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Carbon nanofibers grown on sodalime glass at 500°C using thermal chemical vapor deposition

Cheol Jin Lee [a,*], Tae Jae Lee [a], Jeunghee Park [b]

[a] *School of Electrical Engineering, Kunsan National University, Kunsan 573-701, Republic of Korea*
[b] *Department of Chemistry, Korea University, Jochiwon 339-700, Republic of Korea*

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Abstract

Carbon nanofibers are grown homogeneously on a large area of nickel-deposited sodalime glass substrate by thermal chemical vapor deposition of acetylene at 500°C. The diameters of carbon nanofibers are uniformly distributed in the range between 50 and 60 nm. Most of the carbon nanofibers are curved or bent in shape, but some fractions are twisted. They consist of defective graphitic sheets with a herringbone morphology. The maximum emission current density from the carbon nanofibers is 0.075 mA/cm^2 at 16 V/μm, which is sufficient for commercializing the carbon-nanofibers-based field emission displays.

1. Introduction

Great interest has recently developed in the area of nanostructured carbon materials. Carbon nanofibers (CNFs) are fascinating carbon materials with many potential applications, e.g. field emission displays (FEDs) [1], hydrogen storage [2,3], catalyst or catalyst support [4–6], nanocomposites [7], etc. It is expected that the electron emission property of CNFs can be enough for the field emitters [1]. Sodalime glass, which is commonly used as a low-cost substrate for display panels, deforms at a temperature above ~550°C. In order to develop the CNF-based FEDs, it is therefore highly desirable to grow the CNFs directly on sodalime glass substrate at a low temperature below 550°C.

The synthesis of CNFs was extensively performed using a catalytic vapor-phase growth method at temperatures around 600°C [8–16]. There are a few works that achieved the catalytic CNF growth at temperatures below 500°C. Baker and coworkers reported a growth of CNFs at 400°C over cobalt (Co) and iron (Fe) catalysts using ethylene/hydrogen mixture containing a trace of chlorine [17]. Recently Menini et al. [18] synthesized the CNFs on nickel (Ni)/SiO_2 catalyst using the hydrodechlorination of chlorobenzene at 280°C. The study of field electron emission for CNFs is not so much even though there are many reports for the CNF growth.

In this Letter, we report a homogeneous high-density growth and field electron emission of CNFs grown on a large area of sodalime glass substrate by thermal chemical vapor deposition (CVD) of acetylene (C_2H_2) gas at 500°C. The growth of CNFs has been achieved by employing a two-stage differential heating technique where the

* Corresponding author. Fax: +82-63-469-4744.
E-mail address: cjlee@kunsan.ac.kr (C.J. Lee).

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reactants are heated at 850°C and then brought into a CNF growth zone at 500°C. The structure of CNFs has been investigated using various techniques including scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy.

2. Experimental

A 200-nm-thick Ti film was thermally deposited on a 20 mm × 30 mm-size sodalime glass substrate under a pressure of 10^{-6} Torr, followed by annealing at 200°C for 20 min. Then a 100-nm-thick Ni film was thermally deposited on Ti-deposited sodalime glass substrate. Ti film plays a role as a cathode layer as well as a glue layer between sodalime glass and the Ni film. The quartz CVD reactor consists of two different temperature zones heated independently by resistive heating coils, as described elsewhere [19]. The temperature of the first heating zone is maintained at 750–850°C. The sodalime glass substrates were loaded face down on a quartz boat at the second heating zone under a temperature of 500°C. Before growing the CNFs, the Ni-deposited Ti/sodalime glass substrates were pretreated using NH_3 gas with a flow rate of 200–250 sccm for 20 min. The NH_3 pretreatment is a crucial step to obtain the nucleation sites for the growth of nanostructured carbons [20]. The CNFs were grown using C_2H_2 with a flow rate of 60–120 sccm for 5–10 min at the same temperature range of pretreatment. Argon (Ar) was flowed into the CVD reactor while increasing or decreasing the temperature. The alignment and the structure of CNFs were examined by a scanning electron microscope (SEM) (Hitachi S600) and a transmission electron microscope (TEM) (Philips CM20T, 200 kV). For TEM analysis the CNFs were separated from the substrate in acetone solution using ultrasonic treatment. Peeled CNFs were dispersed on a carbon TEM microgrid. A Raman spectrometer (Renishaw micro-Raman 2000) was also used to identify the structure and the crystallinity of graphitic sheets. Field emission measurement was conducted in a vacuum chamber at 1×10^{-6} Torr. The emission current vs. the applied voltage was measured with an electrometer (Keithley 619).

3. Results and discussion

Fig. 1 shows SEM micrographs for the CNFs grown on Ni-deposited Ti/sodalime glass substrate at 500°C. Fig. 1a shows that high-density CNFs are homogeneously grown on a large area of substrate. Fig. 1b is a magnified SEM image of Fig. 1a, revealing the diameters uniformly dis-

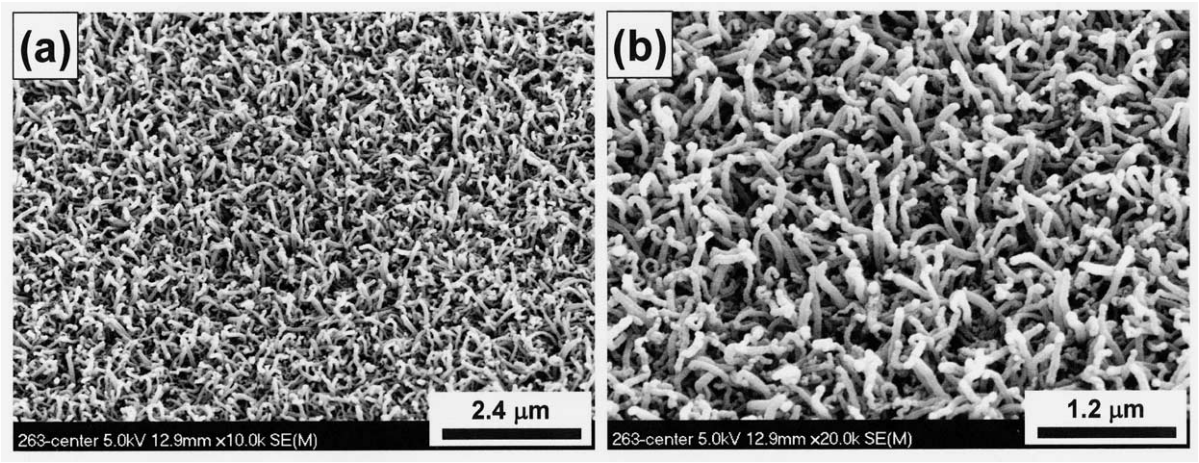

Fig. 1. SEM micrographs for the CNFs grown on a large-area (20 mm × 30 mm) Ni-deposited Ti/sodalime glass substrate at 500°C. (a) High-density CNFs are grown homogeneously on the substrate. (b) The diameters are uniformly distributed in the range 50–60 nm.

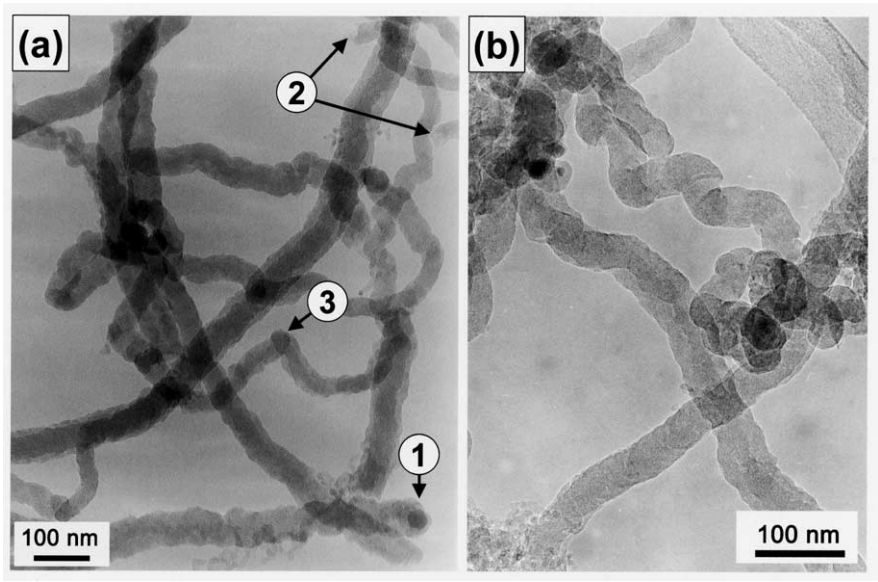

Fig. 2. TEM images for the CNFs grown at 500°C. (a) It reveals the tips encapsulated with the catalytic particles (see arrow ①), the roots separated from the catalytic particles (see arrows ②), and the node of a bent CNF (see arrow ③). (b) Twisted CNFs are also grown.

tributed in the range 50–60 nm. The growth direction of CNFs is approximately perpendicular to the substrate. Most of the CNFs are slightly curved or bent, but some of them are twisted. They have clean surfaces without carbonaceous particles.

As the temperature of the growth zone increases from 500°C to 550°C, the growth of vertically aligned carbon nanotubes (CNTs) is much enhanced [21]. When the temperature is below 480°C, few CNFs are grown. The growth of CNFs is possible only when the temperature of the first heating zone is above 750°C. We tried to grow the CNFs at 500°C following the pretreatment of NH_3 gas at 850°C in a one-stage heating CVD reactor without success. The result indicates that the two-stage differential heating technique provides more activated or decomposed C_2H_2 molecules to the catalytic particles in the growth zone. The activation (or decomposition) process of reactants in gas phase appears as an important step in the overall reaction, even though the detailed mechanism is not known yet.

Baker and coworkers [12] synthesized the CNFs from the decomposition of C_2H_2 over Ni:Cu alloy catalyst and using a mixture of C_2H_2 and hydrogen over Ni catalyst at 600°C. Merkulov et al. [15] reported a growth of vertically aligned CNFs on polycrystalline Ni substrate by plasma-enhanced CVD of C_2H_2 and a mixture of 10% ammonia and 90% helium at 600–700°C. In this work high-purity CNFs are synthesized homogeneously on a large area of Ni-deposited Ti/sodalime glass substrate using thermal CVD of C_2H_2 at the lower temperature 500°C.

Fig. 2a shows TEM images for the CNFs grown at 500°C. Most of CNFs are curved or bent and have no inside hollow. The tips of the CNFs are encapsulated with the catalytic particles (see arrow ①). There are roots separated from the catalytic particles during the ultrasonic treatment in acetone (see arrows ②). The arrow ③ indicates the node of a bent CNF. Fig. 2b shows the growth of twisted CNFs.

Fig. 3 shows HRTEM images for the CNFs grown at 500°C. Fig. 3a show that the CNFs are composed of defective graphitic sheets which are aligned with a herringbone morphology (see arrow marks). The orientation angle between the graphitic basal planes and the fiber axis is about 50°.

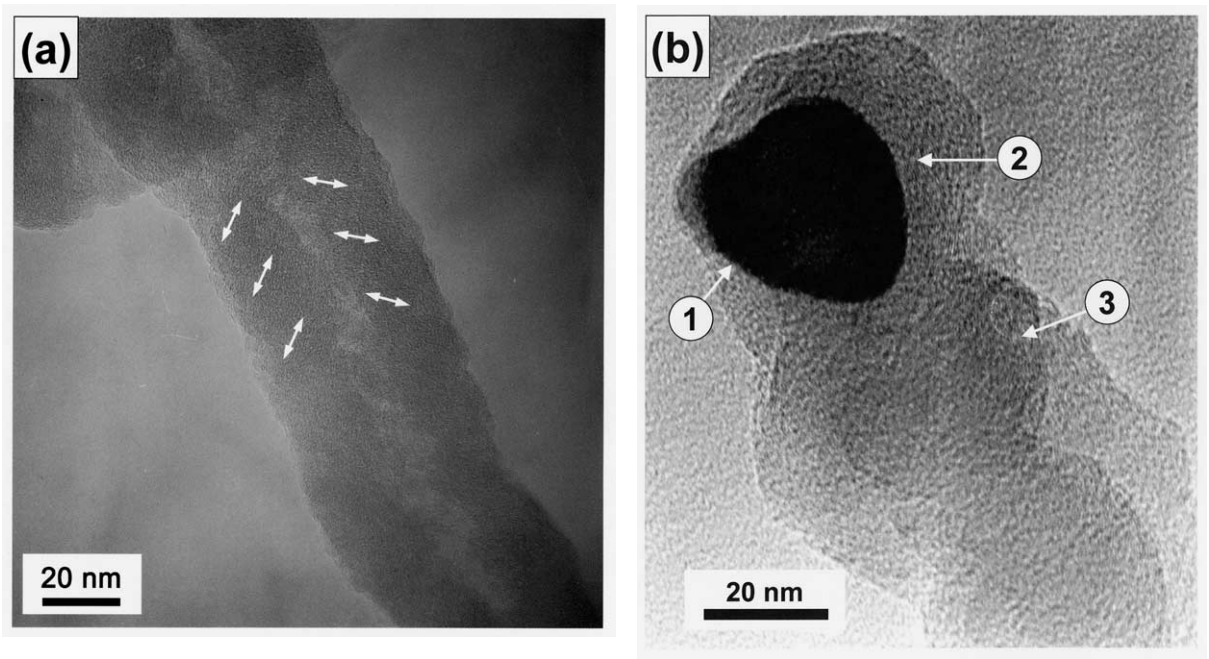

Fig. 3. HRTEM images for the CNFs grown at 500°C. (a) The CNFs consist of defective graphitic sheets aligned with herringbone morphology (see arrow marks). (b) A twisted CNF has encapsulated catalytic particles at the tip (indicated by arrow ①), the fringe of graphitic sheets aligned around the catalytic particle (see arrow ②), and the waving graphitic sheets aligned along the twisted direction (see arrow ③).

Fig. 3b reveals that a twisted CNF has encapsulated catalytic particles at the tip (see arrow ①) and the clear fringe of graphitic sheets around the catalytic particle (see arrow ②). The waving graphitic sheets are aligned along the twisted direction (see arrow ③).

TEM images shows that most CNFs encapsulate the catalytic particle at the tip. All CNFs consist of defective graphitic sheets due to the low growth temperature. The graphitic sheets usually exhibit herringbone morphology, but they are sometimes aligned along the twisted direction.

Fig. 4 shows the Raman spectra for the CNFs grown at 500°C. The excitation laser is a 632.8 nm He–Ne laser. The top spectrum corresponds to the CNTs grown on Ni-deposited SiO_2 substrate at 950°C [22]. Two spectra show mainly two Raman bands at ~1335 cm^{-1} (D band) and ~1580 cm^{-1} (G band). In the spectrum of CNTs grown at 950°C, a D′ band appears at ~1620 cm^{-1} as a bump of the G band. The origin of the D and D′ lines has been explained as disorder features of graphitic sheets [23–25]. For the CNFs grown at 500°C, the D′ and D bands become stronger and broader. Thus the D′ band is completely overlapped with the G band, resulting in a converged

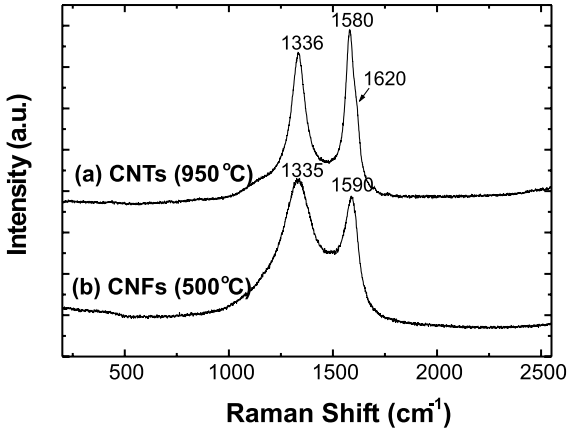

Fig. 4. Raman spectrum of (a) the CNTs grown on Ni-deposited SiO_2 substrate at 950°C and (b) the CNFs grown on Ni-deposited Ti/sodalime glass substrate at 500°C.

peak whose position is at a higher wave number than that of the G band by $\sim$10 cm^{-1}. Tuinstra and Koenig [23] noted a linear relation between the inverse of the in-plane crystallite dimension and the intensity ratio of D and G bands ($I(D)/I(G)$). The value of $I(D)/I(G)$ increases from 0.9 to 1.1 as the growth temperature decreases from 950°C to 500°C. Raman spectrum analysis confirms that the CNFs contain more defective graphitic sheets than the CNTs grown at 950°C.

Fig. 5 is a plot of field emission current density vs. the electric field, for the CNFs grown on Ni-deposited Ti/sodalime glass substrate at 500°C. Indium tin oxide (ITO) is used as an anode for applied voltage. The distance between the anode and the CNF tips was about 50 μm. The turn-on voltage is about 8 V/μm with an emission current density of 0.1 $\mu A/cm^2$. The maximum emission current density is about 0.075 mA/cm^2 at 16 V/μm (i.e. a total bias voltage of 800 V) before electrical breakdown, which is much lower than that of CNTs grown on the Ni/SiO_2 substrate at 950°C, 2.9 mA/cm^2 at 3.7 V/μm [22]. The current density 0.1 mA/cm^2 can produce enough brightness (>1000 cd/m^2) under practical display operating conditions. Therefore, the emission current density from the CNFs grown at 500°C is still sufficient to be applicable for the FEDs. The inset of Fig. 5 indicates that the field emission follows Fowler–Nordheim behavior. The defective graphitic sheets of CNFs are probably responsible for the lower emission current density compared to that of more crystalline CNTs grown at higher temperature.

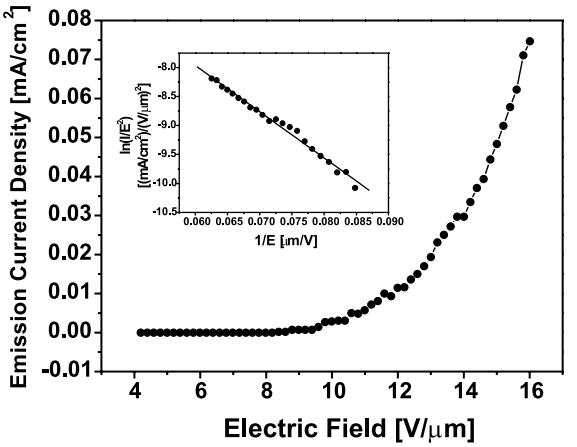

Fig. 5. Field emission current density vs. the electric field, for the CNFs grown on Ni-deposited Ti/sodalime glass substrate at 500°C. The inset shows the Fowler–Nordheim plot.

In summary, we have grown the CNFs on a large area (20 mm × 30 mm) of Ni-deposited Ti/sodalime glass substrate using thermal CVD of C_2H_2 at 500°C. Such low-temperature growth of CNFs has been achieved by a two-stage differential heating technique where the reactants heated at 850°C in the first heating zone are brought into the second heating zone maintained at 500°C for CNF growth. High-density CNFs with diameter in the range 50–60 nm are homogeneously grown on the substrate. Most of the CNFs are curved or bent in shape and composed of defective graphitic sheets with a herringbone morphology. The catalytic particles are usually encapsulated at the tip. Twisted CNFs are also grown with some fractions. All CNFs consist of defective graphitic sheets due to the low growth temperature. The turn-on voltage is about 8.0 V/μm with the emission current density of 0.1 A/cm^2. The maximum emission current density is about 0.075 mA/cm^2 at an applied field of 16 V/μm, indicating that the CNFs grown on the sodalime glass substrate at 500°C can be applicable to FEDs.

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