

Chemical vapor deposition of novel carbon materials

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Abstract

Nanocrystalline diamond thin films have been prepared using hot filament CVD technique with a mixture of CH₄/H₂/Ar as the reactant gas. We demonstrated that the ratio of H₂ to Ar in the reactant gas plays an important role in control of the grain size of diamonds and the growth of the nanocrystalline diamonds. In addition, we have investigated the growth of carbon nanotubes from catalytic CVD using a hydrocarbon as the reactant gas. Furthermore, focused ion beam technique has been developed to control the growth of carbon nanotubes individually. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Chemical vapor deposition; Diamond; Carbon; Scanning electron microscopy

1. Introduction

In recent years, novel carbon materials such as diamond thin films, diamond-like carbon, fullerene, and carbon nanotubes have been intensively investigated because of their great potential applications. A wide array of techniques have been developed for the synthesis of those novel carbon materials, among them chemical vapor deposition (CVD) technique has been proven to be a very versatile tool. For example, CVD technique has been used to synthesis highly oriented diamond thin film [1] and fullerene [2] in the past. More recently, nanocrystalline diamond thin films have been deposited from Ar/CH₄ microwave plasma enhanced CVD without the addition of molecular hydrogen in the reactant gas [3,4]. The nanocrystalline diamond thin films have several desirable characteristics, among them: (a) small grain size and surface roughness of the diamond films, (b) low grain boundary angle, and (c) synthesis from argon domain plasma. These characteristics can be exploited for applications in the cold-cathode electron field emitter for flat panel displays [5], protective coating for vacuum pump sealing [4], diffusion barrier [6] for the Cu interconnect technology, and potential hard transparent coating on oxide or nitride materials for optical applications. In contrast to nanocrystalline diamonds, carbon nanotubes have been demonstrated to be another novel carbon related

material, which has great potential applications in the advanced technology. Normally, carbon nanotubes are produced using carbon arc-discharge [7], laser ablation [8], and thermal catalytic CVD [9–11] techniques. Unfortunately, the formation and growth of carbon nanotubes cannot be controlled individually, which will be important to realize their further applications.

In this paper, we report hot filament CVD synthesis of nanocrystalline diamond thin films using a mixture of Ar/H₂/CH₄ as the reactant gas. Scanning electron microscopy (SEM) and Raman spectroscopy analyses provide evidence of the nanocrystalline diamond phase. It has been found that the ratio of H₂ and Ar in the reactant gas plays an important role in the control of grain size and surface roughness of the diamond films produced from the hot filament CVD system. In addition, the growth of carbon nanotubes from catalyst assisted CVD system has also been investigated. Particularly, in order to control the nucleation sites and then to tailor the growth of carbon nanotubes individually, focused ion beam (FIB) technique has been employed.

2. Experimental

2.1. Hot filament CVD synthesis of nanodiamond

A home-built hot filament CVD system was used for the deposition of diamond thin films. The growth chamber consists of a stainless steel chamber with view ports and feed throughs. The tungsten filament used was mounted vertically with a freestanding end. The typical diameter of

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the tungsten filaments was 0.7 mm in diameter and about 10 cm in length. An a.c. power supply was used with a voltage of 5–10 V and current of 40 to 50 A. Mixtures of precursor gases such as CH_4 , H_2 , and Ar are metered through individual MKS mass flow controllers. The pressure of the deposition chamber is controlled by a valve situated between the deposition chamber and a vacuum pump and monitored by a MKS pressure manometer. The silicon substrate was mounted on a micropositioner for precision positioning of the substrate to filament distance. Note that the silicon substrates were mechanical polished with diamond powder

to provide nucleation seeds of diamond. A thermocouple is mounted right behind the Si substrate. During deposition the substrate temperature was controlled by the distance between the filament and the substrate and typical value of this distance was 0.7 to 2.2 cm while the temperature was between 850 to 950°C.

2.2. Catalytic CVD synthesis of carbon nanotubes

Catalytic CVD synthesis of carbon nanotubes has been demonstrated recently [9–11]. The carbon nanotubes were

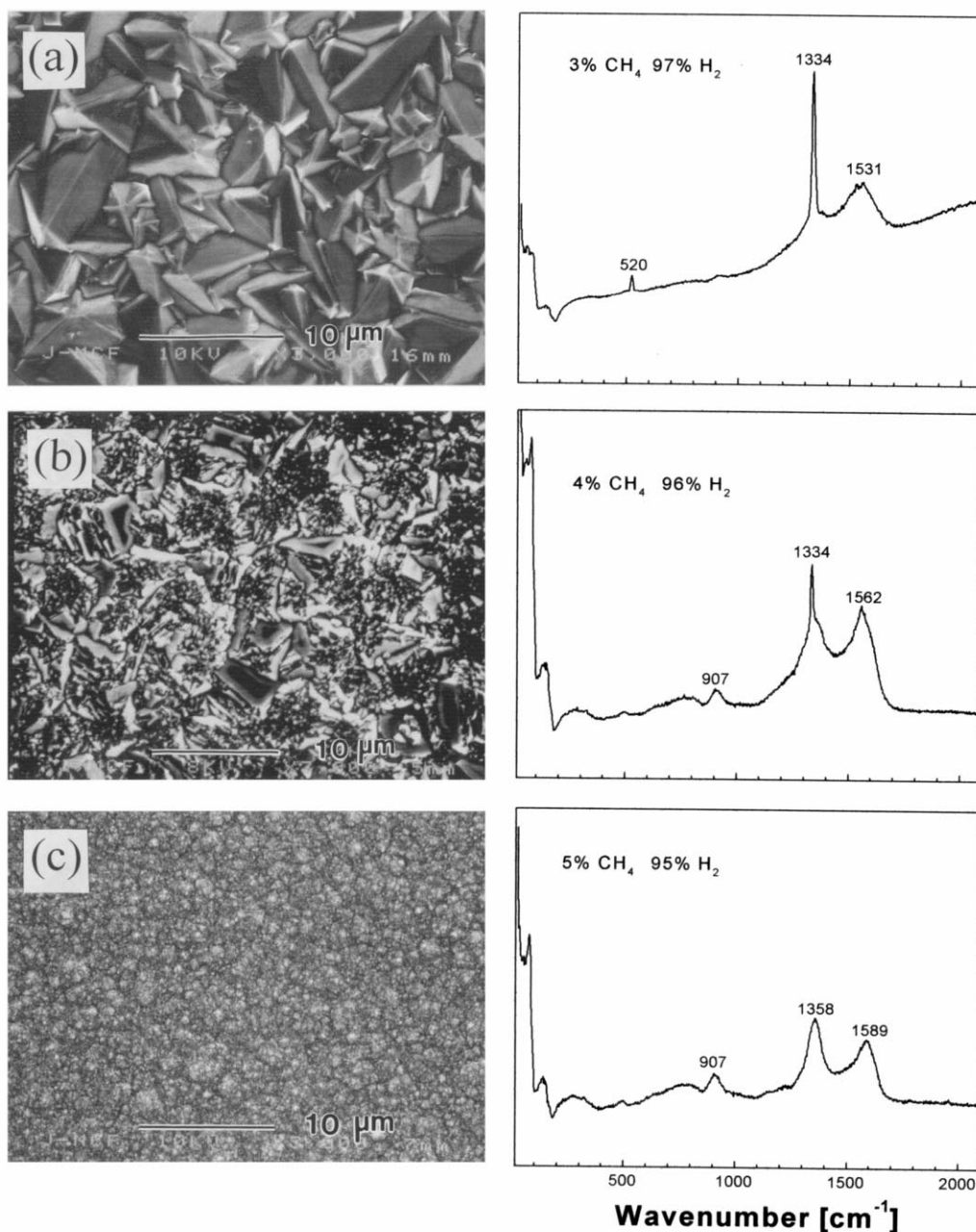


Fig. 1. Surface morphology of diamond thin films as a function of methane concentrations. (a) 3% of CH_4 , (b) 4% of CH_4 , and (c) 5% of CH_4 . The corresponding Raman spectra are shown on the right panel.

grown using a tube furnace. Precursors such as CH_4 , C_2H_2 and C_2H_4 have been employed in our study. In order to stimulate the formation and growth of carbon nanotubes, the catalysts such as Fe thin films, Fe-Ni nanoparticles, or FeSO_4 particles were first deposited on Si substrate. The Si substrate was then placed inside a small quartz tube and inserted into a larger quartz tube inside the tube furnace. The deposition parameters were chosen to be below the

spontaneous decomposition of the hydrocarbon gas such that except for the catalytic growth of carbon nanotubes there was minimum deposition of the other carbon materials. Furthermore, in order to control the formation and growth of carbon nanotubes individually, FIB has been used to drill holes on Si substrate with different diameters and depths. The holes were then filled with FeSO_4 solution and dried in the air. Through the catalytic thermal CVD

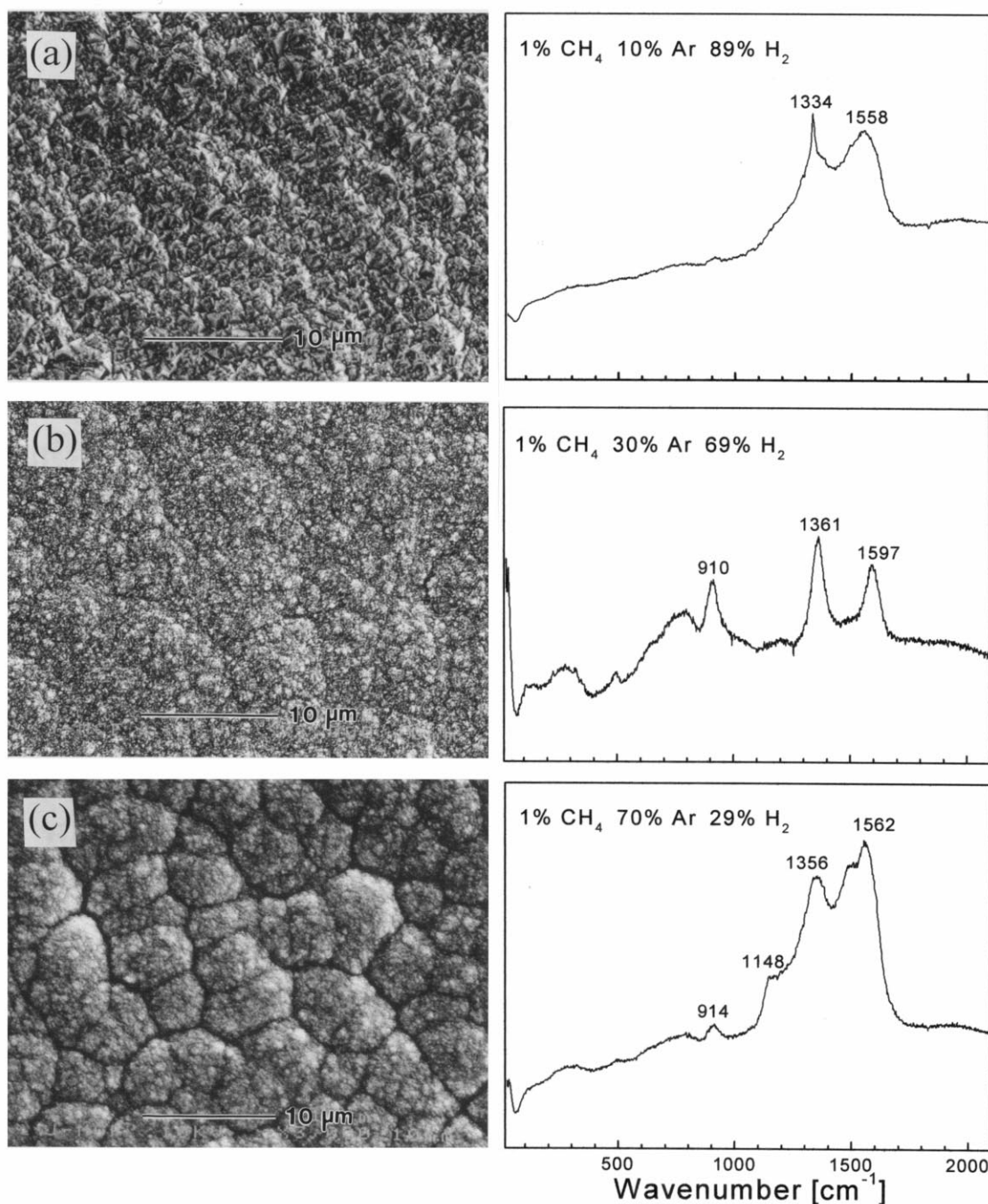


Fig. 2. Transition from microcrystalline to nanocrystalline diamond thin films as a function of Ar concentration in the processing gases with CH_4 concentration kept at 1%. (a) 10% of Ar and 89% of H_2 , (b) 30% of Ar and 69% of H_2 , and (c) 70% of Ar and 29% of H_2 . The corresponding Raman spectra are shown on the right panel.

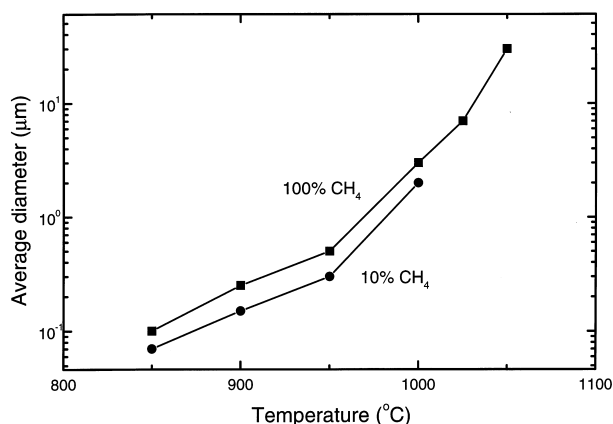


Fig. 3. The diameters of the carbon fiber vs. processing conditions of catalytic CVD synthesis.

process, the carbon nanotubes will be grown from the catalytic particles inside the holes drilled by FIB method.

3. Results

3.1. Hot filament CVD synthesis of nanodiamond

In the first series of experiments, mixtures of methane and hydrogen with different ratios have been employed as the reactant gases for the hot filament CVD processing. Fig. 1 shows SEM micrographs and Raman spectra of diamond thin films grown using 3, 4 and 5% of CH₄ in H₂ atmosphere, respectively. For each thin film deposition, the substrate

temperature was maintained at 950°C and the growth time is about 1 h. As shown in Fig. 1a, microcrystalline diamond films were grown in our CVD system when up to 3% methane was used in the reactant. Grain size of the diamond crystallites in this film is on the order of 5–10 microns, which is quite common for the CVD diamond thin films. Raman spectrum showed intense 1334 cm⁻¹ diamond peak together with a graphitic peak at 1531 cm⁻¹. Note that the Silicon peak at 520 cm⁻¹ also can be seen in the Raman spectrum of 3% CH₄ sample. At 4% of methane, the graduate degradation of the diamond thin films has been found (see Fig. 1b). The grain size of the crystallites is reduced only small amount and grains larger than one micron can be seen. The Raman spectrum of the film also showed reduced diamond 1334 cm⁻¹ peak and a graduate increase of the 1358 cm⁻¹ peak, which is usually associated with amorphous carbon. When the methane concentration is increased to 5%, as shown in Fig. 1c, the sharp 1334 cm⁻¹ peak of diamond disappeared. In its place, the 1358 and 1530 cm⁻¹ peaks showed amorphous carbon and graphitic materials.

In the second series of experiments, thin films have been prepared with a mixture of methane, hydrogen and argon as the reactant gas and the methane concentration has been kept at 1% while the Ar concentration was varied from 10 to 70%. In Fig. 2a, at 10% of Ar, the size of diamond crystallite is greatly reduced to about 0.1 to 1 micron. As the Ar concentration increases to 30%, the grain size is further reduced. Eventually at 70% of Ar, the grain size is the smallest and around a couple of tens nanometers. From micro-Raman spectra, as the concentration of the Ar in the reactant gas being increased, diamond peak at 1334

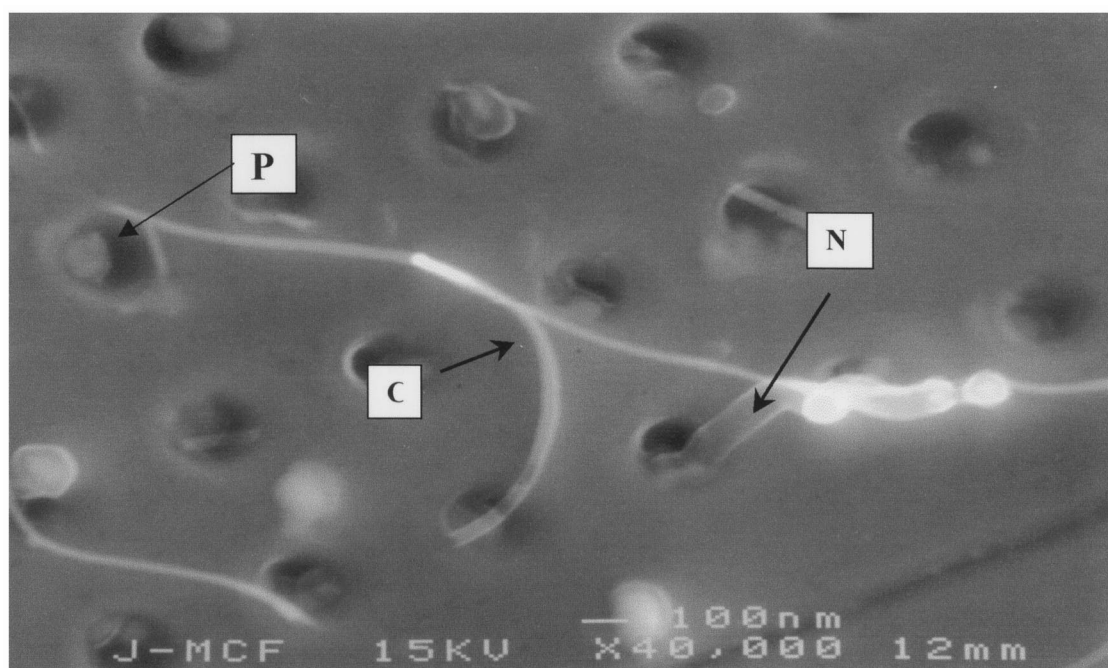


Fig. 4. SEM image shows carbon nanotubes grown from the holes with 100 nm in diameter and 100 nm in depth. (P) iron catalytic nanoparticles, (C) carbon nanotubes with a diameter of 50 nm, (N) carbon nanotubes with a diameter of 100 nm.

cm^{-1} has been broadened, and a shoulder at 1150 cm^{-1} has been gradually developed which has been believed due to the growth of nanocrystalline diamonds [12]. This is the first demonstration which nano-crystalline diamond thin films have been deposited by a hot filament CVD method.

3.2. Catalytic CVD synthesis of carbon nanotubes

For catalytic CVD synthesis of carbon nanotubes, the effects of CVD processing parameters such as substrate temperature on the diameter of the carbon nanotubes or fibers has been systematically studied. In Fig. 3, the size of the carbon fiber vs. the deposition temperature are shown. We observed that the size of carbon fiber is increased with the temperature. This is mainly due to the spontaneous decomposition of the hydrocarbon. The carbon deposited on the walls of the tubes are typically amorphous carbon and can be etched away under pure hydrogen atmosphere at 750°C . For some applications such as using the nanotube as the tip in scanning probe microscopy or as an electron field emitter, carbon nanotubes have been deposited individually at specific locations. To achieve this, we employed a FIB technique to drill holes with 100 nm in diameter and 50 nm in depth on silicon substrate. The substrate was then dip into FeSO_4 solution, dried and wiped several times to ensure the deposition of FeSO_4 into holes. The deposition of carbon nanotubes was carried out using catalytic thermal CVD under typical condition described before. In Fig. 4, a SEM image of a 50 nm nanotube grown out of a hole is shown, suggesting that the growth of carbon nanotubes can be individually located at a specific site, and that FIB technique can be employed to pattern the growth of the carbon nanotubes.

4. Discussions and conclusion

Nanodiamond thin film has been grown by hot filament CVD method for the first time. The results presented here indicated that nanodiamonds could be formed by either increasing the concentration of methane or by reducing the concentration of hydrogen. Nanodiamond formation is closely related to the secondary nucleation rate of diamonds. For the growth of microcrystalline diamonds, atomic hydrogen played an important role in suppressing the secondary nucleation so that the crystallites can grow to micron size. As the hydrogen concentration reduced, there are more opportunities for the secondary nucleation of diamonds, which increases the growth of nanodiamond. During the

growth of nanodiamond films, the suppression of other carbonaceous materials is also important. In the case of plasma enhanced CVD, the high energy density plasma played a major role in suppressing the carbonaceous materials. In our current study, the incorporation of carbonaceous materials seems to be more than in the plasma enhanced CVD case. Further increase of the deposition temperature or reduction of the substrate to filament distance could increase the etching rate of carbonaceous materials.

In the case of nanotube growth, catalytic CVD method has been employed. Various catalysts such as Fe or Fe-Ni nanoparticles, Fe thin films and FeSO_4 particles have been used. We demonstrated that with the use of a FIB apparatus, individual carbon nanotube could be deposit at desirable location on a substrate. This will greatly enhanced the atomic force microscopy application of carbon nanotubes.

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