

Comparative Study of Diamond Films Grown on Silicon Substrate Using Microwave Plasma Chemical Vapor Deposition and Hot-Filament Chemical Vapor Deposition Technique

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Abstract—Diamond films on the p-type Si(111) and p-type(100) substrates were prepared by microwave plasma chemical vapor deposition (MWCVD) and hot-filament chemical vapor deposition (HFCVD) by using a mixture of methane CH₄ and hydrogen H₂ as gas feed. The structure and composition of the films have been investigated by X-ray Diffraction, Raman Spectroscopy and Scanning Electron Microscopy methods. A high quality diamond crystalline structure of the obtained films by using HFCVD method was confirmed by clear XRD-pattern. SEM images show that the prepared films are polycrystalline diamond films consisting of diamond single crystallites (111)-orientation perpendicular to the substrate. Diamond films grown on silicon substrates by using HFCVD show good quality diamond and fewer non-diamond components.

Key words: Diamond, HFCVD, MWCVD

INTRODUCTION

Diamond is one of the most important materials for advanced engineering due to its unique and extreme properties in hardness, wear resistance, good thermal expansion coefficient and room temperature thermal conductivity of any known material as well as low coefficient of friction. Applications include coatings for machine cutting tools, heat sinks for electronic devices and protective coatings for aerospace component. Diamond can be synthesized by various methods [Alder and Charistian, 1961; Bundy, 1963; Choi et al., 1994; Kanda et al., 1994; Lux et al., 1992; Stephan et al., 1992; Yin et al., 2001]. Unfortunately, due to the high cost, limited size, and uneasily controlled impurities of natural and synthetic high-pressure, high-temperature (HPHT) diamond, the diamond applications have in fact been limited in comparison to its great potential. CVD diamond can overcome these difficulties and is the most promising avenue available for synthetic diamond [Shendorova et al., 2002]. The major CVD diamond-techniques are the hot-filament, arcjet-torch, AC- and DC-discharge, radio-frequency plasma, and microwave plasma methods. Carbon is unique in that simple changes in its local bonding can give rise to materials as diverse as diamond, graphite, fullerene, carbon nanotubes, and disordered, nanostructured and amorphous carbon [Shendorova et al., 2002]. That is why diamond nucleation and growth, particularly on non-diamond substrates, is an issue of current interest for growing diamond films for electronic and optical applications. In a previous study, we reported the growth of Lonsdaleite diamond on flashed and reconstructed Si(100) and the nucleation of diamond on carbon nanotubes as a seed

layer by HFCVD [Ansari et al., 2004; Cheim et al., 2003]. In this communication, we study the diamond grown films on silicon substrate by using HFCVD and MWCVD. A mixture of CH₄/H₂ was used as the feed gas. The film structure and composition were characterized by SEM, XRD and Raman methods.

EXPERIMENTAL

1. Microwave Chemical Vapor Deposition (MWCVD)

The diamond depositions were conducted in a 2.45-GHz Applied Science Technology (ASTex), USA, made AX-2115 system with a stainless-steel vacuum chamber of cylindrical shape of 18 cm diameter and 30 cm high, as presented schematically in Fig. 1(a).

Silicon wafers (111) orientation was used as substrates. In order to diamond nucleation enhancement, Si-substrates were scratched by diamond powder of up to 10 μm size. After loading Si-substrate into vacuum chamber, it was evacuated to a base pressure of $<10^{-6}$ torr by the high vacuum system. Then a mixture of 3 sccm (standard cubic centimeter per minute) of 99,999 pure methane CH₄ and 300 sccm of 99,999 pure hydrogen H₂ is inlet into chamber by gas system; gas flow rates were controlled by MFC (mass flow controller) with a precision of 0.1 sccm and 1.0 sccm for methane and hydrogen, respectively. Total pressure in the chamber was kept at 50 torr $\pm$ 1 torr during deposition time. Base substrate temperature T_s with accuracy ± 1 °C was measured by thermocouple and controlled by substrate heater and surface substrate temperature T_s^{pyr} was measured by optical pyrometer. Two series of samples have been deposited under conditions summarized in Table 1.

2. Hot-Filament Chemical Vapor Deposition (HFCVD)

All experiments were carried out on p-Si(100) substrates scratched manually by using diamond paste with 1 μm particles. The particles

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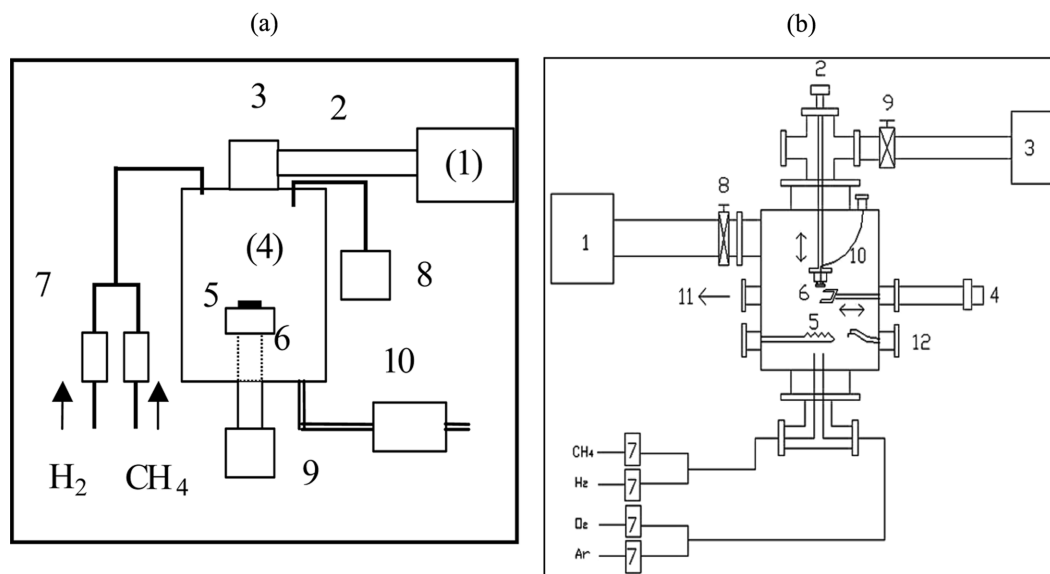


Fig. 1. Schematic diagrams of (a) MWCVD and (b) HFCVD reactors.

- (a)
1. Magnetron head 2.45 GHZ
 2. Wave guide
 3. Wave coupler
 4. Stainless-steel vacuum chamber
 5. Substrate
 6. Substrate holder
 7. Gas sources and gas supply system
 8. Optical pyrometer
 9. Substrate heater with substrate locator
 10. Vacuum system with turbo pump

- (b)
1. Turbo pump (520L/S)
 2. Sample manipulator
 3. Turbo pump (56 L/S)
 4. Load-lock
 5. W-filament
 6. Substrate holder
 7. Mass flow controller
 8. Needle valve
 9. Gate valve
 10. K-type thermocouple
 11. Analysis chamber
 12. Power connector

Table 1. Deposition conditions

Sample	Flow rate CH ₄ , sccm	Flow rate H ₂ , sccm	Total pressure torr	T _s , °C	T _s ^{pyr} , °C	Time, hours
A	1	100	50	700	1,060	3
B	1	100	30	750	2,150	2

were washed with acetone and de-ionized water. The system was evacuated to a base pressure $\sim 10^{-9}$ torr. Tungsten filament was positioned at a 5 mm distance from the substrate, as presented schematically in Fig. 1(b) and heated to $2,150 \pm 50^\circ\text{C}$ as measured using an optical pyrometer Minolta TR-630, Japan. A gas mixture of H₂ (99.999%) and CH₄ (99.5%) in 1 : 100 proportions was introduced in the deposition chamber at a flow rate of 100 sccm, so that the pressure inside the chamber rose to 30 ± 2 torr. Deposition was carried out for two hours.

X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy were used for film investigations.

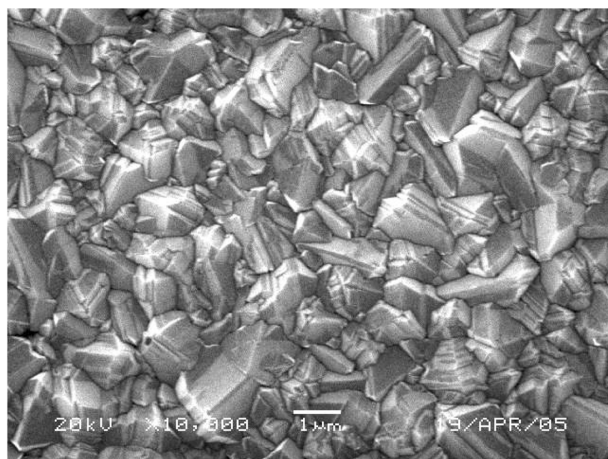
RESULTS AND DISCUSSION

Surface morphology: Typical SEM images of diamond film on scratched Si(111) and Si(100) by using Microwave chemical vapor deposition (HWCVD) and hot-filament chemical vapor deposition (HFCVD) techniques are illustrated in Fig. 2. It is clear from (a) that the film was composed from particles of different size from

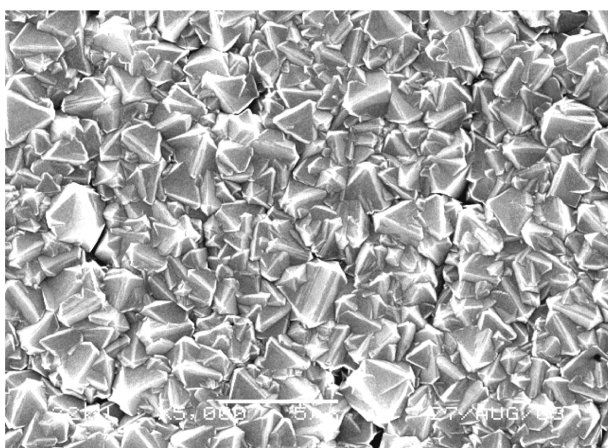
nano- to micro-scale. Here the grown film impression is that the particles are larger and a careful examination of sample (b) shows that there are many triangular platelets on top of bigger crystals. These triangles have sides $\sim 1.5 \mu\text{m}$ in length and they are (111) oriented crystallites. This type of surface morphology is typical for diamond (111)-directions growth [Stammle et al., 2002]. These facts indicate that the nucleation and growth processes really continuously occurred during deposition time.

The crystalline structure of the films was characterized by XRD and the patterns are presented in Fig. 3. In both types of sample, a peak at the Bragg angle of $\sim 43.9^\circ$ is observed indicating the diffraction from (111)-plane. This peak corresponds to typical cubic diamond peak as can be seen in the JCPDS cards (06-0675).

Diamond grown films were also analyzed by micro Raman spectroscopic technique. Raman scattering is very powerful means for characterization of carbon-bonding [Ferrari, 2002]. Carbyne has no crystalline structure and gives Raman peaks at a wavenumber $\sim 2,100 \text{ cm}^{-1}$ [Ferrari et al., 2003]. Graphite has crystalline structure A_g-type, characterized by flat hexagonal layer of covalent sp²-bonded



(a)



(b)

Fig. 2. SEM images of (a) Diamond film grown on scratched Si (111) surface using MWCVD and (b) Diamond film grown on scratched Si(100) surface using HFCVD.

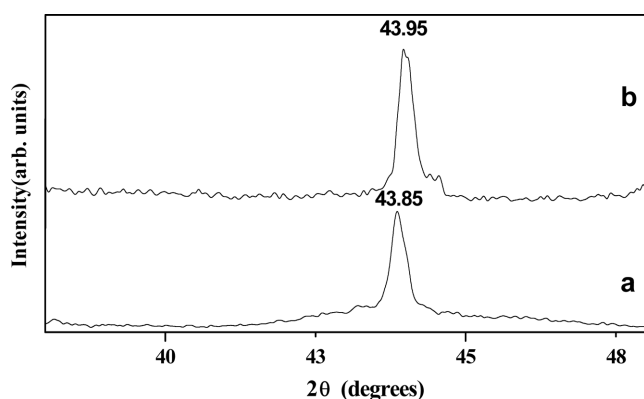


Fig. 3. XRD images of (a) Diamond film grown on scratched Si (111) surface using MWCVD and (b) Diamond film grown on scratched Si(100) surface using HFCVD.

carbon atoms and van der Waals force between the layers. It depends on the degree of graphitic ordering and there must exist two bands near $\sim 1,580\text{ cm}^{-1}$ and $1,355\text{ cm}^{-1}$ in the Raman spectrum called

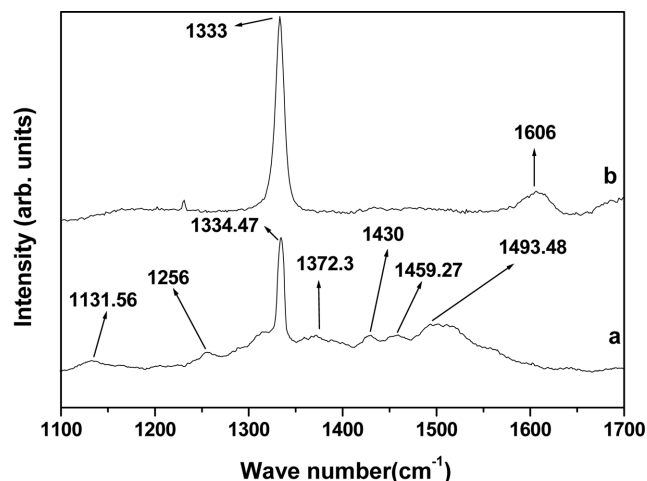


Fig. 4. Raman images of (a) Diamond film grown on scratched Si (111) surface using MWCVD and (b) Diamond film grown on scratched Si(100) surface using HFCVD.

G-band (Graphite) and D-band (Disordered graphitic rings in the flat hexagonal layers) [Ferrari, 2002]. Diamond has crystalline structure A_4 -type, characterized by tetrahedral sp^3 -bonded carbon; and a typical Raman peak of natural crystalline diamond is located at $\sim 1,332\text{ cm}^{-1}$. For CVD diamond, commonly composed from separate crystallites, there may be observed Raman peaks at $\sim 1,060\text{ cm}^{-1}$, $1,150\text{ cm}^{-1}$, $1,260\text{ cm}^{-1}$, and $1,475\text{ cm}^{-1}$ due to short-range of diamond ordering (nanodiamond) [Ferrari and Robertson, 2001; Petrov et al., 1999]. The Fig. 4 presents typical Raman spectra for the two types of samples prepared. Raman shows no peak at $\sim 2,100\text{ cm}^{-1}$ and that confirms no carbyne (sp^1 -hybridization) in the films. Fig. 4(a) shows very sharp and strong peak with FWHM at $\sim 9\text{ cm}^{-1}$ and at $\sim 1,334.47\text{ cm}^{-1}$, that is a typical cubic diamond peak. The observed small peaks at $\sim 1,064\text{ cm}^{-1}$, $1,135\text{ cm}^{-1}$, $1,255\text{ cm}^{-1}$ obviously are due to nanodiamond. The large and broad peak at $\sim 1,503\text{ cm}^{-1}$ is due to a mixture of sp^2 - and sp^3 -carbon, called diamond-like carbon (DLC) [Ferrari and Robertson, 2001]. The nature of small peaks which often appeared at near $\sim 1,373\text{ cm}^{-1}$, $\sim 1,429\text{ cm}^{-1}$, and $\sim 1,455\text{ cm}^{-1}$ like shown in Fig. 4(a) is still questionable. A peak at $\sim 1,447\text{ cm}^{-1}$ was reported to be for nanodiamond [Petrov et al., 1999]. We suggest that these peaks are due to metastable states because they are not always appearing and their locations are not fixed, but a little bit changed. The other opinion for these peaks can be due to the mixture of disordered tetrahedral sp^3 -carbon presented at the grain boundaries with small portion sp^2 -carbon (for DLC: $sp^2/sp^3 \sim 30\%/60\%$) or hydrogen generated tetrahedral sp^3 -C:H. For the first situation, the mixture can be identified as defected (or nano-) diamond. The Raman spectrum of the film grown by HFCVD technique (Fig. 4b) is similar to the well reported spectra with a sharp peak at $1,333\text{ cm}^{-1}$ which is a typical diamond peak and a broad peak corresponding to graphitic phase at $1,606\text{ cm}^{-1}$.

CONCLUSION

A comparative study of the growth of polycrystalline film on Si-substrate was carried out by using hot filament chemical deposition (HFCVD) and microwave plasma chemical vapor deposition

(MWCVD) using a mixture of methane and hydrogen as feed gas. It was found that films prepared by HFCVD are better in quality than MWCVD prepared films. SEM and Raman spectra indicate that the obtained film should be composed from diamond crystallites A_4 -type cubic structure ranging from nano- to micro-scale. Raman spectra also confirm that the prepared films consist mostly of sp^3 -bonded carbon in the diamond structure, and only a small portion of sp^2 -bonded carbon coexists together with sp^3 -carbon in the thin boundaries between diamond crystallites. There is no sp^2 -bonded carbon in the graphitic ordering in the prepared film.

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