

# Synthesis of CN Nanostructures by Hot Isostatic Pressure Apparatus and Their Field Emission Properties

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Carbon–nitrogen (CN) nanofibers were synthesized in argon–nitrogen gas mixture at 75 MPa by high isostatic pressure (HIP) apparatus using a graphite resistive heater. The CN nanofibers were grown in random with the diameter of about 200 nm and the length over 5  $\mu$ m. The structures obtained can be divided bamboo-like, spring-like, and bead necklace-like CN nanofibers. The nitrogen content of up to 8.4% was found in CN nanofibers by EELS analysis. Field emission results showed that the density of field emitters and the field enhancement factors changed by surface treatments and that CN nanofibers contained glass frit. The screen-printed CN nanofiber had a turn-on field of 2 V/ $\mu$ m.

Keywords: Carbon Nanostructures, High Isostatic Pressure (HIP), TEM, Field Emission.

## **1. INTRODUCTION**

Carbon-nitrogen (CN) nanostructures, novel carbon form, have interesting properties because of their novel electronic properties and high mechanical strength.<sup>1</sup> CN nanostructures can be used in numerous potential applications such as high hydrogen storage,<sup>2</sup> chemical sensors,<sup>3</sup> field effect transistors<sup>4</sup>, and field emission display (FED). Carbon nanotubes (CNTs) emitters directly grown into submicrometer gate holes.<sup>5</sup> Researchers have investigated the possibility of using CN nanostructures as electron emitters and the synthesis of nitrogen (N)-doped CNTs because the N can enhance the mechanical and conducting properties of CNTs.<sup>6,7</sup> Several groups have produced CN nanostructure containing nitrogen. Lee et al. reported the growth of nitrogen-doped CNTs on the silicon substrate by thermal CVD.8 Terrones et al. observed aligned CN nanofibers by pyrolyzing mixtures of ferrocene and melamine at 950-1050 °C under an Ar flow.9 The field emission current density of nitrogen-doped (2.62 wt%) nanotubes on silicon wafer, which were obtained by

floating-catalyst CVD techniques, was over 23.8 mA/cm<sup>2</sup> at 17 V/ $\mu$ m.<sup>10</sup>

In this letter, we report the synthesis of CN nanofibers by the HIP method at 1400 °C under an argon–nitrogen gas mixture pressure of 75 MPa. We also investigate the structure and nitrogen content of the synthesized CN nanofibers by transmission electron microscopy as well as the field electron emission properties.

### 2. EXPERIMENTAL DETAILS

CN nanofibers were fabricated in the water-strictly cooled hot isostatic pressure device (HIP). The block scheme of the HIP device is shown in Figure 1(a). In our experiments, we used the HIP apparatus, designed for the maximum pressure of 350 MPa. Its inner dimensions for mounting a heater and screens were as follows: Check valve (6) was used to better stabilize the pressure during the experiment. High gas pressure was created by a one-stage piston gas compressor (2). The upper part of gas compressor is shown in Figure 1(a). The compressor worked without any liquid lubricant and therefore it maintained the high purity of the gas mixture. The HIP apparatus (1) was a three-layer

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**Fig. 1.** The Block scheme of the experimental unit: (a) The block diagram of high isostatic pressure (HIP) unit: (1) HIP Apparatus; (2) High pressure gas compressor; (3) Gas-cylinder (or cylinders); (4) Shut off valve; (5) Manometer; (6) Check valve. (b) The scheme of the heating unit of HIP apparatus: (1) Carbon resistive heater; (2) Copper contacts; (3) Supporting graphite ring; (4) Graphite screen; (5) Upper cover; (6) Thermocouple. A, B, and C—places of black cotton wool-like product accumulation and E-hot zone of heater.

steel cylinder with an outer water-strictly cooler and inside free volume 40 mm in diameter and 200 mm height to mounting heating unit. The main view of the HIP apparatus is shown in Figure 1(a). A carbon heater was used as the carbon source. The shape of the graphite heater and the heat shielding are shown in Figure 1(b). Carbon vapor was obtained by using a graphite resistive heater (U = 7-10 V I = 200-220 A). The heater was made of ultra pure graphite with Fe content of less than 0.003 mass%. The heat shield was manufactured from graphite and it contained ring 3, plug 4, and cylinder 5. The heating zone with the thickness equal to 0.7 mm was made in the middle part of the heater 1. Carbon deposit was taken from the top part of the heater (zone A). The argon-nitrogen mixture of gases in equal content was prepared in the mixture unit ((3) in Fig. 1(a)). The gas pressure was 75 MPa, synthesis duration 40 min, and temperature of 1400 °C. The temperature was monitored by a Type A thermocouple. Carbon was evaporated by direct resistive electrical

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heating. The carbon deposit was investigated by JSM-6700F (Hitachi S-4300) scanning electron microscopy (SEM), CM20 (Philips Electron Optics), transmission electron microscopy (TEM) operated at an accelerating voltage of 200 kV, VG 601 UX scanning transmission electron microscope (STEM), and Raman spectroscopy (Jobin Yvon, LabRam HR). The electron energy loss spectroscopy (EELS) was carried out in a STEM, a VG 601 UX, equipped with a GATAN 666 spectrometer providing a spatial resolution of 1 nm. For Raman measurement, laser excitation was achieved with the 514.5 nm line of Ar<sup>+</sup> laser at 0.5 mW.

The mixture of CN nanofiber paste, which consisted of the CN nanofibers, glass frit, ethyl cellulose, and terpineol was screen-printed onto an indium tin oxide (ITO)-coated soda lime glass. Cathode plate coated CN nanofibers underwent binder burn-out at 380 °C in ambient N<sub>2</sub>. Green phosphor used in cathode ray tube (CRT) was printed on the ITO glass of the anode plate. The field electron emission characteristics were measured by computer-controlled DC power supply at pressure of about  $10^{-6}$  Torr. The distance between anode and cathode was 900  $\mu$ m, and the emission area (printed pattern size) was  $1 \times 1$  cm<sup>2</sup>.

#### 3. RESULTS AND DISCUSSION

Different structures were found in the A-zone. Figure 2 shows the representative SEM and TEM images and the corresponding EELS spectra of these CN nanofibers. The CN nanofibers with the diameter of about 200 nm and length over 5  $\mu$ m were grown at random. The structures obtained can be divided into three groups in Figure 2(b): bamboo-like nanofibers, spring-like nanofibers, and bead necklace-like CN nanofibers, of which the latter type had the most complex structure. These nanofibers consisted of intersections of graphene layers. Curved intersected graphene layers inside the fiber appeared primarily because of the nitrogen atoms in the graphene layers. Nitrogen may have effectively substituted the carbon atoms at the fringes of graphene layers and cause their bending.<sup>12</sup> This corrugated-like structure was explained in Refs. [11, 13] as the formation of pyridine-like bonds between nitrogen and carbon atoms. These bonds characterize mainly the edges of graphene layers and can explain the curved shape of the layers. Figure 2(c) shows a TEM image of the bead necklace-like CN nanofiber and EELS spectra at selected points corresponding to the chemical composition of the nanofiber. The EELS spectrum of CN nanofiber shows the N K-edge at 401 eV and the C K-edge at 284 eV. As shown in a representative EELS, the nitrogen in the nanofiber was mainly located at the centre of the tube. The nitrogen concentration in bamboo-like CN nanofibers was calculated to be about 3-4%, and that in the bead necklace-like CN nanofibers was 8.4%. Comparing the near-edge structure of different N K-edge, we can associate



Fig. 2. (a) SEM image of the carbon nanostructures fabricated by HIP method, (b) TEM image of nanofibers observed in the deposit from A-zone; structure of bamboo-like nanofiber, bead necklace-like nanofiber, and spring-like CN nanofibers, and (c) TEM image of bead necklace-like nanofiber and the corresponding EELS spectra at selected points. The inset show magnification of N-edge structures (nitrogen content;  $1-2.5\pm0.4\%$ ,  $2-7.4\pm0.2\%$ ,  $3-2.6\pm0.5\%$ ,  $4-8.4\pm0.2\%$ ,  $5-7.0\pm0.2\%$ ,  $6-6.8\pm0.2\%$ ).

the peak occurring at 401 eV in Figure 2(c) (inset) to trivalent nitrogen-replacing carbon in a hexagonal lattice.<sup>13</sup> Although the role of nitrogen in structure formation as

well as in the modification of material properties is not completely clear, we believe that interstitial nitrogen in the graphite lattice leads to the development of defective **RESEARCH ARTICLE** 



Fig. 3. Raman spectrum of CN nanofibers formed by HIP.

structures. Even a small difference between C–C and C–N bond lengths (0.1422 and 0.1429 nm, respectively)<sup>14</sup> can cause large inner tensions in the growing layer, giving rise to elastic deformations and the bending of layers. A bead necklace-like CN nanofiber shows nitrogen concentration of 2.5–7.4% in region I (points 1–3) and 6.8–8.4% in region II (points 4–6). The average value of N content was 5.8%. When the nitrogen content in the CN nanofibers increased, more faults appeared in the structure.

The typical Raman spectrum of CN nanofibers is shown in Figure 3. The D band (1355  $cm^{-1}$ ) is associated with the defective structure of the graphite sheet, whereas the G band (1575 cm<sup>-1</sup>) indicates single crystals of graphite.<sup>15</sup> The peak at 1348  $cm^{-1}$  is the D band, and the other at 1596 cm<sup>-1</sup> is the G band. The intensity ratio of D band to G band  $(I_D/I_G)$  of CN nanofibers was 0.9. The Raman spectra bands of a sample were different from those of CNTs. Keskar et al. reported that with increasing nitrogen concentration, the intensity of the D band at 1350 cm<sup>-1</sup> increased gradually relative to that of the G-band in single-wall carbon nanotubes (SWNTs) by CVD.<sup>16</sup> In Lee et al. paper, as the nitrogen content increases, the relative amount of crystalline graphitic sheets reduces and the value of  $I_{\rm D}/I_{\rm G}$ increases from 0.48 to 0.66 as the N content increases from 2.0% to 4.7% in CNTs obtained by thermal CVD.<sup>8</sup> Thus, as a result of the strong peak intensity at about  $1350 \text{ cm}^{-1}$ , the presence of nitrogen induces the formation of disordered CN nanofibers (corrugated-like structures).

Based on SEM, TEM, EELS, and Raman information, the nitrogen atoms, introduced into growing nanofibers, caused strong tension and large deformation. Elastic deformation led to the strong bending of layers, corrugated nanofiber surfaces, and formed diaphragms inside the nanofibers.

Figure 4(a) shows the I-V curves of the printed-CN nanofiber after different surface treatments. The inset shows the corresponding Fowler-Nordheim (F-N) plot. From Figure 4, samples A, B, and C were measured to turn-on field of 2 V/ $\mu$ m, 2.7 V/ $\mu$ m, and 2.9 V/ $\mu$ m.



**Fig. 4.** (a) *I*–*V* characteristics and the inset shows the F-N plot of the CN nanofibers measured after different surface treatment and (b) SEM image of printed sample B after soft roller surface treatment: (A) printed-CN nanofiber without glass frit after soft roller surface treatment; (B) printed-CN nanofiber containing glass frit after soft roller surface treatment; (C) printed-CN nanofiber containing glass frit after adhesive taping surface treatment.

Here, the turn-on field was defined as 1  $\mu$ A/cm<sup>2</sup>. The turn-on field is different because of the density of CN nanofiber emitters and change of surface morphology by soft roller and adhesive taping treatment. Sample A displayed relatively higher field emission current at low voltage than samples B and C containing glass frit as filler materials. Samples B after soft roller and C after adhesive taping treatment obtained field emission current of 400  $\mu$ A/cm<sup>2</sup> and 120  $\mu$ A/cm<sup>2</sup> at the applied voltage of 3700 V (4.1 V/ $\mu$ m), respectively. These field emission characteristics indicate that the density of emitters was relatively higher in sample B than in sample C. Sample A was measured 150  $\mu$ A/cm<sup>2</sup> at 2650 V. At above the applied voltage, the emission current cannot be measured because of loose adhesion between CN nanofibers and the cathode plate. The F-N equation describes the quantum mechanical tunneling mechanism. The F-N plot is expressed by  $\ln(I/V^2)$  versus 1/V and fitted by high-voltage and low-voltage regions. The field enhancement factors ( $\beta$ ) calculated from the F-N plot for samples A, B, and C

were 168, 802, and 857 in the low-voltage ranges and 570, 2156, and 4592 in the high-voltage ranges, respectively, for an assumed work function of 4.5 eV for graphite. Each plot has two straight lines of different slopes. The transition of the F-N slopes are related to complex factors such as space charge effect, resistance of emitter and interaction between the CN nanofibers with different geometry, and the randomly arrayed CN nanofiber paste during field emission.<sup>17</sup> However, in this case, the difference in these  $\beta$  values and the change in the F-N slopes were explained by the increase of perpendicularly well-protruded CN nanofibers due to glass frit such as filler or bonding materials, randomly distributed CN nanofibers onto the cathode substrate and the change of surface morphology by surface treatment. Figure 4(b) shows the SEM image of the protruded CN nanofibers on the surface of sample B after soft roller treatment. These results showed that the CN nanofibers protruded over the surface as a result of mechanical surface treatment and vertically aligned to the cathode substrate.

# 4. CONCLUSIONS

In summary, we synthesized CN nanofibers by HIP process in a nitrogen–argon gas mixture. Bamboo-like, spring-like, and bead necklace-like CN nanofibers were found in the deposit. The nitrogen content of up to 8.4% was found in CN nanofibers by EELS analysis. The Raman spectra of CN nanofibers indicated two strong bands 1348 and 1596 cm<sup>-1</sup>. The printed-CN nanofibers were obtained turn-on field of 2–2.9 V/ $\mu$ m. The glass frit strengthened the field emission stability as voltage increased and vertically arranged the CN nanofiber tips. Also, adhesive taping as surface treatment controlled the emitter density and removed loosely bonded emitters.

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