Fabrication of efficient field emitters with thin multiwalled carbon nanotubes using spray method

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Abstract

Thin multiwalled carbon nanotube (t-MWCNTs)-based field emitters are made by use of a spray method. The number of tube walls is between 2 and 6, with the corresponding outer diameters between 3 and 6 nm. They were dispersed in dichloroethane and sprayed onto metal-deposited indium tin oxide glass. After heat treatment, they were found to be tightly adhered to metal electrode. Excellent field emission characteristics were exhibited, with a large field enhancement factor and low turn-on voltage, comparable to those of single-walled CNTs. However, the t-MWCNTs demonstrated a significantly lower degradation rate than SWCNTs in the emission current. This high emission stability was attributed to their stable edge structures, similar to conventional large-diameter MWCNTs. Therefore, t-MWCNTs could be utilized as an alternative material for field emitters.

Keywords: Carbon nanotubes; Coating; Field emission

1. Introduction

A large field enhancement factor, high electrical conductivity, and environmental stability are prerequisites for an efficient field emitter. For this reason, carbon nanotubes (CNTs) have been considered as one of the best field emitters [1] due to their unique properties such as high aspect ratio, chemical inertness, high mechanical strength, and high electrical conductivity. Recently, singlewalled carbon nanotubes (SWCNTs) have been reported to have a large field enhancement factor, low threshold voltage, and high emission currents [2], but substantial degradation of emission currents presents a serious drawback for application to the field emission displays [3]. In contrast to SWCNTs, multiwalled CNTs (MWCNTs) have shown high emission stability, however, a small field enhancement factor has resulted in low emission current [4]. Doublewalled carbon nanotubes have been studied for this purpose, but the poor production rate and following purification process of catalysts presents a serious bottleneck [5]. Thin multiwalled CNTs (t-MWCNTs) have been synthesized with high catalyst efficiency such that no further purification process is required [6]. Therefore, these t-MWCNTs, with small number of walls of 2–6 and small diameters below 6 nm, could be an alternative for this purpose due to their intermediate structural properties between SWCNTs and MWCNTs [7].

CNT-based field emitters have been fabricated by various methods such as direct growth [8], suspension-filtering [3], electrophoresis [9], and screen printing [2]. One may easily control the alignment, density, diameter, and length of nanotubes using the direct chemical vapor deposition (CVD) growth method. However, this approach is often limited by the scalability of the substrate size and growth temperature. Whereas large area deposition of nanotubes can be realized using the screen-printing method, a
substantial degradation of emission tips caused by oxygen gases that are out-gassed from the organic vehicles in the paste cannot be avoided. In addition, this method could not permit measurement of the intrinsic field emission nature of nanotubes, due to the surface modification of nanotubes. Suspension-filtering and electrophoresis methods are also disadvantageous due to the large substrate size, and the particularly weak adhesion of CNTs to the substrate makes these approaches impractical. The spray method, which is an easy and convenient method to deposit nanotubes for cathodes, can achieve large area deposition and suppress degradation of emission tips [10]. However, the poor adhesion of nanotubes to the electrode, and the dispersability of nanotubes are serious drawbacks to overcome.

The purpose of this paper is twofold. The first is to overcome the hurdles in the fabrication of CNT-based field emitters, by using the spray method mentioned above. Adhesion between nanotube and electrode was resolved by introducing indium layers on indium tin oxide (ITO)-coated glass substrate, followed by heat treatment [11]. The 1,2-dichloroethane (DCE) solvent is used as a good dispersant for CNTs followed by sonication and centrifugation [12]. Another is to find the best CNTs among several existing CNTs that present field emission characteristics. The spray technique is introduced to fabricate field emitters using several CNTs such as SWCNTs, t-MWCNTs, and MWCNTs. It is found that the t-MWCNTs demonstrated the best field emission characteristics, following the merits of SWCNTs and MWCNTs.

2. Experimental

To maintain uniform distribution of CNTs on the substrate, it is a prerequisite to disperse CNTs in the solvent. Furthermore, the solvent should be vaporized easily during the spray method, and the CNTs should remain on the sample exclusively in order to prevent agglomeration of CNTs after spray. It has been well known that DCE is a good dispersant for CNTs without surface modification, and easily vaporized in ambient conditions [12]. The dispersion process consists of sonication of 50 mg CNTs in 100 ml of DCE solvent for 100 h and a centrifugation at a speed of 2370g (5000 rpm) for 30 min to precipitate some undissolved CNTs. The as-grown t-MWCNT using the catalytic thermal CVD method was used directly for dispersion because of its high purity of the sample [6]. Their diameters typically ranged from 3 to 6 nm and they were mostly bundled to several nanotubes with lengths similar to those of SWCNTs. We also used some other samples for comparison of emission stability. Arc discharge-synthesized SWCNTs with diameters of 1.0–1.2 nm and CVD-synthesized MWCNTs with diameters of 10–15 nm (Iljin Nanotech, Korea) were purified by heat treatment in air ambient, followed by nitric acid treatment.

After decanting the supernatants with care, CNTs/DCE solution was sprayed on the prepared ITO glass. For strong adhesion between nanotubes and ITO glass, a thin indium metal layer with a thickness of 100 nm was deposited on ITO glass using thermal evaporator. The spraying conditions such as Ar pressure, nozzle diameter, and distance between substrate and nozzle were optimized for uniform deposition of the nanotubes. Fig. 1(a) presents a schematic of the proposed spraying system. After spraying the nanotubes, the substrate was annealed at 350°C for 10 min in Ar atmosphere. Thin indium layers were melted and diffused onto nanotube walls during heat treatment, resulting in strong adhesion between CNTs and the ITO glass.

3. Results and discussion

Fig. 1(b) presents the cathode of t-MWCNTs-based field emitters over 1 × 1 cm². Fig. 1(c) presents a SEM image of the t-MWCNT, where all t-MWCNTs were uniformly distributed over the area. Neither appreciable aggregates nor catalysts were visible in the image. The surface activation enabling preferential alignment along the vertical direction was achieved using an adhesive tape [13], prior to emission measurement. A considerable amount of t-MWCNTs that did not form stable adhesion with electrodes were removed using an activation process. As a consequence, the underly-
ing indium domains were clearly visible after taping. Yet, numerous t-MWCNTs that were strongly bound to the indium layer still remained in the sample, as presented in Fig. 1(d).

Fig. 2(a)–(c) demonstrates SWCNTs, t-MWCNTs, and MWCNTs-based field emitters after activation process, respectively. After activation process, numerous CNTs were aligned preferentially in the vertical direction. This preferential alignment gives rise to large field enhancement factor, resulting in high emission current density and low turn-on field. Since the equivalent amount of CNTs in all three samples is used, it is expected that the density of SWCNTs would at least be several times higher than that of t-MWCNTs, because the mass of SWCNTs is lighter than that of t-MWCNTs for the same length. The amount of supernatant SWCNTs should be larger than those of t-MWCNTs or MWCNTs after centrifugation. However, it was observed that the emitter density of SWCNTs was very similar to that of t-MWCNTs, as presented in Table 1. This might be caused by the more prominent bundling effect of SWCNTs than t-MWCNTs. As presented in Fig. 2(a) and (b), the bundle size of SWCNTs is similar to that of t-MWCNTs. The bundling effect can be also conjectured by the sharp tip of the bundles, compared to the bottom section. This is also an advantage of t-MWCNTs, where it demonstrates much less prominent bundling effect and hence better dispersability in DCE. It is also observed that many t-MWCNTs and MWCNTs were curly, though this trend was more severe in MWCNTs than t-MWCNTs. However, these nanotubes could become straight under high applied bias during field emission measurements [14]. Therefore, this is not currently of concern at this point.

Fig. 3 presents the current density–electric field (J–E) characteristics and the corresponding Fowler–Nordheim (FN) plots of SWCNTs, t-MWCNTs, and MWCNTs-based field emitters. These three samples were fabricated in the same manner as discussed before and their field emission characteristics were examined in a diode type with a dc bias inside a vacuum chamber, where the base pressure was 5 × 10^-7 Torr. In order to remove the emission noise and instability, the high-voltage annealing for three samples was carried out until the fluctuation of emission currents was less than 2%. In Fig. 3(a), t-MWCNTs revealed the highest current density of approximately 1.52 mA/cm² at 3.5 V/lm for all three samples. In addition, the turn-on field of t-MWCNTs was lower than that of MWCNTs, as presented in the FN plot of Fig. 3(b). This is attributed to the higher field enhancement factor of t-MWCNTs than that of MWCNTs, as presented in Table 1. In fact, the field enhancement factor is proportional to the aspect ratio of nanotubes, i.e., the higher the field enhancement factor is, the lower the turn-on field and higher the current density. On the other hand, it is also noted that the turn-on field of t-MWCNTs was similar to that of SWCNTs. This can

<table>
<thead>
<tr>
<th>Density (cm⁻²)</th>
<th>E_{turn-on} (V/µm)</th>
<th>J_{E=3.5 V/µm} (mA/cm²)</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT</td>
<td>8.2 × 10⁸</td>
<td>1.85</td>
<td>1.25</td>
</tr>
<tr>
<td>T-MWCNT</td>
<td>7.8 × 10⁸</td>
<td>1.90</td>
<td>1.52</td>
</tr>
<tr>
<td>MWCNT</td>
<td>7.0 × 10⁸</td>
<td>2.44</td>
<td>0.65</td>
</tr>
</tbody>
</table>

The turn-on field was calculated as a starting field of the linear region (S1) at the FN plot. The field enhancement factor was determined from the slope of the linear region, β = -BΦ¹/²/S, where B is just a constant, Φ is the work function, and S is the slope which is determined from the linear slope (S1) of the FN plot. It is assumed that the work function of the nanotube is 5.0 eV of graphite.

Fig. 2. SEM images of (a) SWCNTs, (b) t-MWCNTs, and (c) MWCNTs-based field emitters after surface activation, respectively. The scale bars are 2 µm.
be ascribed to the less bundling effect of t-MWCNTs than SWCNTs, as presented in Fig. 2, resulting in a comparable field enhancement factor of t-MWCNTs to SWCNTs.

The emitter density and field emission characteristics for these three kinds of CNTs were measured from SEM images, \( I-V \) curve, and the related FN plot, and listed in Table 1. As mentioned previously, the emitter number-density of three kinds of nanotubes is quite similar, whereas the field enhancement factor, turn-on field, and emission current density under 3.5 V/\( \mu \)m are quite different. It is generally known that the emission current depends on the field enhancement factor, as well as emitter density [15]. Since the field enhancement factor is mainly affected by the aspect ratio and inter-tube spacing, t-MWCNTs with higher aspect ratio than MWCNTs can give rise to a higher emission current. It is also noted that values of the field enhancement factor for three CNTs is a little larger than those reported in much literature [15–17]. Nilsson and his co-workers reported that the field enhancement factor is the largest when the ratio of the intertube distance to nanotube length approximately reaches 2 [16]. More recently, Suh and his co-workers insisted that the largest field enhancement factor could be obtained at the nanotube length, similar to the intertube distance [15]. In fact, the length and inter-tube distance of vertically aligned CNTs grown by thermal CVD are approximately ~10 \( \mu \)m and 100 nm, respectively, resulting in small field enhancement factor of approximately several hundred, due to the large screening effect [17]. In this case, the nanotube length is approximately 4.3 times longer than inter-tube spacing, and thus the screening effect in samples still exists, but the effect is much less significant compared to the CVD-grown samples, resulting in large field enhancement factor in the samples. Two regions are observed, with different slopes in the FN plot, as presented in Fig. 3(b). At the low field region (S1), SWCNTs show superior field emission characteristics over others, as listed in Table 1. However, in the high field region (S2), the emission current density of t-MWCNTs is higher than that of other nanotubes. This can be explained in terms of the tip stability of nanotubes.

Fig. 4(a) presents the degradation rate of the emission current density (\( J/J_i \)) at the same electric field of 2.8 V/\( \mu \)m. The initial current density (\( J_i \)) of SWCNTs, t-MWCNTs, and MWCNTs was 0.17, 0.19, and 0.09 mA/cm\(^2\), respectively. These current densities were relatively large, to visual-
ize the tip degradation vividly within a relatively short time. It is clearly observed that the emission current density of SWCNTs drastically decreases to 10% after 12 h. It is also noted that the current degradation rate of t-MWCNTs is similar to that of MWCNTs, even though the initial current density of t-MWCNTs is much higher than that of MWCNTs. The emission current of nanotubes decreases, when the nanotube tip attached with residual oxygen gases is degraded by Joule heating under a high electric field [18]. In fact, the out-gassing from the cathode is one of the main reasons of vacuum deterioration, resulting in degradation of emission currents. In the proposed approach, the spray method using the CNT/DCE solution is advantageous for high vacuum levels, since there are no organic vehicles as out-gassing sources, compared to the conventional screen printing with paste [2]. This was observed using the residual gas analysis measurement and will be reported elsewhere. In addition, the structural modification of the nanotube tip by the ion bombardment of residual gases could reduce the emission current at the high electric field region. Therefore, the current degradation rate of CNTs would depend on the physical strength of a particular CNT tip, and thus it can be concluded that the stable emission of t-MWCNTs is attributed to the chemical and physical stability similar to MWCNTs [19]. The photo image of the emission pattern from t-MWCNTs with a size of 3 × 3 cm² is presented in Fig. 4(b). The uniform and extremely bright electron emission from t-MWCNTs is retrieved using phosphor-coated ITO glass as an anode when the applied electric field and emission current density were 3.1 V/μm and 0.5 mA/cm², respectively. This plane-type field emission, not a spot-type, is attributed to the uniform length, diameter, and density of t-MWCNTs emitters in the whole area.

4. Conclusion

The field emission characteristics of t-MWCNTs have been investigated together with SWCNTs and MWCNTs-based field emitters, fabricated by spraying the dispersed nanotubes/DCE solution. The indium thin layers were deposited and annealed for the strong adhesion between substrate and nanotubes. It is found that t-MWCNTs have a higher current density and lower turn-on field than MWCNTs, due to the higher field enhancement factor. It was observed that the current degradation rate of t-MWCNTs was very similar to that of MWCNTs, however, SWCNTs drastically decreased their currents over a period of 12 h. This stable emission of t-MWCNTs compared to SWCNTs was attributed to their chemical and physical stability, similar to MWCNTs. Therefore, t-MWCNTs could be utilized as an alternative material for the application to field emitters.

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References