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Composited BCN/carbon fibers prepared by hot-filament chemical vapor deposition

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ABSTRACT

The combined BCN/carbon fibers with porous configuration have been successfully prepared by hot-filament chemical vapor deposition (HF-CVD). The composited materials consist of carbon fiber inside covered by the cylindrical BCN films. The differences in the surface morphology and the diameter of the composite fibers are related to the different reactant gases. It is demonstrated that the elements of B, C, and N are chemically bonded with atomic-level BCN hybrid in the composite fibers. The resistance of the composite fibers is about 300 Ω which is 10 times higher than that of the isolated carbon fibers (27.5 Ω). When the applying voltage increases up to 8–15 V, the BCN films have been broken down and the resistance of composite fibers decreases to the typical value of the carbon fibers. The composite fibers with porous configuration have the strongly capacity to adsorb oxygen. The findings suggest that the combined BCN/carbon fibers are favorable for achieving high performance nano-optoelectronic and sensor devices.

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1. Introduction

In recent years, the compound boron-carbon-nitride (BCN) has attracted considerable attention for potential applications especially in the optoelectronic fields because the band gap of BCN can be adjusted with the composition [1]. Furthermore, various structural features of BCN have been realized [2]. In general, the BCN products were deposited on silicon substrate by chemical vapor deposition (CVD) [3,4] and physical vapor deposition (PVD) [5]. For example, the BCN films synthesized on the diamond film were reported to improve the field emission of diamond [6]. The other important carbonaceous material, carbon fiber (CF), has been widely applied in many fields owing to their outstanding electrical, thermal, and mechanical properties. Considering the unique properties of BCN, it is desirable to fabricate the combine the BCN/carbon fibers having potential wide applications (e.g., applied as high performance electrochemical electrode and absorption waves materials). Furthermore, CFs used as the substrate for BCN is favorable to prepare long BCN fibers and to enhance the electrical properties of BCN fibers.

In this paper, the BCN-coated CFs are prepared by hot-filament chemical vapor deposition (HF-CVD). The carbon fiber is proposed as either the template or the carbon source during the BCN growth. Analyzed by FTIR spectroscopy, the elements of B, C, and N are

chemically bonded with atomic-level B–C–N hybrid in the products. The combined BCN–CFs show a varied resistance applied under different voltages.

2. Experimental

The synthesis of BCN/CF composite structure was carried out in a HF-CVD system [7]. N_2 , CH_4 and/or carbon fibers, and trimethylborate (B(OCH $_3$) $_3$) were used as the precursor source of N, C, and B, respectively. The B(OCH $_3$) $_3$ was loaded in the chamber during the growth process by bubbling the H_2 gas through the liquid B(OCH $_3$) $_3$ precursors (the ambient temperature was kept at 25 °C). The carbon fibers were placed on a molybdenum substrate. The vertical distance between the filament and carbon fibers was \sim 1 cm. The temperatures (measured by an infrared thermometer) of the filament and substrate were about 2000 °C and 400 °C, respectively. The deposition pressure was kept at 30 Torr and the lasting time was 2 h. The detailed growth parameters for different samples (samples a–d) are summarized in Table 1 (for simplification, the B-flow rate is expressed by the corresponding bubbling H_2 flow rate)

The morphology and chemical composition of the samples were characterized by scanning electron microscopy (SEM, JSM-6480LV) equipped with electron energy dispersive X-ray spectroscopy (EDX). The chemical bond structure information of BCN was analyzed by Fourier transform infrared spectroscopy (FTIR, NICOLET AVATAR 370 DTGS spectrometer) from 400 to 4000 cm⁻¹. The samples were mixed with KBr powder and pressed into a pill for the IR transition examination. The resistance of samples was obtained

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Table 1 Deposition parameters for samples (a)–(d), B flow rate = carrier H_2 flow rate for bubbling $B(OCH_3)_3$.

Sample	Reaction gases	Flow-rate ratio (in sccm)
a	=	=
b	H ₂ :B:N ₂	390:5:5
С	H ₂ :B:N ₂ :CH ₄	390:5:5:3
d	B:N ₂	5:5

from the current–voltage (I-V) curves measured using Keithley sourcemeter 2400 by the two-point probe method. Two copper wires were attached on the two ends of the CFs and BCN/CFs bundles using silver paste as electrodes. All the examinations were performed at room temperature.

3. Results and discussion

3.1. Analysis of FTIR

The FTIR spectra of the samples a-d are shown in Fig. 1. For sample a of pure CFs (curve a), there is a broad peak of around 1630 cm⁻¹ appearing in the region of 1550 cm⁻¹ to 1750 cm⁻¹ (see in the inset), which is related to the typical hexagonal net of graphite [8]. The curves (b)-(d) are the IR spectra of the products synthesized under different growth conditions. The two absorption peaks at around 820 cm⁻¹ and 1375 cm⁻¹ are attributed to the B-N-B bending mode and B-N stretching modes of BCN, respectively [9]. Note that the intensities of the characteristic peaks at 820 cm⁻¹ (1375 cm⁻¹) for sample b (sample d) is stronger than that for samples c and d (samples b and c), which means that the strength of the vibration modes are varied dependent on the intrinsic features of those samples synthesized under different growth conditions. The peak at 880 cm⁻¹ found in samples b-d are assigned to the characteristic peak of B(OCH₃)₃, which might be absorbed on the products. The intensities of this characteristic peak for samples b and c are stronger than that for sample d, suggesting that the decomposition ratio of B(OCH₃)₃ for sample d is higher than that for samples b and c

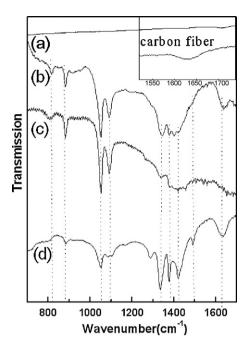


Fig. 1. IR transmission spectra of samples a–d. The inset shows the enlarged curve in the region of $1550-1750\,\mathrm{cm}^{-1}$ for sample a.

synthesized in the H_2 -rich ambient. The adsorption peak at around $1050\,\mathrm{cm}^{-1}$ originates from c-BN phase, which generally appears in BCN films [10]. Similarly, the peak at around $1100\,\mathrm{cm}^{-1}$ is corresponding to the B–C vibrations from amorphous B_x C phase [11], and the peak at $1330\,\mathrm{cm}^{-1}$ is from the amorphous BN phase [12]. The adsorption peaks at $1425\,\mathrm{cm}^{-1}$ and $1500\,\mathrm{cm}^{-1}$ are resulted from C=N [13]. The band centered at around $1625\,\mathrm{cm}^{-1}$ attributed to sp² C–N vibration [5] appears in the spectra of samples b and d, while nearly absent for sample c. It is worth pointing out that the introducing H_2 plays an important role in the formation of BCN structure

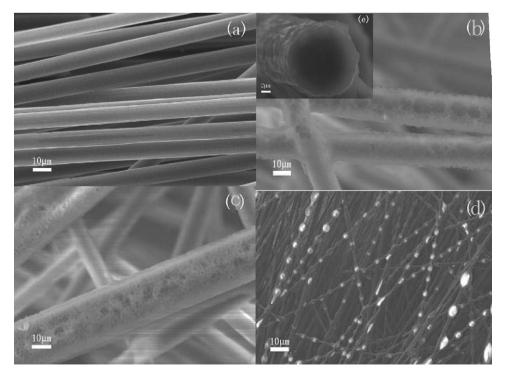


Fig. 2. SEM images of the samples a-d. The inset is the cross-section images of sample b.

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