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Nucleation of Diamond over Nanotube Coated Si Substrate Using Hot Filament Chemical Vapor Deposition (CVD) System

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Abstract−We studied the use of carbon nanotubes as a seeding layer for the nucleation of diamond on Si (100) substrate by using a hot filament chemical vapor deposition (HFCVD) system. Prior to deposition, substrates were seeded with multi-wall carbon nanotube (MWCNT) powder which was prepared separately. MWCNTs were used as nucleation precursors. The diamond grains grew essentially over the nanotubes with a higher growth density in comparison with the un-seeded substrates. The scanning electron microscopy (SEM) image of surface morphology shows crystallites of cauliflower shaped grains. The micro Raman spectroscopic results show a sharp peak at 1,332 cm^{-1} corresponding to diamond phase. X-ray photoelectron spectroscopic study show the presence of carbon (C_{1s}) phase.

Key words: HFCVD, Diamond, Carbon Nanotubes Seeding

INTRODUCTION

Over the past 40 years, a variety of techniques have been evolved for the synthesis of diamond including high pressure high temperature (HPHT) processes, chemical vapor deposition (CVD), physical vapor deposition (PVD) etc. The CVD process is one of the most important technological developments since it gives a high quality diamond coating on pre-shaped parts and on a variety of substrates including insulators, semiconductors and metals ranging from single crystal to amorphous materials. The success in growing good quality and dense diamond by using CVD lies in various enhancing techniques, viz. surface pretreatment, scratching, seeding with nucleation precursors, electrical biasing, covering/coating, ion implantation, pulsed laser irradiation, carburization and use of noble gases along with the hydrocarbon gases [Lawrence and Kania, 1995; Baranauskas et al., 2000].

The nucleation mechanism on non-diamond substrates, which has been outlined in many reports, is as follows. First, an activated species (high energy carbon atom or hydrocarbons), which is supplied from the respective plasma, migrates on the substrate forming a cluster at a stable site. This process is achieved with much difficulty, since the produced cluster tends to evaporate due to the presence of high density hydrogen plasma and high substrate temperature. In order to overcome such problems, either the carbon concentration in the raw material is increased or the substrate surface is pre-treated (scratching). Also, the substrates with high carbon affinity are selected to stabilize the diamond nucleus. Thus the cluster produced is easily transformed into the diamond nucleus by plasma energy [Yugo et al., 1997].

The diamond nucleation mechanism is generally clear; however, the structure of the precursor and the transition mechanism from an amorphous carbon cluster to a diamond nucleation remain unclear. In this paper, an attempt is made to study the nucleation of diamond grains on silicon substrate seeded with multi-wall carbon nanotubes (surface pre-treatment) by using an HFCVD system with a gaseous mixture of H_2 and CH_4. Morphological data obtained by SEM and characterizations by XPS and Raman spectra are discussed.

EXPERIMENTATION

Diamond films were deposited by using HFCVD as reported earlier [Cheim et al., 2000, 2003]. A mirror polished side of p-type Si (100) wafers of size 15×7×0.5 mm^3 was used for deposition. The seeded/unseeded substrates were loaded onto a sample holder and the assembly was then transferred to the high-vacuum reaction chamber. The substrate was aligned at the center of the reaction chamber, just above the filament. The filament (15 mm long and 5 mm cross sectional dia.) was horizontally installed at the center of the chamber perpendicular to the gas flow direction. Distance between the substrate and filament was kept as ~5 mm which was adjusted by the manipulator.

For seeding, multi-wall carbon nanotubes (powder form) were used, which were prepared by catalytic pyrolysis [Fazle et al., 2001]. Seeding of Si substrate with separately prepared carbon nanotubes was carried out in the following way. 1% of MWCNT was mixed in a pre-prepared 10% polyvinyl alcohol (PVA) solution and was dispersed in the PVA solution by using ultrasonic vibrations for uniform dispersion. The substrates were then dipped in the solution for 1 min followed by drying in hot air for a few minutes. PVA was chosen as a dispersing medium since it can be easily evaporated at low temperatures. Fig. 1a and 1b show top view SEM images of dispersed MWCNT at different places on the seeded Si substrate. It is seen that the dispersion is not very uniform as the carbon nanotubes are coagulated forming clumps.

A mixture of high purity H_2 (99.999%), CH_4 (99.95%) was introduced from the bottom side of the setup and the flow rates were

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‡ This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

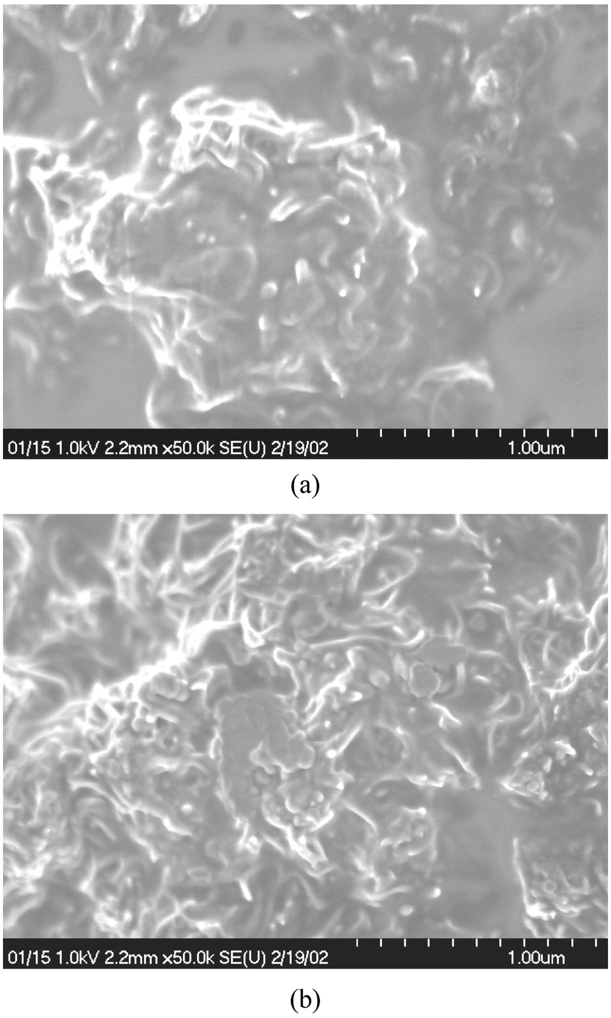


Fig. 1. (a) & (b) Top view SEM image of carbon nanotubes coated on Si substrate at two different places (carbon seeded Si substrate before diamond deposition).

controlled by using mass flow controllers (MFC). Reaction gases consisting of 1 vol% of CH_4, and 100 vol% of H_2 were supplied in a total flow rate of 100 sccm and the total gas pressure inside the reaction chamber was kept constant as 30±2 Torr, throughout the deposition process. The deposition was carried out at a substrate temperature of ~950 °C and the filament temperature was maintained at 2,400±50 °C, which was measured by optical pyrometer (Minolta TR-630, Japan). The substrate was heated by filament radiation and its temperature was measured by thermocouple, which was adjusted to touch the substrate from the backside. The deposition was carried out for two hours.

The morphological study of the grown film was carried out by Scanning Electron Microscope (SEM, JSM-6400, JEOL, Japan) and Field Emission SEM (Hitachi S-4700). For structural analysis X-ray photoelectron spectroscopy and Micro Raman spectroscopy with He-Ne laser (λ=632.8 nm, Renishaw) were used.

RESULTS AND DISCUSSION

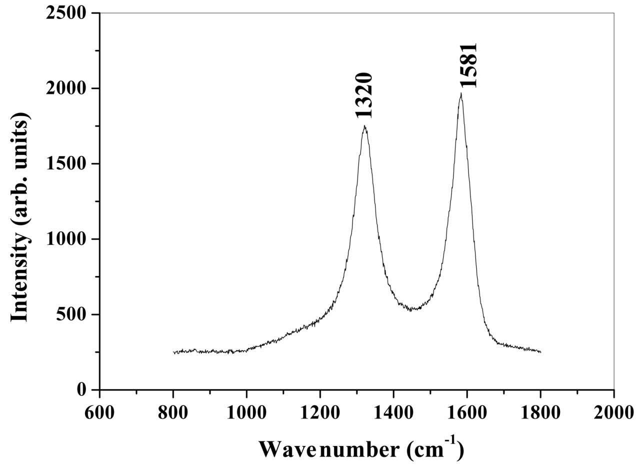
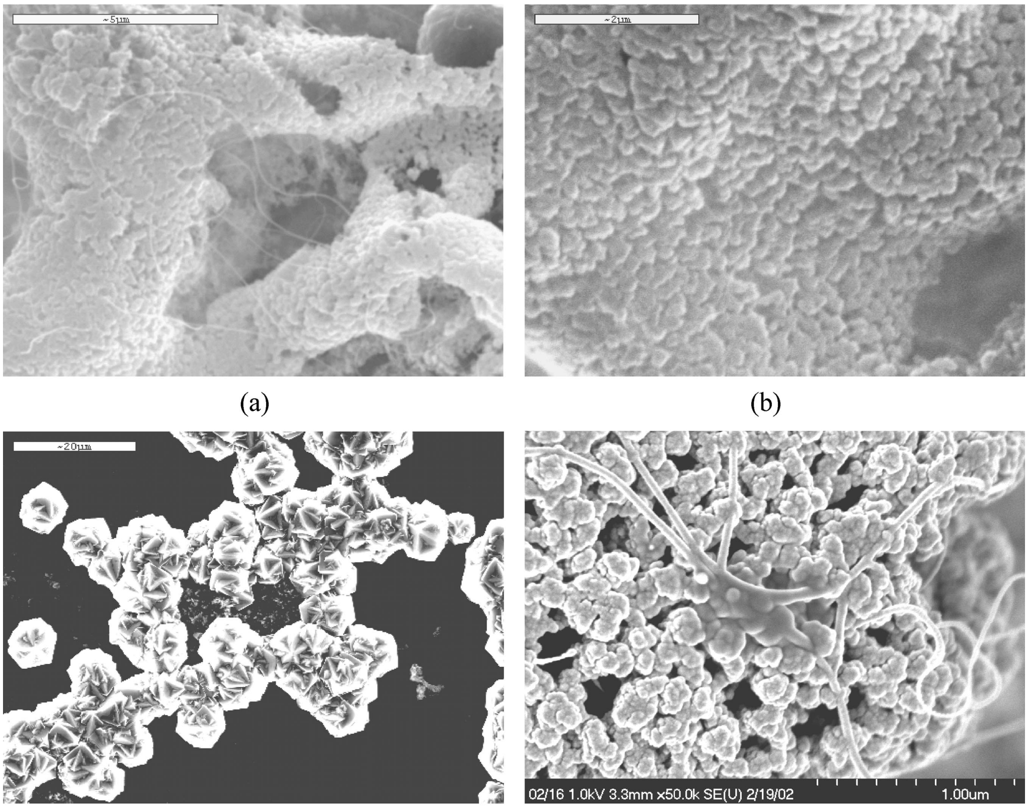


Fig. 2. Raman spectrum of the carbon nanotubes seeded on Si substrate (before diamond deposition).

Micro Raman spectroscopy was used to investigate the elements and structure of the seeding material (i.e., carbon nanotubes) as well as the grown film. Fig. 2 shows the Raman spectrum of the seeding material indicating the graphite structure. The G-band at 1,581 cm^{-1} reveals that the CNTs are multi-walled CNTs. The D-band at 1,320 cm^{-1} indicates the existence of defects or carbonaceous (amorphous carbon) particles on the surface of CNTs. It is suggested that the D-band mainly indicates the defective feature of graphite sheets. In the spectrum, it is noticed that the relative intensity of G-band to D-band is close to unity, indicating good crystallinity of graphite sheets. Therefore, it can be concluded, based on Raman studies, that the CNTs have a high crystallinity multiwalled structure with some defects on the wall surface. The radial breathing modes were not observed in the present case and hence data not presented.

Fig. 3a and 3b show top view SEM images of the diamond film deposited on CNT seeded substrate and Fig. 3c is the SEM image of the film grown on unseeded substrate. From Fig. 3a and 3b, it is seen that the diamond grains apparently grow over the carbon nanotubes and less over the other places. Fig. 3b shows a high magnification image where grains are seen to be of cauliflower shape. It is seen that the diamond has grown on the seeded CNT, which is not flat and much rougher than the mirror polished Si surface (as also seen in Fig. 1a and 1b). In order to calculate surface nucleation density, the number of diamond nuclei per unit area should be determined by dividing the number of grains visible in SEM images by the effective substrate area. In the present case, the effective substrate area cannot be easily measured from the SEM image and hence a rough estimate of surface nucleation density is given assuming a smooth surface, which is ~3×10^{10} cm^{-2} whereas for deposition without seeding (Fig. 3c), scattered diamond grains are seen with very low surface growth density (5×10^{7} cm^{-2}). Fig. 3d shows FE-SEM image of the film, which clearly shows that the diamond grains are grown entirely on the carbon nanotubes. The average size of the grains is ~50 nm.

Fig. 4 shows the Raman spectrum of the films deposited on the carbon nanotube seeded substrate. It shows a very intense and broad peak at 1,332 cm^{-1}, which corresponds to a diamond and a small peak at 1,570 cm^{-1} corresponding to a non-diamond carbon phase. This indicates that the quality of the deposited film is good. The



(a) (b)

(c) (d)

Fig. 3. SEM images of (a) diamond deposited on CNT seeded substrate (b) diamond deposited on CNT seeded substrate with higher magnification (c) diamond deposited on un-seeded substrate and (d) FE-SEM image of diamond deposited on MWCNT seeded substrate.

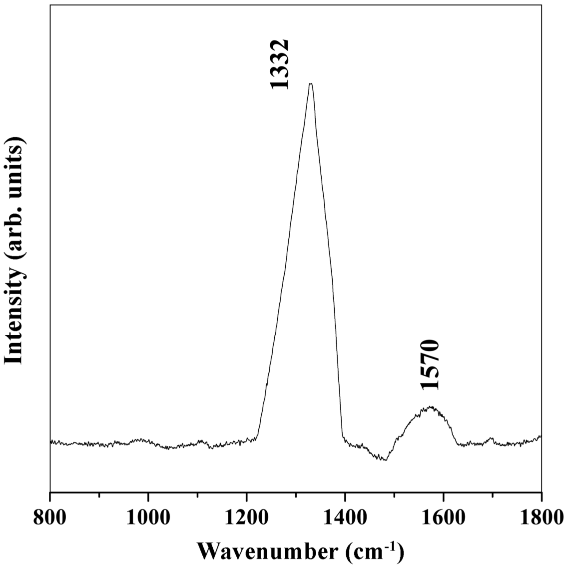


Fig. 4. Raman spectrum of the diamond film deposited on MWCNT seeded substrate.

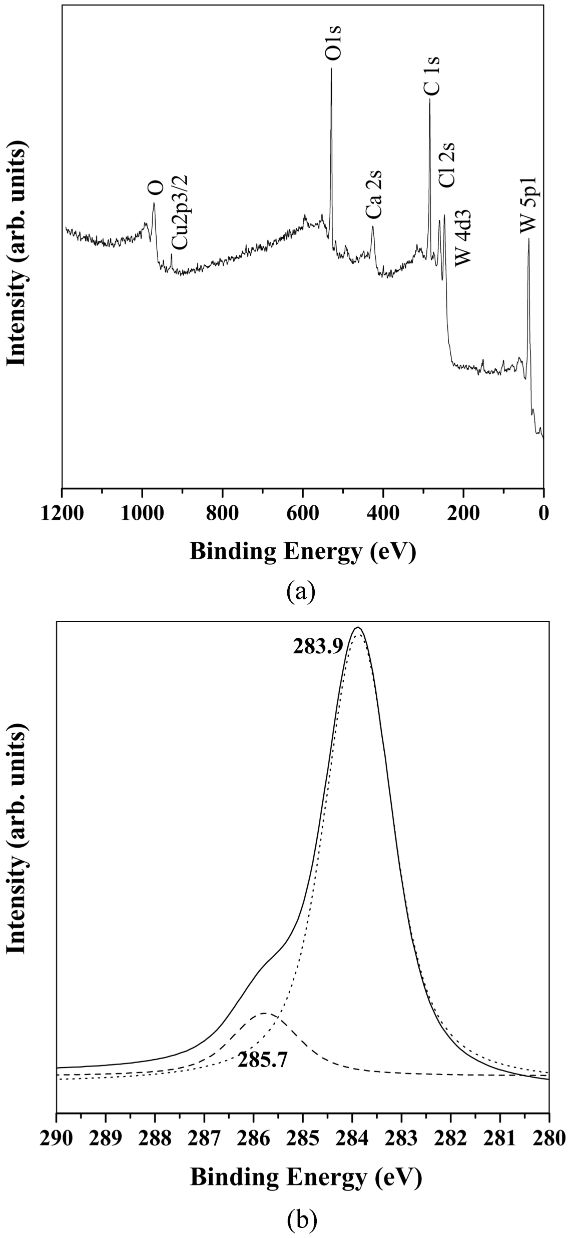
peak broadness indicates that strains are developed in the film during deposition.

Fig. 5a shows a wide scan XPS of the grown diamond film. It shows peaks corresponding to various shells of tungsten, carbon, calcium, oxygen and copper. Traces of tungsten are seen which are likely to be on the surface of the film and must have evaporated from the hot filament. The appearance of $Cu_{2p3/2}$ peak is due to the substrate holder since samples were mounted on Cu holder for XPS study.

The core level (C_{1s}) XPS spectrum of the diamond film is presented in Fig. 5b. It is seen that the peak at 283.9 eV is a C_{1s} peak, which clearly confirms that the film composition is basically carbon.

An attempt is made to fit the core level C_{1s} XPS curves by using Shirley-type base line with mixed Gaussian (30%) and Lorentzian (70%) profile and controlled FWHM. The entire curve fitting was carried out with chi-squared value less than 2 eV, which is reported to be good value for best fitting [Crist, 2000]. The corresponding curves are shown in Fig. 5b. It can be seen there are two peaks at 283.9 eV and 285.7 eV. The appearance of these two peaks can be related to the crystallinity of the grown film, which indicates that film is not fully crystallized and contains amorphous carbon.

Hou et al. [2002] have also reported growth of diamond on carbon nanotube nucleated substrate. The differences in the present and their work are as below: (i) in the present work, substrates were not scratched with diamond paste or sandpaper, (ii) The deposition time in the present work was only 2 hrs, whereas in their case it was 3.5 hrs. Surface growth density in the present work is ~3×10^{10} cm^{-2}



(a)

(b)

Fig. 5. (a) Wide scan XPS spectrum of the films deposited at 950 °C for two hours on MWCNT seeded Si substrate. (b) Core level C_{1s} XPS spectra and curve fitting of the diamond films deposited at 950 °C for two hours on MWCNT seeded Si substrate.

whereas they reported it to be ~2×10^9 cm^{-2}. This indicates that the growth rate in the present work is slightly higher than the reported work. Higher growth rate in the present work may be due to the higher substrate temperature in comparison with the work reported by Hou et al. [2002].

It is well known that the nucleation enhancement by scratching is due to the minimization of interfacial energy on sharp convex surfaces, breaking of number of surface bonds or dangling bonds at sharp edges, strain field effect, rapid carbon saturation and surface oxide removal. Another method of nucleation enhancement is the preparation of non-volatile graphitic particles. These particles can form precursor molecules under the typical CVD condition of hydrogenation in the atomic hydrogen environment. Seeding of the substrate surface with CNT results in preparation of such surfaces as in the present work. Raman studies showed that the CNTs are crystalline but have some defects on the wall surface. The other reason of nucleation enhancement with CNT is due to allotropes of carbon having some structural resemblances and same chemical bond of sp^3. The seed layer can act as a template for the growth of diamond. Additionally, in HFCVD due to the H_2 (atomic hydrogen) ambient, the carbon nanotubes break into pieces lengthwise and form nano-anions like structure due to the defects in the nanotubes. The phenomenon is similar to that of the breaking of surface bonds or dangling bonds at the sharp edges. The sp^3 bonds at the broken ends turn to dangling bonds. Furthermore, due to H_2 and high temperature, the sp^2 bonds at the middle of the tubes can open and turn into sp^2 dangling bonds, and finally turn into sp^3 bonds again [Meilunas et al., 1991; Gruen et al., 1994; Terrones and Mackay, 1992]. This results in countless heterogeneous nucleation sites and the improvements of nucleation and growth for diamond. As can be seen in Fig. 3a, the growth of diamond is mostly on the agglomerated nanotubes and is very rare on other places. This indicates that the formation of nano-anions and separation action of hydrogen is strong and hence growth of diamond is high. The appearance of a non-diamond carbon phase indicates that the nanotubes are in a clump form, and thus the reaction area between carbon nanotubes and hydrogen during deposition is very small. The diamond that nucleates from broken carbon nanotubes ends and graphite phase of CNTs results in a non-diamond phase (graphite). Therefore in order to have a uniform growth of quality diamond over a large area, the carbon nanotubes need to be coated uniformly over the substrate. Nucleation enhancement with CNT seed layer can also be attributed to the physical and chemical effects associated with changes to the surface and changes to the gas chemistry in the immediate vicinity of the substrate surface. The seed layers may promote carbon saturation at the substrate surface, and provide high energy sites or nucleation centers, which is one of the basic requirements for the diamond nucleation.

CONCLUSION

We have successfully nucleated a high density diamond on Si substrate using carbon nanotubes as a nucleation precursor in an HFCVD system. The diamond grains grew essentially over the nanotubes with a higher growth density in comparison with the un-seeded substrates. The scanning electron microscopy (SEM) image of surface morphology shows crystallites of cauliflower shaped grains. The Raman spectra show a good quality film with a peak at 1,333 cm^{-1}. An XPS study shows the presence of C_{1s} phase with partly crystalline film. The quality of the films can still be improved with better quality of carbon nanotubes and uniform dispersion of carbon nanotubes over substrate. Future work can be to improve the quality of diamond and to deposit over a large area. Different types of carbon nanotubes can also be tried as a seeding layer for variation in growth parameters.

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