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Growth of carbon nanotube field emitters on single strand carbon fiber: a linear electron source

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Abstract
The multi-stage effect has been revisited through growing carbon nanotube field emitters on single strand carbon fiber with a thickness of 11 \( \mu m \). A prepared linear electron source exhibits a turn-on field as low as 0.4 \( V \mu m^{-1} \) and an extremely high field enhancement factor of 19 300, when compared with those results from reference nanotube emitters grown on flat silicone wafer; 3.0 \( V \mu m^{-1} \) and 2500, respectively. In addition, we introduce a novel method to grow nanotubes uniformly around the circumference of carbon fibers by using direct resistive heating on the continuously feeding carbon threads. These results open up not only a new path for synthesizing nanocomposites, but also offer an excellent linear electron source for special applications such as backlight units for liquid crystal displays and multi-array x-ray sources.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The selective placement of carbon nanotube (CNT) field emitters in vacuum electronics is extremely important for applications such as electron sources in field emission displays (FEDs) \cite{1, 2}, backlight units (BLUs) for liquid crystal displays (LCDs) \cite{3, 4}, multi-array x-ray sources \cite{5}, and parallel electron beam lithography systems \cite{6}. Since the first report on CNT film using a filtration method \cite{7}, various approaches for preparing CNT films have been reported; screen printing, spray coating, and direct growing. The direct growth of CNTs using chemical vapor deposition (CVD) or plasma-enhanced chemical vapor deposition (PECVD) is only achievable on the patterned catalytic layer, which is normally deposited prior to the CNT growth on various substrates including glass and silicone wafers. To improve the uniformity of the growth, an additional diffusion barrier is inserted between the substrate and the catalysts \cite{8}, mainly because the CNT growth is performed under typical PECVD conditions even over 700 \( ^\circ \)C. The CVD method yields fine gate hole structures of typical dimensions 1–10 \( \mu m \), leading to a dense integration of gate holes. Various advantages that emerge from the CVD approach, however, will be valuable only when they are implemented in techniques that can be scaled for large substrates at low cost. Furthermore, due to the CVD temperature being limited by the sustainable temperature of the substrate during the process, the CNT products are not graphitized perfectly in the usual case, compared to those from arc discharge or laser ablation \cite{9}. Therefore, we still need technological breakthroughs in material quality with lower defective states, low-cost operation, high throughputs, and suitable mass production, especially in large substrate sizes.

Linear electron sources with CNT field emitters have been proposed for application in luminescent tubes \cite{10, 11}, where screen printed or CVD grown CNTs were formed typically on
metal wires 0.27–1.00 mm in diameter. However, electron sources based on metal wires are expected to suffer from several limitations such as: (a) to integrate linear emitters with high resolution in devices such as CNT BLUs or x-ray sources, a much thinner metal wire under 10 µm is preferred, and (b) using metal wires as cathode material, their large thermal expansion generated by Joule heating during field emission may cause considerable effects. From the electrical view point, the carbon fibers (CFs) can be categorized as a semi-metal that increases electric conductivity with increasing temperature over 1650 °C, and then decreases due to the governing phonon scattering, as usual metallic materials do. In their favor, the CFs have excellent thermal properties such as an extremely low thermal expansion coefficient (\(\gamma \leq 5 \times 10^{-6} \text{K}^{-1}\)), and good stability at an elevated temperature (\(\sim 3000^\circ\text{C}\)) in oxygen-free ambient. Therefore, the CF threads can be a promising cathode material for the field emission devices.

In terms of hybrid structure, the CNTs have been deposited in the direction normal to the CF for the purpose of reinforcement in the mechanical strength of CF/polymer composites [13–17]. This selective reinforcement by CNTs resulted in improved CF/polymer matrix interfacial load transfer. In the previous works, the CF bundles usually dipped into catalytic solutions such as ferrofluid, cobalt nitrate, or ferrocene. Because such formed catalysts tend to diffuse into the CF, an amorphous Si layer has been deposited onto the CF as a diffusion barrier [17]. Meanwhile, an extremely high field enhancement factor (\(\gamma\)) over 10 000 has been observed from the multi-staged structures including CNT/CF composites [17–22]. Ren et al [23] also reported the superior field emission properties from the CNTs grown on CF, which were interpreted by their own ‘multi-stage effect’ [24]. Though this effect has been verified in some specific physical situations such as that the CNT emitters grown on a multiple geometrical system show extremely high \(\gamma\) as a product of all those corresponding values of the constituent stages, i.e. \(\gamma_1 \times \gamma_2 \times \cdots \times \gamma_{\text{CNT}}\) for example, it still needs more experimental verification and analysis.

In the above instances, the CF bundles are usually placed onto a supporting substrate to grow CNTs in the CVD chamber, in which only the surfaces exposed to mass transport of gaseous reactants are supposed to lead to a good coverage of CNTs. In this paper, a single strand of CF was continually supplied and heated electrically (Joule heating) through two rotating electrodes in a carbonaceous gas ambient to generate uniform CNTs around the CFs without any problems with mass transport.

2. Experiment

The pitch-based CFs (K63712-12K, Mitsubishi Chem. Ltd) used in this work have 12k fiber tows with a filament diameter of 11 µm, and the strands were cut to 20 cm in length for the preparation of samples. The room temperature electrical resistivity of the CF is about \(10^{-1}\) Ω cm. Before catalyst deposition on CFs for CNT growth, the sizing material was removed by heat treatment at 450°C for 30 min in the air ambient. The catalyst deposition was then followed by two different preparation methods; a conventional thin film deposition and electroless plating. A 2 nm thick layer of catalytic metal (Invar; Fe 54% Ni 42% Co 6%) was prepared using electron beam evaporation at a chamber pressure of \(10^{-9}\) Torr (sample A). For the electroless plating process, dipping CF into Pd–Sn colloid solution was first processed for seed formation on the CF surfaces. The electroless plating involves a neutralizing process of the Pd–Sn modified surface by adsorption of Ni cations on the negatively charged seeds. The details of the plating bath compositions and process conditions are listed in Table 1. The thickness of the plated Ni

### Table 1. Bath composition and the plating condition for electroless Ni plating.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Content (l)</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etching</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>15 ml</td>
<td>60 °C, 5 min</td>
</tr>
<tr>
<td>Neutralizing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>15 ml</td>
<td>45 °C, 5 min</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>26 ml</td>
<td></td>
</tr>
<tr>
<td>Glycol acid</td>
<td>24 ml</td>
<td></td>
</tr>
<tr>
<td>Poly(oxyethylene)ononylphenylether</td>
<td>1.8 ml</td>
<td></td>
</tr>
<tr>
<td>Conditioning</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 sodium tri nitro tri acetone</td>
<td>0.048 ml</td>
<td>60 °C, 5 min</td>
</tr>
<tr>
<td>Lauryltrimethylammonium chloride</td>
<td>3 ml</td>
<td></td>
</tr>
<tr>
<td>Tri ethanol amine</td>
<td>2.6 ml</td>
<td></td>
</tr>
<tr>
<td>2-amino ethanol</td>
<td>1.5 ml</td>
<td></td>
</tr>
<tr>
<td>Poly(oxyethylene)alkyl ether</td>
<td>1 ml</td>
<td></td>
</tr>
<tr>
<td>Copper sulfate pentahydrate</td>
<td>0.2 ml</td>
<td></td>
</tr>
<tr>
<td>Pd–Sn colloid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>9 g</td>
<td>25 °C, 3 min</td>
</tr>
<tr>
<td>Stannous chloride</td>
<td>17.5 g</td>
<td>(Repeat three times in ultrasonic bath)</td>
</tr>
<tr>
<td>Palladium chloride</td>
<td>0.225 g</td>
<td></td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>3.1 ml</td>
<td>25 °C, 4 min</td>
</tr>
<tr>
<td>Fluoroboric acid</td>
<td>13 ml</td>
<td>(Repeat twice in ultrasonic bath)</td>
</tr>
<tr>
<td>Gluconic acid</td>
<td>0.8 ml</td>
<td></td>
</tr>
<tr>
<td>EL Ni–P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium phosphate</td>
<td>25 g</td>
<td>40 °C, 5 s</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>7.95 g</td>
<td></td>
</tr>
<tr>
<td>Nickel sulfate</td>
<td>32 g</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>3 ml</td>
<td></td>
</tr>
<tr>
<td>Malic acid</td>
<td>6.5 g</td>
<td></td>
</tr>
</tbody>
</table>

Malic acid 6.5 g, Ammonia 3 ml, Nickel sulfate 32 g, Glutamic acid 7.95 g, Gluconic acid 0.8 ml, Fluoroboric acid 13 ml, Gluconic acid 0.8 ml, Lauryltrimethylammonium chloride 3 ml, Tri ethanol amine 2.6 ml, 2-amino ethanol 1.5 ml, Poly(oxyethylene)alkyl ether 1 ml, Copper sulfate pentahydrate 0.2 ml, Palladium chloride 0.225 g, Hydrogen fluoride 3.1 ml, Fluoroboric acid 13 ml, Gluconic acid 0.8 ml, Sodium phosphate 25 g, Glutamic acid 7.95 g, Nickel sulfate 32 g, Ammonia 3 ml, Malic acid 6.5 g.
layer on the CF was controlled to be around 15 nm. During the plating, about 4 wt% phosphorous (P) was incorporated into our prepared Ni film. The catalytic layer formation using an electronless process—a typical liquid-based surface redox reaction—has advantages in both mass production and uniform deposition on a bumpy surface with less shadow effect, compared to the other physical deposition processes such as sputtering or evaporation.

To heat the CF strand resistively, we designed a system with two rotating electrodes separated by 4 cm (see the illustration in figure 1). Through one electrode, the prepared CF was to be supplied in the gaseous chamber, and at the same time, the counter electrode holding an end of the supplied fiber starts to wind up for the continuous CVD process. The typical supply speed was set to be 8 mm min$^{-1}$. After evacuating the reaction chamber (base pressure 1 × 10$^{-3}$ Torr), acetylene ($\text{C}_2\text{H}_2$) as a carbon source and argon (Ar) as a carrier gas were supplied with a flow rate of 200 sccm and 500 sccm, respectively. The process pressure was 10 Torr. The temperature of the fiber during the CNT growth was measured to be about 650$^\circ$C using an optical pyrometer, when DC bias 5.5 V was applied in between the rotating electrodes.

To investigate the surface morphologies and microstructures of the prepared CNTs, a scanning electron microscope (SEM, S-4500, Hitachi), a transmission electron microscope (TEM, H-9000NA, Hitachi) with an acceleration voltage of 300 kV, and a micro-Raman spectrometer (633 nm Ar laser, Renishaw) were used. Electron field emission properties were characterized in an ultra-high vacuum (UHV) chamber (1 × 10$^{-6}$ Torr) under a diode configuration with a cathode-to-anode gap ($D$) 700 μm. Such a large gap (emitter tip length $\ll$ tip-to-anode gap) was chosen so as to reduce any possible measurement error, especially in the evaluation of the applied electric field. In the measurements, maximum gain in the $D$ was expected to be about 15 μm in the case of a CNT/CF strand, compared to that in the case of a CNT/Si wafer. Thus, our $I$–$V$ data can hold only a maximum 2% of error. Additional measurement error is expected to be generated in a small gap regime (emitter tip length $\gg$ tip-to-anode gap), where a large dependence of the estimated $γ$ values on the gap can be induced by the nano-configuration effect [24, 25].

Prior to the CVD process, the catalyst layers prepared by two different methods were commonly heat treated at 650$^\circ$C for 30 s in vacuum to form nano-clusters of the catalysts. While the clusters formed by electron beam evaporation (sample A, figure 2(a)) showed uniform sizes (3–5 nm), relatively large clusters with wide size distribution (10–80 nm) were obtained from the electronless plating (sample B, figure 2(b)). As a natural consequence, the grown CNT morphologies followed the same patterns as the catalyst clusters. A well aligned and uniform CNT array 5 μm in length was obtained from sample A (figures 2(c) and (d)). It should be noted that CNTs were not grown on the side of the fiber, where inevitably no catalyst is deposited during the evaporation process. By contrast, a relatively disordered array with shorter length (1–2 μm), and less uniform morphology with large variation in CNT diameter was observed from sample B (figures 2(e) and (f)), which is due to the limit in the plating process to form a thinner continuous film, compared to those deposited by a low pressure vapor process. In spite of this limit, the CNTs were grown all around the CF without a dead surface in sample B.

From the TEM investigation with energy dispersive x-ray (EDX) analysis, as shown in figure 3, the Invar catalyst cluster sizes in sample A were in the range 3–5 nm (figure 3(a)). The grown CNTs in sample A showed about 7 nm in outer diameter (3–4 walls) with a 5 nm inner hole (figure 3(b)). Meanwhile, 10–15 nm of Ni clusters (figure 3(c)) and thicker CNTs with outer diameter 15–20 nm (12–15 walls) were mainly observed in sample B (figure 3(d)).

Micro-Raman spectra were investigated for both of the samples, as shown in figure 4. Two representative peaks are assigned at around 1350 cm$^{-1}$ (D band) and 1580 cm$^{-1}$ (G band). The second harmonic peak of the D band at 2700 cm$^{-1}$, historically named the G$'$ band, is also observed in the spectra [26]. The ratio between D and G intensities ($I_D/I_G$) is often used as an index of the degree of crystalline perfection of the graphite structure. The estimated $I_D/I_G$ values are 0.335 for the bare CF, 0.804 for the CNTs in sample A, and 0.992 for sample B, respectively. Attributed to the fact that the carbon precursors dissolved in a smaller catalytic particle can easily diffuse and precipitate as a two-dimensional (2D) graphene structure, fewer defective CNTs in sample A were detected, compared to those in sample B. It is out of the question that the much higher graphitization temperature, over 1500$^\circ$C for the CF preparation, yields such a low index.

3. Results and discussion

Figure 1. Schematic diagram of the resistive heating system and an illustration of the experimental apparatus.
Figure 2. SEM images of (a) Invar nanoparticles, (b) Ni nanoparticles on carbon fiber after thermal treatment without carbon gas source-C₂H₂. SEM images of CNTs grown by resistive heating from: (c), (d) thin Invar layers (sample A) and (e), (f) Ni layer (sample B) on carbon fibers as a catalyst for CNT growth.

Figure 5(a) plots the $I-V$ characteristics for the prepared samples and a plot obtained from nanotubes grown on the Si wafer is used as a reference. In this case, the CNTs were deposited on n-type Si (4 mm × 4 mm) using the same catalyst layer as sample A. The reference sample turned on electron field emission at ~3 V μm⁻¹ and reached ~500 μA at over 4.2 V μm⁻¹. The turn-on fields were dramatically lowered for the CNTs/CF samples: sample B showed about 1.0 V μm⁻¹ and 0.4 V μm⁻¹ for sample A, reaching 500 μA at 1.7 V μm⁻¹ and 0.7 V μm⁻¹, respectively. The Fowler–Nordheim plots [27], as shown in the inset of figure 5(a) indicate that such improved field emission properties for our CNTs/CF samples are caused by the enhanced $γ$ values from 2500 (reference) to 8700 (sample B) and 19 300 (sample A), respectively.

Our CNTs/CF cathodes can be approximated as a two stage system [24] with a common CF bottom stage. The overall $γ_{tot}$ in the two stage system yields

$$γ_{tot} = γ_{CNT}γ_{CF} = \left(\frac{l}{l+d}\right)\left(1 + \frac{d}{r}\right)\left(\frac{L}{L+d}\right)\left(1 + \frac{d}{R}\right).$$

(1)

Here, $l$ and $r$ are the length and radius of the CNT, $L$ and $R$ correspond to the diameter and radius of the CF, respectively. $d$ indicates the distance between the CNT tip and anode. Under the large gap regime as in our case, equation (1) can be readily reduced to $γ_{tot} = γ_{CNT}γ_{CF} = \left(\frac{l}{l+d}\right)\left(\frac{L}{L+d}\right)\left(1 + \frac{d}{R}\right)$. However, the last term $L/R$ is only valid for the tip geometry. For the cylinder (CF) and plate (anode) geometry as in our geometry, the $γ_{CF}$ should be written as $γ_{CF} = 0.9\frac{D−2R}{R\ln[D−2R]}$. 


Figure 3. TEM images of the initial growth stages with EDX analysis (a, c), and the grown CNTs (b, d). (a) and (b) are of sample A, and (c) and (d) are of sample B. The marked circles in (a) and (c) indicate the EDX analyzing points.

Thus, we obtain $\gamma_{\text{CF}} = 0.9 \times \frac{290 - 11}{5.5 \times (5.5 - 5.5)} \approx 23$. For sample A, $\gamma_{\text{CNT}}$ can be assumed to be 2500, that is, the same value as obtained from the CNTs/Si reference, so thus about an eight-fold increase in $\gamma_{\text{tot}} \sim 19300$ is estimated with assistance from the underlying CF structure. The same analysis for sample B showed about a nine-fold enhancement in $\gamma_{\text{tot}} \sim 8700$, compared with $\gamma_{\text{CNT}} \sim 900$ of the CNTs grown on electroless Ni/Si ($I-V$ not shown here). The experimentally deduced $\gamma_{\text{CF}}$ amounts to 8–9 for $D = 700 \mu$m, which is quite a reasonably acceptable value because the calculation was done on the infinite cylinder and plate geometry without a bottom electrode (ITO in our experiment).

To support our results qualitatively, an additional electrostatic simulation was conducted with commercial software (OPERA 3D, v. 12) to investigate the electric field distribution using the finite element method. The simulation geometry was set to have a flat anode (0 V) located above the CNT/CF cathode (100 V) at a 500 $\mu$m distance with $r$, $l$, and $R$ of 10 nm, 5 $\mu$m, and 5 $\mu$m, respectively. The zone map representation of the simulated electric field showed the same tendency that a higher electric field is concentrated on the tip edge in the case of the CNT on a curved stage than that on a flat stage (12.7 versus 3.7 V $\mu$m$^{-1}$), as shown in figure 5(b). A field emission image, as shown in figure 5(c), was obtained on a phosphor (ZnS:Cu, Al) coated anode plate from sample A with a 15 mm length. A uniform linear emission image along the CF strand was observed at an applied electric field as low as 0.6 V $\mu$m$^{-1}$.

Figure 4. Raman spectra of carbon fiber and CNTs grown by resistive heating of carbon fiber.

4. Conclusion

In conclusion, we report on a method to make a linear electron source for which the CNTs were grown on single strand CF by direct resistive heating. Both e-beam evaporated Invar and electroless plated Ni were used as catalyst layers. The former yielded CNTs with better crystallinity and uniformity than those produced by the latter. Such prepared linear emitters exhibited a turn-on field as low as 0.4 V $\mu$m$^{-1}$, and an extremely high $\gamma \sim 19300$, contrasted with the CNT emitters grown on the flat wafer. It is estimated that the underlying CF structure enhances the overall $\gamma$ by about eight or nine times, based on the ‘multi-stage effect’. Our results open not only a new path for synthesizing nanocomposites, but also offer an excellent linear electron source for special applications such as in backlight units for liquid crystal displays and multi-array x-ray sources.
Figure 5. (a) Field emission characteristics of CNTs on Si wafer and carbon fiber (samples A and B), where the inset shows their Fowler–Nordheim plots. (b) Local electric field distribution around the CNT tip with different substrate geometry and (c) a field emission image of CNT/CF (sample A) was observed at an electric field of 0.7 V μm. (Scale bar means 1 cm.)

References