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Effects of ammonia plasma treatment on the surface characteristics of carbon fibers

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Abstract

Carbon fibers were grown from cobalt catalysts with larger size (>100 nm), and the size distribution can be controlled by pretreatment. Pretreated cobalt catalytic-layers were observed as islands, which can enhance the growth of carbon fibers. The carbon fibers were treated by ammonia plasma in a PECVD system. High-energy ammonia plasma not only can cause damage but also adsorb on carbon fibers. The ammonia plasma treatment resulted in the etching effect. It is also observed that the more treatment time, the more disorder in structures of carbon fibers. The N–H functional groups were found on the surfaces of ammonia plasma treated carbon fibers and this observation can be further investigated to develop chemical sensor application.

Keywords: Microwave CVD; Carbon fibers; Plasma treatment

1. Introduction

The applications of carbon nanotubes to practical use of electronic and energy storage devices are still limited by a number of reasons [1–3]. A chemical functionalization of the sidewalls can change the electronic properties of nanotubes and enhance the performance in hydrogen storage, secondary battery, and chemical sensor. However, the sidewall functionalization is not easily accessible, since the open ends of carbon tubular materials are more reactive than the sidewall due to the presence of dangling bonds. Moreover, the bonding nature of ammonia carbon fibers is far from being clearly understood.

In the production of high quality gas sensor device, capable of real-time in situ of gases detection are needed. On the other hand, a precise control of chemical functionalization and understanding of the related structural modification are the key ingredients prior to the real applications.

Chemical vapor deposition (CVD) have been used for the growth of carbon fibers in the presence of catalyst particles [4–7]. The nano-size effects show unique size distribution and hollow geometry, which result in unique electrical, mechanical and chemical properties. Among them, CVD technique is a simple and low-cost method and can be operated at relatively low temperatures, especially with plasma enhancement [8].

In this work, the surface properties of carbon nanotubes and carbon fibers treated by ammonia plasma in a PECVD system were investigated. The interactions between the surface of nanomaterials and ammonia plasma were discussed. This leads to some interesting possible applications, such as gas adsorbents. In gas adsorption, carbon fibers can adsorb impurities by exposing in external environment and cause variations of the electrical properties. Therefore, the gas sensing behavior of carbon fibers will be the interesting subject. In fact, carbon materials have shown considerably

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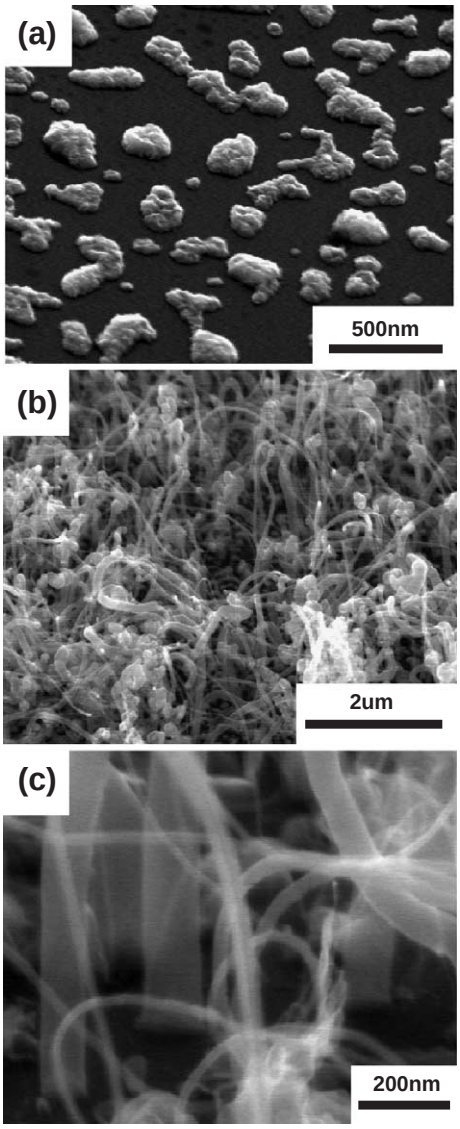

Fig. 1. SEM images. (a) The islands were induced by 10-min hydrogen plasma treatment, (b) 10-min hydrogen plasma treatment and synthesis of carbon fibers, (c) the various diameters of tubular structures including carbon fibers and few carbon nanotubes.

complex properties of microstructure depending on preparation and post-treatment. The chemical control of the carbon fibers was studied and interactions between molecular species and carbon fibers and their effects on bonding properties were investigated. The effects of ammonia plasma treatment on carbon fibers will be interpreted as a result of the ammonia-induced changes on carbon fibers' morphology.

2. Experimental

2.1. Preparation and synthesis of carbon fibers

The substrates used in this experiment were 6-in. p-type (100) orientated silicon wafers with resistivity of 15–25 Ω cm. 30 nm cobalt films were deposited with a power of 800 W and a sputtering pressure of 6.4 mTorr (0.85 Pa).

A 915 MHz microwave plasma chemical vapor deposition (MPCVD) system was used for growth of carbon fibers. The base pressure of the system was below 2×10^{-3} Torr. The applied microwave power was 800 W and the chamber pressure was 20 Torr.

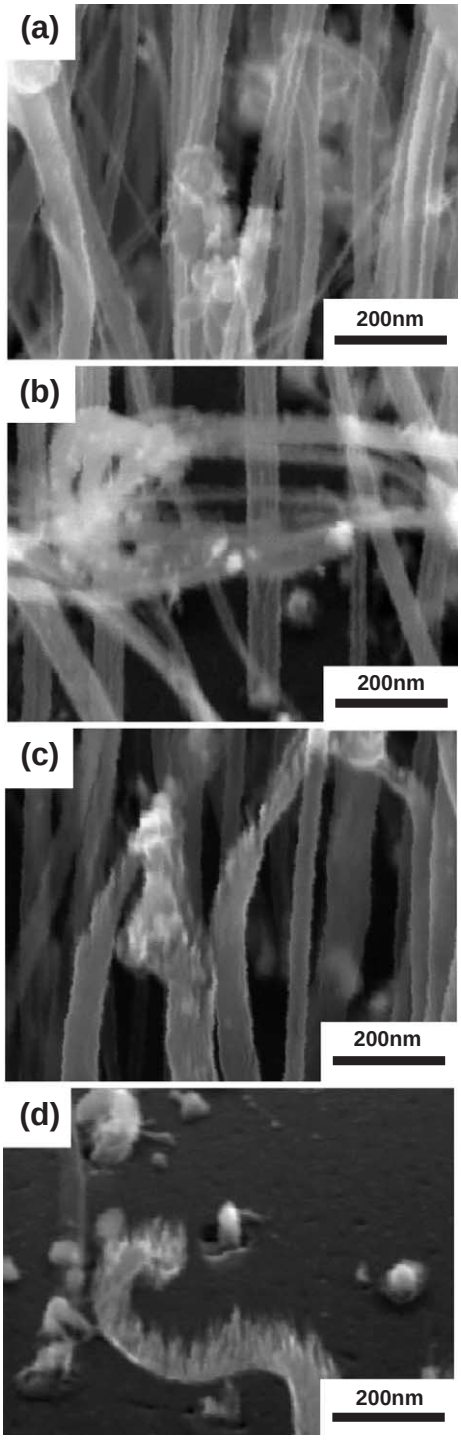

Fig. 2. SEM images of carbon fibers post-treated by NH_3 plasma for 1, (b) 3, (c) 5, (d) 10 min. The open sidewalls of carbon fibers treated from 3 to 10 min are clearly seen.

In the processing, the substrates were heated via a graphite heater. The cobalt-coated substrates were first pretreated by hydrogen plasma at 630 °C for 10 min. The cobalt catalysts were formed on silicon substrates. Gas mixtures of hydrogen (100 sccm) and methane (50 sccm) were then flowed into the chamber at 630 °C for 10 min for synthesis of carbon fibers.

2.2. Ammonia plasma treatment and analysis of carbon fibers

The carbon fibers were ex situ post-treated by ammonia plasma in a PECVD system. The power was 800 W and the pressure was 0.3 Torr during post-treatment. The ammonia plasma post-treatments were conducted at 250 °C for 1, 3, 5, and 10 min. The cobalt catalyst particles were examined using scanning electron microscopy (SEM). The resulting carbon fibers were examined using SEM and Raman spectroscopy. Chemical compositions were analyzed by Fourier Transform Infrared spectroscopy (FTIR), thermal desorption atmospheric pressure ionization mass spectrometry (TDS-APIMS) and X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

3.1. Syntheses of carbon fibers

The cross-sectional SEM image of the cobalt film with 10-min hydrogen plasma treatment is shown in Fig. 1(a). The islands induced by hydrogen plasma treatment are clearly observed. After methane and hydrogen were introduced into the system for 10 min, carbon fibers can be grown from the catalyst islands, as shown in Fig. 1(b). The various diameters of tubular structures including carbon fibers and few carbon nanotubes are shown in Fig. 1(c).

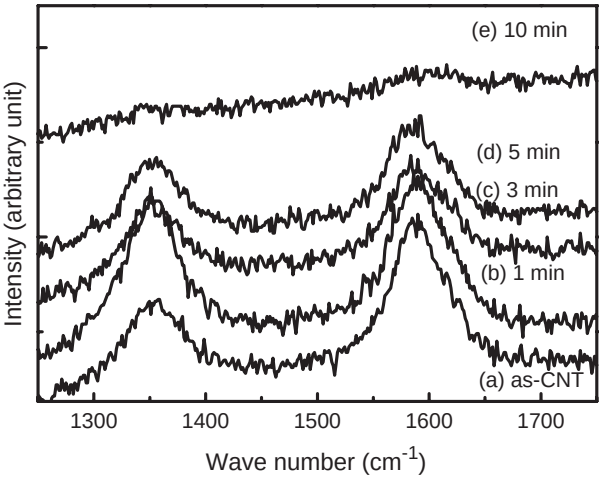

Fig. 3. Raman spectra of carbon nanotubes post-treated by NH_3 plasma: (a) as-grown CNT, (b) 1 min, (c) 3 min, (d) 5 min, (e) 10 min post-treatments.

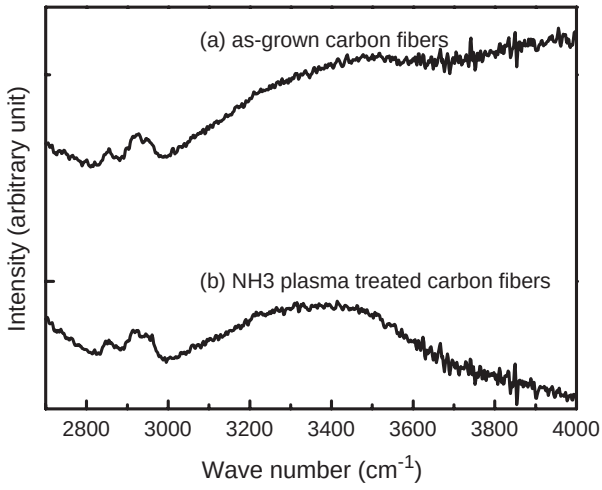

Fig. 4. FTIR spectra of carbon fibers post-treated by NH_3 plasma: (a) as-grown, (b) N–H stretching vibration bands at 3200–3400 cm^{-1}.

3.2. Characteristics of carbon fibers with ammonia plasma treatment

After completing the growth of carbon fibers, the samples were ex situ post-treated by ammonia plasma in a PECVD system. SEM images of samples with various post-treatment time are shown in Fig. 2. The open sidewalls of carbon fibers treated from 3 to 10 min are clearly seen. This open-end form can induce the adsorption of N–H molecular. 10-min ammonia plasma post-treatment caused the destruction of the microstructures of carbon fibers.

In order to investigate effects of ammonia plasma post-treatments, Raman spectroscopy was employed to analyze the resulting carbon fibers. The peaks at 1350 and 1580 cm^{-1} represent the diamond related structure, i.e., D band, and the graphite related structure, i.e., G band. It is observed that the more ammonia plasma treatment time, the more increasing D band, as shown in Fig. 3. However, the intensity decreased for the sample with 10-min ammonia

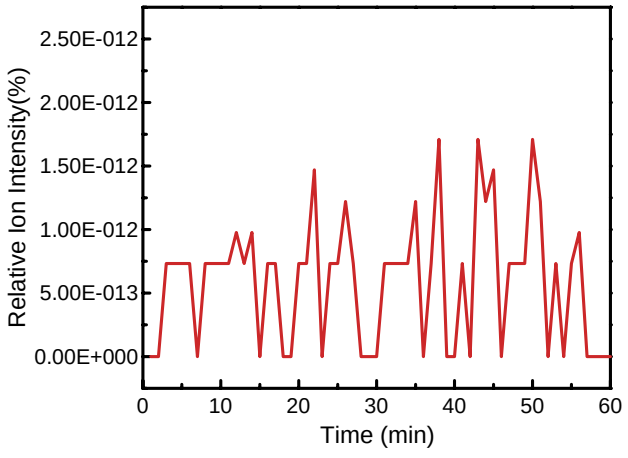

Fig. 5. High desorbed N–H functional groups are observed for carbon fibers with ammonia plasma treatments.

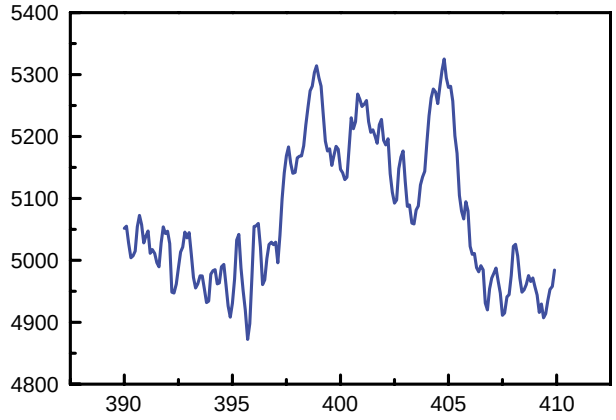

Fig. 6. N 1s XPS spectrum of carbon fibers with NH_3 plasma post-treatments.

plasma treatment, and it was well consistent with SEM observations.

Effects of ammonia plasma treatment have been observed by FTIR absorption spectra. The peak at 2800–2950 cm^{-1} is attributed to C–H stretching vibration. N–H stretching vibration bands at 3200–3400 cm^{-1} are observed and provided further information concerning ammonia plasma effects on the surface of carbon fibers, as shown in Fig. 4.

The TDS results provide adsorption information on the carbon fibers. Highly desorbed N–H functional groups are observed for carbon fibers with ammonia plasma treatments, as shown in Fig. 5. This is probably the cause of increased chemical bond in carbon fiber and thus induces adsorption capability.

XPS has been widely used to characterize the chemical states and the core-level electronic bonding situations in compounds [9,10]. In this experiment, bonding analysis of the carbon fibers showed several N–H functional groups on the surface of carbon fibers after ammonia plasma post treatments. The functional groups are chemisorbed at the outer surface of the carbon fibers wall and can be shown in Fig. 6.

4. Conclusion

In summary, carbon fibers were further ex situ treated by ammonia plasma in a PECVD system. It has been observed that high-energy ammonia plasma can cause damage to microstructures of carbon fibers. The surface chemical states of carbon fibers were analyzed by FTIR, TDS, and XPS. N–H functional groups and bonds were observed after ammonia plasma post treatments. Further theoretical and experimental studies are required for more detailed understanding of ammonia carbon fibers system.

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