technique using $H_2:CH_4$ (100:1 sccm) gas mixture. The effect of substrate pretreatment on the structure and morphology of the deposited films have been investigated. It was found that the pretreatment of the substrate enhances the growth rate and leads to significant change in the surface morphology of the deposited films when the time of pretreatment is high enough (30 minutes). A successful attempt has been made to incorporate boron in easy and simple way in the deposited diamond films. It was found that the presence of boron introduced cauliflower type features to diamond crystallites on micron scale. The Raman spectrum for the deposited film after 30 minutes substrate treatment exhibited sharp peak at 1332.4 cm^{-1} indicating presence of diamond (sp^3) phase only while Raman measurement corresponds to the boronated diamond film deposited under the same conditions indicates peak corresponding to diamond (sp^3) phase at 1333.3 cm^{-1} and additionally a wide peak contribution near 1550.6 cm^{-1} due to non-diamond (sp^2) phase, and since both types of films are deposited in identical deposition conditions except presence of boron in the later case, the variation in morphological features is expected to be due to presence of boron only. The presence of boron at the growing diamond surface could lead to secondary nucleation and modify the morphological features of result-

ing diamond films^[22].

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