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Well-aligned graphitic nanofibers synthesized by plasma-assisted chemical vapor deposition

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Abstract

Well-aligned graphitic nanofibers on a large scale have been grown on Ni(100) wafers by plasma-assisted hot filament chemical vapor deposition using a mixed gas of nitrogen and methane. A two-stage control of the plasma intensity has been used in the nucleation and growth stages of the fibers. The growth direction of the fibers is perpendicular to the substrate surface and the plasma-induced Ni particles serve as a catalyst. The diameter of the fibers is in the range 50–500 nm, mostly between 100–200 nm, controlled by the size of the nickel particles. The growth mechanism of the fibers is described based on structural information provided by scanning electron microscopy and transmission electron microscopy. © 1997 Published by Elsevier Science B.V.

1. Introduction

The synthesis and characterization of carbon fibers have been topical for many years [1–4]. The discovery of carbon nanotubes with fullerene structure [5] has inspired a wide range of research both in science and technology, owing to their unique properties and potential applications [6,7]. Large quantities of carbon tubes can now be synthesized either by arc discharge [8,9] or the thermal deposition of hydrocarbons [10,11]. However, most challenging in all of these processing techniques is the aligned growth of straight carbon filaments, vitally important in many practical applications of carbon fibers in microelectronics. Several attempts [12,13] have been made to synthesize aligned carbon nanotubes. For example, Li et al. [14] have recently developed a method using chemical vapor deposition catalyzed by iron nanoparticles embedded in mesoporous silica to grow the aligned carbon nanotubes, but the preparation of the substrate is a tedious process.

In this Letter, we report the growth of well-aligned graphitic nanofibers on a Ni(100) substrate by bias-assisted hot filament chemical vapor deposition (HFCVD). The graphitic fibers can be formed by controlling the experimental condition and a uniform plasma can lead to the aligned growth of the fibers. The microstructures of the grown fibers was analyzed using scanning electron microscopy and transmission electron microscopy. A growth mechanism of the fibers is also proposed.

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2. Experiments

The HFCVD is a conventional method for growing diamond films [15] using mixed gases of hydrogen and hydrocarbons such as methane or acetone. Recently, this technique has been developed to synthesize crystalline carbon nitride films using a mixed gas of nitrogen and methane [16], where the detailed experimental apparatus has been described. In the present work, a gas mixture of high purity nitrogen (99.999%) and methane (99.9%) was used as a gas source, using a total gas flow rate of 70 sccm with a methane concentration of 2.0 vol%. Single crystalline Ni(100) wafers were used as the substrate, polished by 1.0 μm diamond paste and ultrasonically cleaned in acetone before deposition. A deeply carbonized tungsten filament was used to dissociate the introduced gases and generate a plasma between a Mo foil mesh installed above the filament and the substrate. The distance between the filament and the substrate was typically 6–8 mm. The nucleation and growth of the nanofibers proceeded in two steps. After the vacuum chamber was pumped to 1×10^{-3} Torr, the mixed gas was admitted to the chamber while maintaining a pressure of 50 Torr, and the filament was heated to about 2000°C. A negative bias ($V_{mesh} - V_{subst} < 0$) of 315 V was then applied to generate a discharge plasma. This process lasted for about 5 min and is called the nucleation stage, during which the substrate temperature was controlled at 900–950°C as measured by a thermocouple fixed to the back of the substrate. In the next step, the bias voltage was decreased to 270 V to grow fibers. The final length of the fibers depended on the deposition time, at a growth rate of about 20 μm/h. The substrate temperature during this growth stage was about 800°C. A layer of dark film on the Ni(100) surface was visible by eye after 5 min growth. The as-grown films were examined first by a Hitachi-450 SEM.

3. Results and discussions

Fig. 1 (a) shows an SEM image of a film grown for 30 min. Well-aligned fibers are seen distributed uniformly over a large area, with the length of the fibers being about 10 μm. Details of the morphological structure of the fibers are shown in an enlarged image (Fig. 1(b)). The fibers are straight with a diameter in the range 50–500 nm, most with 100–200 nm. The distribution of the fiber is uniform with a density of the order of $10^8/cm^2$. There are small particles decorating the tips of the fibers, and some tiny crystals also adhered to the surface of the fibers.

To establish the nature of the fibers and particles, TEM (JEOL 4000EX) specimens were made by transferring the carbon fibers to a holey carbon films. Fig. 2 shows a low magnification TEM image of the carbon fibers. The inner tube is not completely hollow but interconnected via graphitic layers. The crystal at the tip is covered by a layer of a carbon-like film. The bending directions of the interconnected bridges are the same and there is a large space left between the Ni particle and the carbon fiber, suggesting the particle was progressively pushed up during the growth.

Fig. 3(a) shows a high-resolution TEM image of the region next to the Ni particle, where bunching of the graphitic layers is apparent. Regions further away from the Ni particle show an ordered graphitic structure. Fig. 3(b) gives the TEM image recorded from the middle section of a carbon fiber, exhibiting the ordered graphitic structure. Analysis of the fibers by energy dispersive X-ray spectroscopy (EDS) found no other elements but carbon. The particles at the tips of each carbon fiber are pure Ni and they are believed to originate from the Ni substrate during the first stage of intensive plasma etching.

The fibers shown in Figs. 1 and 2 are different from the conventional nanotubes reported in the literature with fullerene structure [5,17], and also different from earlier solid carbon fibers produced by the thermal decomposition of hydrocarbons [18,19]. From a structural point of view, the carbon fibers here are similar to the spiral fibers grown using a mixed valence oxide carbonization process [20], but the growth mechanism may be different.

A relatively strong plasma was used in the nucleation stage to generate Ni particles on the smooth Ni substrate, which acted as a catalyst for carbonizing methane. The accumulated carbon tends to diffuse towards the substrate side, thus the Ni particles are floated by the growing graphitic fibers. The continuous carbonization of the gas by the Ni particles thus leads to the growth of the carbon fibers. This growth

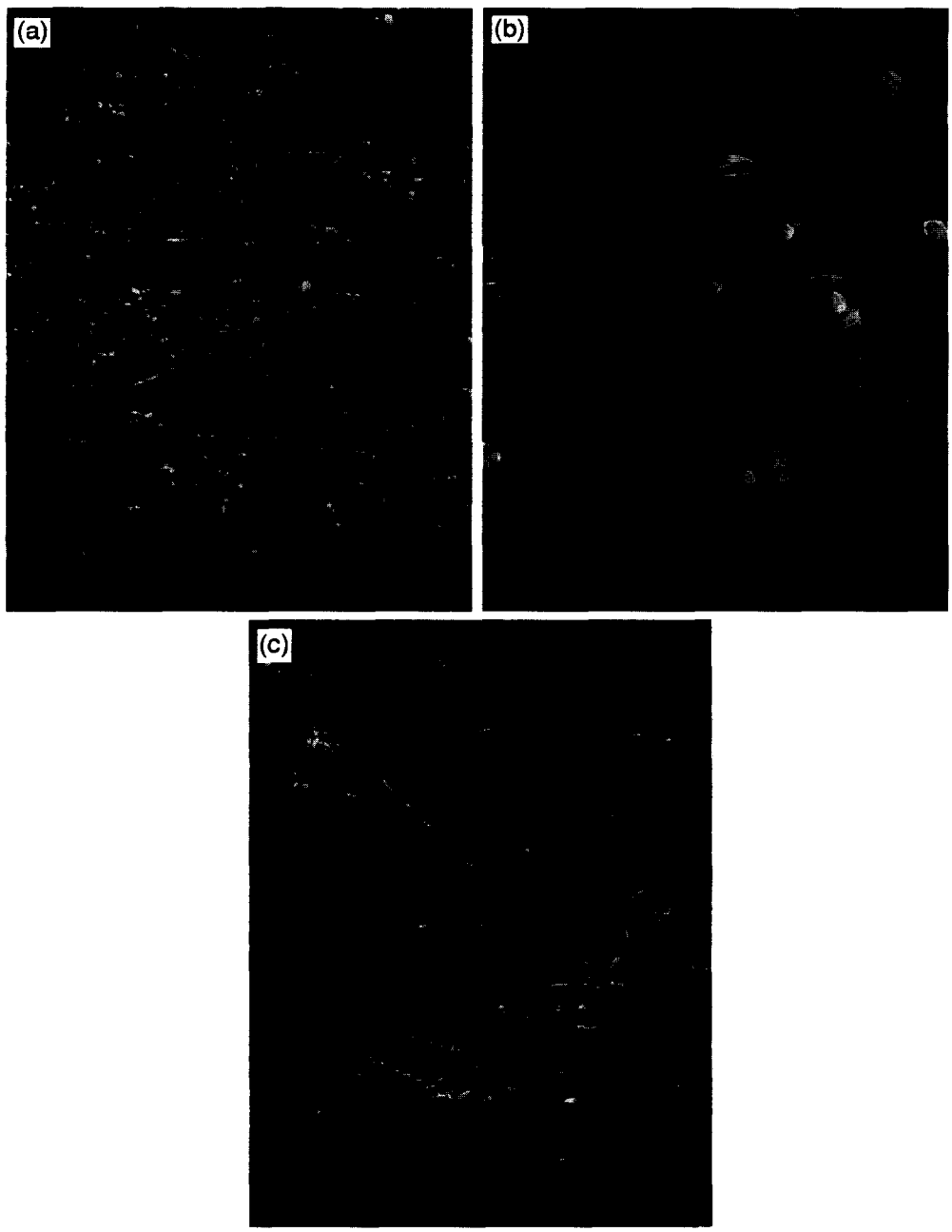

Fig. 1. SEM photos of graphitic fibers grown on Ni(100) wafers, (a) in the center area, (b) a magnified photo of (a), (c) the fibers grown on the edge of the substrate, showing more random growth of than in (a).

mechanism is different from the mechanism proposed for carbon nanotubes [17,22], in which the carbonization is believed to occur at the surface of the catalyst particles; in that case the particles serve as a substrate for the growth, thus carbon atoms tend to diffuse along the tube towards the growth front of the tube, which could be an open end. Here, the surface diffusion of the activated hydrocarbons or

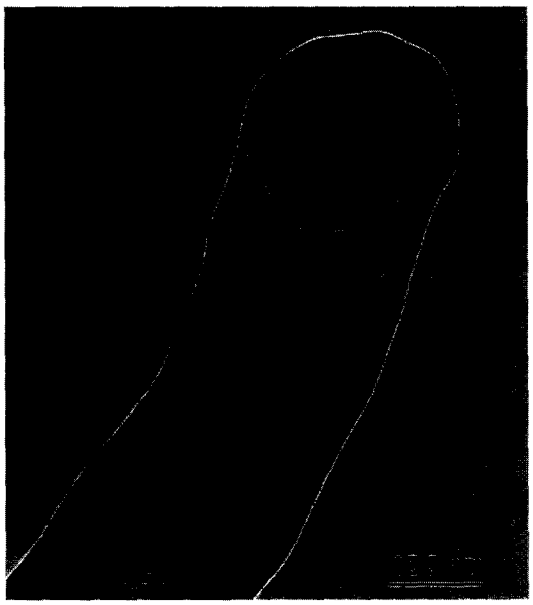

Fig. 2. TEM image of a carbon fiber with a Ni particle at the tip.

carbon species on the surface of the tip Ni crystals is the main transporting channel for forming the hollow-shaped fibers, as in the model suggested by Oberlin and Endo [4] but different from the result of Baker [18] who showed that carbon diffusion through the catalyst particle is the rate-determining step. The self-assembly of the inner graphitic layers should be take place during growth, forming a wider inner diameter in the middle area of the fiber.

If the substrate was not treated by a strong plasma at the beginning, no carbon fibers could be grown on the substrate. Moreover, the plasma condition used in the nucleation stage is not suitable for further growth, since only numerous nickel particles were formed on the surface but no carbon fibers. This result indicates that the plasma etching is too strong to induce any growth. Therefore, the nucleation and the growth conditions of the graphitic fibers are different, but this situation is expected if the substrate is smooth. If the catalyst particles pre-exist on the substrate surface before the deposition, the nucleation stage is not needed.

The most striking feature of the carbon fibers reported here is their alignment, and to our knowledge there is no report of the aligned straight carbon fibers synthesized using the technique of thermal decomposition of hydrocarbons. The most successful technique for producing aligned nanotubes is by Li et al. [14] using CVD catalyzed by iron nanoparticles embedded in mesoporous silica. In contrast, our method is much simpler, the only requirement being a nickel wafer.

We believe that the discharge plasma generated uniformly on the substrate surface is critical leading to the aligned growth of fibers. At the edge of the Ni substrate, the plasma was not as uniform as that in the central region owing to the 'edge effect', thus the growth of the fibers in this area seems more random, as shown in Fig. 1(c). Yudasaka et al. [21] reported the CVD growth of carbon nanotubes on a quartz substrate coated with different thicknesses of nickel films, but no aligned tubes were found. Furthermore,

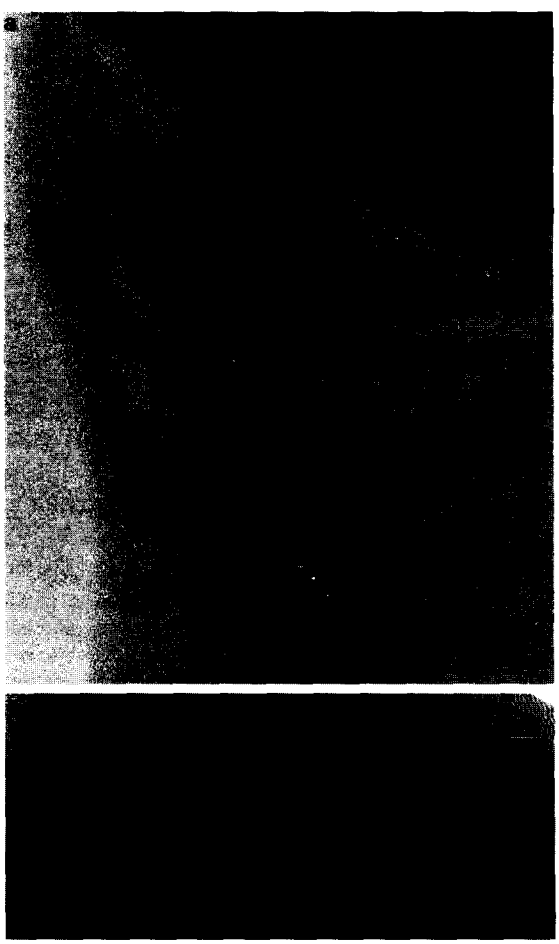

Fig. 3. (a) High-resolution TEM image of the carbon fiber recorded (a) from the tip region and (b) from the middle section, showing the layered graphitic structure.

they found that when the diameter of the Ni particle is larger than 50 nm, the graphite layer prefers to wrap up on the particle surface. In our case, the diameter of the Ni particles at the tips is mostly in the range 100–200 nm; thus, the fiber size is predetermined by the particle size. On the other hand, it is easy to see that some smaller Ni particles stick on the outer walls of the fibers (Fig. 1). These particles are believed to be derived from the relatively thin fibers grown at the beginning, but later competition from large fibers may terminate their growth. Smaller fibers may be more readily etched by the plasma, leaving some small dangling Ni particles.

A high filament temperature is also important to fiber growth because it can promote the dissociation of hydrocarbons, especially methane. No carbon fibers can be grown if the temperature drops below 900°C in conventional CVD using methane as the carbon source [19]. When the hot filament was turned off and the growth relied on the discharge formed on the substrate surface, a completely different product was obtained, to be reported elsewhere. Furthermore, the dissociation and activation of nitrogen seems to play a minor role in forming carbon fibers.

4. Conclusion

In conclusion, well-aligned graphitic fibers have been synthesized via bias-assisted hot filament chemical vapor deposition using a mixed gas of nitrogen and methane. The discharge plasma and its uniformity are the key for the growth of aligned fibers. The growth mechanism is revealed using the microstructural information provided by scanning electron microscopy and transmission electron microscopy.

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