CARBON NANOSTRUCTURES SYNTHESIZED THROUGH GRAPHITE ETCHING

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Introduction

Interest in developing new process to synthesize well-aligned carbon nanostructure films has been growing steadily in recent years. Well-aligned carbon nanostructures, including nanotubes (CNTs), nanofibers (CNFs) and nanocones (CNCs), have been usually synthesized by chemical vapor deposition (CVD) [1-9]. Well-aligned CNTs has been achieved by (1) embedding catalyst nano-particles in nanopores [1], (2) utilizing very dense growth which forces the tubes to align parallel to each other [2], (3) by growth under plasma conditions and/or by application of a bias voltage to the substrate [3], and (4) by control of the direction of the incoming flux of the carbon source [4]. Recently, CNFs aligned at a controlled variable angle to the substrate was achieved using PECVD in a gas mixture of C_2H_2 and NH_3 when the substrate was placed close to the edge of the substrate holder [5]. Tubular graphite cones have been synthesized on iron needles by microwave plasma CVD (MPCVD) with N_2 and CH_4 as the reaction gas [6]. Synthesis of carbon nanostructures with conical and cylinder-on-cone shapes was also realized using PECVD in a gas mixture of C_2H_2 and NH_3 [7]. Recently, we have synthesized well aligned CNT and CNC films with various orientation angles by using hot filament CVD (HFCVD) in a CH_4/H_2 gas mixture [8,9].

It is known that diamond films can be deposited by using hydrogen alone if graphite is used as carbon source [10]. Recently, we have deposited high quality submicron crystalline diamond films on Si substrate with a high growth rate through graphite etching in a HFCVD reactor without plasma discharge [11]. In this paper, we report a novel plasma-enhanced hot filament process for synthesis of various carbon nanostructures based on hydrogen etching of graphite. During this process, pure hydrogen is used for DC glow discharge and the carbon source originates from hydrogen etching of a graphite plate served also as substrate holder. The nanostructure features of the well-aligned graphitic and diamond films synthesized on Si substrates will be presented.

2. Experimental methods

The experiments were performed using a home-built HFCVD system described earlier [8]. The filament was a coiled tungsten wire of 0.3 mm in diameter and was heated by an ac power supply at a voltage of 30 ~ 40 V and current of 9 to 10 A. A thermocouple

was mounted right behind the substrate to measure the substrate temperature. The typical substrate temperature was 700 ºC and the distance between filament and substrate was typically 8 mm. P-type (100)-oriented mirror polished Si wafers were used as substrates. The substrates were either untreated or pretreated using one of the following two methods: (i) coated with a diamond film of 7μm by HFCVD, and (ii) coated with a thin nickel (Ni) film of 20 nm by DC biased ion sputtering in an argon plasma discharge. As a carbon source, a graphite plate was placed beneath silicon substrates. After substrates were placed on the substrate holder, the deposition chamber was pumped down to a base pressure of 2.7 Pa using a rotary pump. Then pure hydrogen gas was introduced using a mass flow controller at a constant flow rate of 35 sccm. When the working pressure was stabilized at the preset value in the range 5.32 Pa to 1.99 kPa (typically 1.04 kPa), a current was passed through the tungsten filament coil. A DC glow discharge between the filament (anode) and the substrate holder (cathode) was initiated. The discharge voltage and current were approximately 300 V and 100 mA, respectively. After a typical deposition time of 1.5 hr, a trough was formed on the graphite surface closest to the filament.

The deposited films were analyzed by a Scanning Electron Microcopy (SEM), Micro-Raman Spectroscopy and Transmission Electron Microscopy (TEM). The Raman spectra were obtained using a Renishaw micro-Raman System 2000 spectrometers operated at a laser wavelength of 514.5 nm (argon laser). The spot size was around one micrometer.

3. Results and discussions

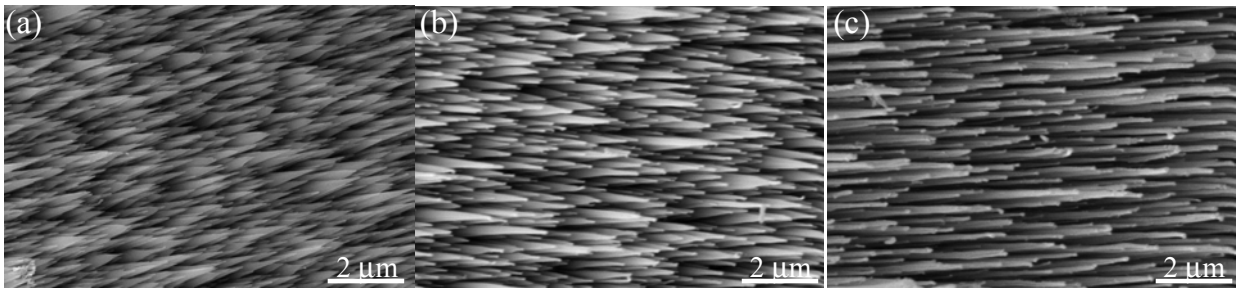

Figure 1. SEM micrographs of the films (located at the right edge of the samples) grown on (a) untreated mirror polished Si (top-right), (b) CVD diamond-coated Si and (c) Ni coated Si

Figure 1 presents typical SEM micrographs of the films on Si substrates (located at the right edge) with different pretreatment. Deposition of well aligned nanocones can be seen on untreated and CVD diamond-coated Si substrates (Fig.1 a,b). Well aligned carbon nanotubes are grown on Ni-coated substrate (Fig.1 c) (see following paragraphs for further confirmation of the CNC and CNT features). These nanostructures are tilted away from the sample center. In the central region of the sample (Fig. 2), the alignment orientation of the nanocones or nanotubes is perpendicular to the sample surface. In the regions around the sample edges, orientations of the aligned nanocones or nanotubes gradually deviate from the substrate normal and point away from the sample center. Compared to our early experiments to synthesize the aligned CNTs when methane was

mixed in the hydrogen discharge as carbon source [8], we found the similar properties of the nanostructures of the CNTs and CNCs grown with the new process: (a) The alignment angle depends on the working pressure and the distance from the edge, (b) the alignment orientation of the nanocones or nanotubes appears to be determined by the direction of the electric field lines on the sample surface. Therefore, the orientation of the nanocones or nanotubes can also be controlled by adjusting the working pressure, presumably due to the change of the electric field line directions in the cathode region at different pressures.

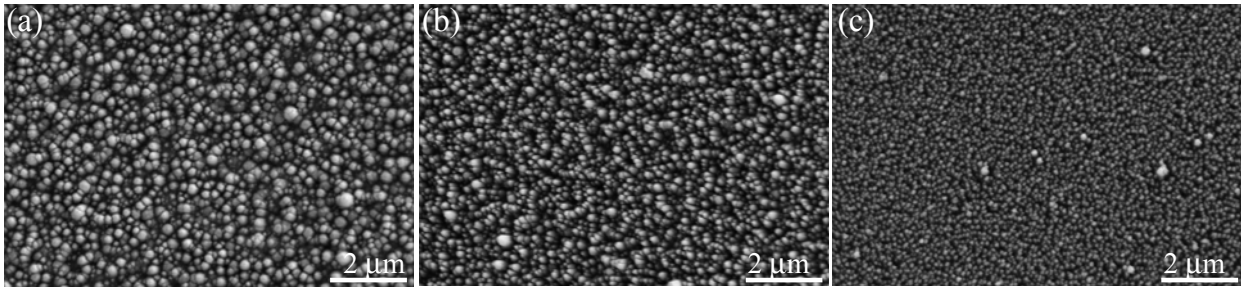

Figure 2. SEM micrographs of the films (located in the central region of the samples) grown on (a) untreated mirror polished Si, (b) CVD diamond-coated Si, and (c) Ni coated Si

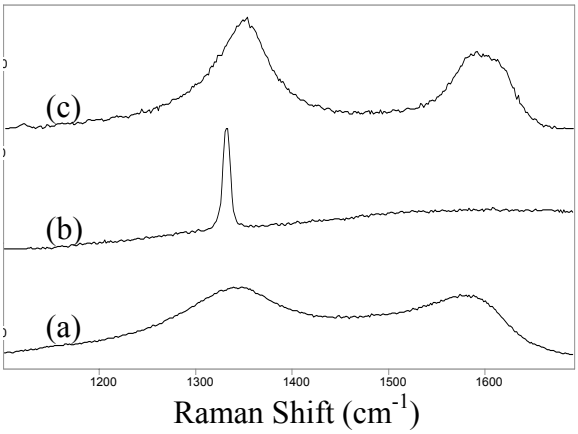

Figure 3. Typical Raman spectra of films grown on (a) untreated Si, (b) diamond-coated Si and (c) Ni-coated Si

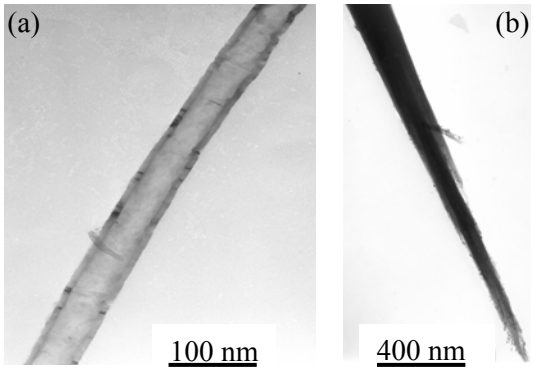

Figure 4. TEM image of typical carbon (a) nanotube and (b) nanocone

Figure 3 a-c show Raman spectra (in the range of 1100 – 1700 cm $^{-1}$) of the films shown in Fig. 1a, b and c. Two broad peaks centered at 1350 cm^{-1} (D- band) and 1590 cm $^{-1}$ (G-band), which are the signatures of the graphitic structure of carbon, are seen in Fig.3 a and c, suggesting that the nanocones formed on untreated Si surface and the nanotubes grown on Ni-coated Si surface are of graphitic nature. However, the Full Width at Half Maximum (FWHM) of D- and G-band of CNTs is smaller, indicating that the graphitic structure of CNTs is more perfect. This result suggests that nickel promotes formation of graphitic structure. On the other hand, a sharp strong peak at

1332 cm^{-1}, which is the signature of diamond, was observed in Fig. 3b, confirming that the nanocones grown on CVD diamond-coated Si surface are of diamond nature. The broad peak between 1450 and 1650 cm^{-1} in Fig.3 b, signature of non-diamond carbon, is low, suggesting that the diamond is of high quality. Similar results were obtained under different working pressures.

The nanotubes and nanocones were further analyzed by TEM. Figure 4 (a) shows the TEM image of a typical carbon nanotube. It clearly shows that the nanotube is a hollow tube, not a solid fiber. The outer diameter of this carbontube is about 40 nm. The inside hollow diameter is about 30 nm. Figure 4 (b) shows a TEM image of a typical graphitic nanocone (grown on untreated Si surface), which seems to indicate a solid cone with a sharp tip. The diameter of the tip is close to the diameter of the nanotube. The roots of cone are in submicron scale.The image of diamond nanocone is similar to that of the graphitic nanocone. The diamond or graphitic nanocone films are solid with nanometer-size tips and submicron scale roots. One potential application of the nanocones is to be used as tips for scanning probe microscopy with greater rigidity and easier mounting than carbon nanotubes.

Well aligned CNC and CNT films have been synthesized by HFCVD in pure hydrogen gas plasma. During the synthesis process, the graphite plate is subject to active etching by hydrogen. The etched graphite forms hydrocarbon radical, which acts as precursors of CNT and CNC growth. The growth process is believed to be similar to that in the gas mixture of hydrogen and hydrocarbon.

4. Conclusion

Growth of carbon nanocones and naotubes was investigated through graphite etching in a plasma enhanced HFCVD reactor. Well-aligned graphitic nanocone, diamond nanocone and carbon nanotube films with variable alignment angles can be obtained on untreated mirror polished, CVD diamond-coated and Ni-coated Si substrate, respectively. The alignment orientation of the nanocones or nanotubes appears to be determined by the direction of the electric field lines on the sample surface.

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