Ar, O$_2$, CHF$_3$, and SF$_6$ plasma treatments of screen-printed carbon nanotube films for electrode applications

Zhongyu Hou*, Bingchu Cai, Hai Liu, Dong Xu

The National Key Laboratory of Micro/Nano Fabrication Technology, Key Laboratory for Thin Film and Microfabrication of Ministry of Education, Research Institute of Micro/Nano Science and Technology, Shanghai JiaoTong University, Shanghai 200030, China

**ABSTRACT**

This paper investigates the consequence of the material property and the plasma gas chemistry (herein referred to the plasma gas-feeding species and methods) on the electrode performance in plasma treatments of screen-printed carbon nanotube (CNT) films. Four plasma gases (Ar, O$_2$, SF$_6$, and CHF$_3$) and three gas-feeding methods were examined. The surface morphology, microstructure, and composition of 11 sample groups have been carefully characterized. Tests of the CNT film electrode subjected to gas discharge and field emission show that surface morphology modification is the most influential factor in respect of lowering the onset voltages. In detail, O$_2$/Ar (O$_2$ followed by Ar) and Ar + CHF$_3$ + SF$_6$ (mixed three gases) treatments are the best choices for ionization and field emission applications, respectively. The relevant results are even better than that of the samples of aligned CNT films prepared by chemical vapor deposition. The underlying mechanisms are modeled by two opposing processes (etching and coating), which phenomenally produce three competing effects, i.e., CNT protruding, bundle forming, and neo-nanostructure forming. The results and the correct behavior of our model suggest that the plasma gas chemistry is the most fundamental factor in the process of plasma treatments of CNT films.

© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

Direct incorporation of carbon nanotubes (CNTs) into some conventional devices such as in field emission, gas electronics, and electrochemistry can significantly improve the expected performance [1-4]. This is mainly due to its superior aspect ratio for electric field convergence [5,6], good chemical stability, high thermal conductivity, and mechanical stiffness [7,8]. Recent explorations of the application of CNTs to the microelectromechanical system (MEMS) devices show that slurry-based screen printing technology for the patterning of CNT film (CNTF) is efficient for CNTF-based MEMS device fabrications [9-11]. In addition, some field emission (FE) commercial products have been realized based on screen-printed CNTFs, such as by Samsung, ERSO/ITRI, and ISE. The main reason why screen-printed CNTFs is accepted by the industry is that it satisfies the need of low-cost and large area production; besides, its field emission yields, operation voltage and other performance are comparable with those of aligned CNTFs prepared by high cost technologies, e.g., the chemical vapor deposition (CVD) method. However, the random arrangement of CNTs in screen-printed CNTFs needs to be optimized or activated [12]. Such treatments are also necessary sometimes for those aligned CNTFs. Consequently, intense efforts have been made on the plasma treatments of CNTFs for FE applications, recently [12-35]. Unfortunately,
many self-consistent approaches are developed independently, which are lacking in comparisons under the same experimental conditions. The plasma–CNTs interaction and the field emission property evaluation in this field are very sensitive to CNTs’ original state, methods of CNTFs’ preparation, experimental setups of the plasma treatment, and the FE test condition; this results in some incompatible and puzzling conclusions in this field. For example, in the case of argon plasma treatment, Kim et al. concluded that Ar plasma treatment of CNTFs can improve the FE property significantly [12], whereas Liu et al. asserted that Ar plasma can destroy the FE property of CNTs [24]. Another example is the hydrogen plasma treatment, Zhang et al. [13] concluded that C–H bonds cannot be introduced by H-plasma, whereas such effect was confirmed in Ref. [26]. Such situation has greatly limited the understanding and application of those technologies.

In this paper, plasma treatments on the screen-printed CNTFs have been systematically examined under the same conditions. Four ‘representative’ plasma gases (Ar is for physical treatment, O₂ is for oxidation reaction, SF₆ is for fluorination reaction, and CHF₃ is for hydrogen contained fluorination reaction) were considered in our experiments. Furthermore, the gas-feeding methods have been sorted into three categories of single component, multiple components, and sequential method. The surface morphology, microstructure, and composition changes in those plasma-treated samples have been carefully examined. Besides, the authors argue that the gas discharge experiment in the air should be considered as an efficient supplemental method to the FE testing to evaluate the CNTF property. Consequently, the experimental results of both field emission and gas discharge tests have been demonstrated. Based on the results, a qualitative model has been proposed to describe the physical processes involved herein. Technically, the study conclusively supports that the plasma treatment is an effective method for the performance optimization of screen-printed CNTF electrode in the areas concerned with field emission electrons and ionization gas molecules.

2. Experimental

2.1. CNTF preparation

Multiwalled carbon nanotubes (MWCNTs), purchased from NH Co. Ltd., are 15 μm and 45 nm in mean length and diameter, respectively. The MWCNT powder (1 g) was mixed with the organic solvent (10 g), which was composed of ethyl cellulose and turpentine with the mass ratio of 1.7:98.3. They were blended into the MWCNT slurry through steel ball milling method for 30 min. The slurry was screen-printed on a glass substrate, which was sputter-deposited with a Cr/Au thin film of 30/270 nm in thicknesses. After annealing under 350 °C for 20 min, the thickness and unit area of the CNTFs are 3 ± 0.4 μm (profiler method) and about 25 mm², respectively. The thickness of the CNTF sample without the plasma treatments is measured by the FEM observation. It is also measured by a Vecco Dektek 6 M surface profiler; during the measurements, the sampling results of the CNTF surface and the Au film surface were both averaged across their respective sampling distances of 400 μm; furthermore, the results of five different sampling lines were averaged to enhance the data quality. Yet the FEM method yielded the outputs of about 0.1–0.3 μm thicker.

2.2. Plasma treatment

The plasma treatment was performed in a reactive ion etching (RIE) commercial apparatus (NEXTAL 100). The plasma was operated by a radio-frequency (RF) plate electrode with digitally tunable RF power, DC bias, gas feed species, gas flow rate, chamber temperature, and working pressure. Table 1 is the list of our experimental parameters. The RF power and chiller temperature were set to 40 W and 22.5 °C, respectively. In every sample group (eight samples), five samples were treated for process uniformity concern and three samples for the etch rate. The thicknesses of the CNTF samples after the plasma treatments were measured by a Vecco Dektek 6 M surface profiler. The error in the evaluation of etch

<table>
<thead>
<tr>
<th>Sample group</th>
<th>Plasma gas</th>
<th>Work pressure (mTorr)</th>
<th>Gas flow rate (sccm)</th>
<th>Bias voltage (V)</th>
<th>Load (W)</th>
<th>Tune (cycles)</th>
<th>Etch time (s)</th>
<th>Etch rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A*</td>
<td>Ar</td>
<td>40, 80</td>
<td>10, 50</td>
<td>760</td>
<td>300, 400</td>
<td>4500, 4600</td>
<td>100</td>
<td>7.69, 9.48</td>
</tr>
<tr>
<td>B*</td>
<td>O₂</td>
<td>40, 80</td>
<td>10, 50</td>
<td>715</td>
<td>300, 390</td>
<td>4750, 4985</td>
<td>100</td>
<td>28.12, 37.92</td>
</tr>
<tr>
<td>C*</td>
<td>SF₆</td>
<td>40, 80</td>
<td>10, 50</td>
<td>100</td>
<td>70, 80</td>
<td>1750, 1800</td>
<td>100</td>
<td>4.87, 6.12</td>
</tr>
<tr>
<td>D</td>
<td>CHF₃</td>
<td>40, 80</td>
<td>10, 50</td>
<td>750</td>
<td>270, 350</td>
<td>4500, 5300</td>
<td>100</td>
<td>2.23, 3.72</td>
</tr>
<tr>
<td>E</td>
<td>CHF₃ + SF₆</td>
<td>80</td>
<td>10 + 10</td>
<td>190</td>
<td>60</td>
<td>2500</td>
<td>150</td>
<td>9.73</td>
</tr>
<tr>
<td>F</td>
<td>O₂ + SF₆</td>
<td>40</td>
<td>30 + 10</td>
<td>260</td>
<td>60</td>
<td>1800</td>
<td>150</td>
<td>9.51</td>
</tr>
<tr>
<td>G</td>
<td>O₂ + SF₆</td>
<td>80</td>
<td>30 + 10</td>
<td>200</td>
<td>50</td>
<td>1800</td>
<td>150</td>
<td>23.67</td>
</tr>
<tr>
<td>H</td>
<td>Ar + O₂</td>
<td>80</td>
<td>20 + 20</td>
<td>740</td>
<td>400</td>
<td>5000</td>
<td>150</td>
<td>38.01</td>
</tr>
<tr>
<td>I</td>
<td>Ar + CHF₃ + SF₆</td>
<td>80</td>
<td>30 + 10 + 10</td>
<td>320</td>
<td>250</td>
<td>2600</td>
<td>150</td>
<td>3.99</td>
</tr>
<tr>
<td>J*</td>
<td>O₂/Ar</td>
<td>80</td>
<td>30/30</td>
<td>710/670</td>
<td>390/400</td>
<td>4985/4600</td>
<td>90/90</td>
<td>90/90</td>
</tr>
</tbody>
</table>

a Samples have been analysed using EDX and TEM.
b Two groups were treated with work pressure of 40 and 80 mTorr while the gas flow rate was fixed at 50 sccm in both cases.
c Two groups were treated with gas flow rate of 10 and 50 sccm while the work pressure was fixed at 80 mTorr in both cases.
rate came from the CNTF thickness measurement, which was estimated to be less than ±0.7 μm [30]. The etch rate for different treatment parameters have also been shown in Table 1. In this table and the text, ‘+’ and ‘/’ are used to represent that several gases are mixed together (herein referred to as ‘multiple components’) and one gas is followed by another (herein referred to as ‘sequential method’), respectively.

2.3. Characterization and tests

The surface morphology, microstructure and composition changes in the CNTFs before and after the plasma treatments were examined by the field emission scanning electron microscopy (FESEM) (Philips Sirion 200, 5 kV), transmission electron microscopy (TEM) (JEM 2010, 200 kV), and energy dispersive X-ray (EDX) detector fixed in the FESEM apparatus, respectively. For the FESEM observation, no samples were deposit-covered with Au thin films to keep the original morphology less interfered. The gas ionization test in the air (101 kPa) was performed by the similar approach described in Refs. [2,10,19]. The background vacuum for field emission property testing was 1 × 10⁻⁴ Pa. The apparatus is illustrated in Fig. 1. The CNTFs were negatively biased during the test. The room temperature and relative humidity are in the range of 23 ± 5°C and 50% ± 1%, respectively.

3. Results and discussion

3.1. The surface examinations

3.1.1. Surface morphology examinations

Firstly, the results of the surface morphology examination are shown as follows: Figs. 2–4 demonstrate the FESEM images of the surface morphology after the plasma treatments with gas feeding of single component, multiple component, and sequential method, respectively. The modified surface morphology after plasma irradiation can be characterized by three features, i.e., protruding, bundling, and neo-nanostructure forming, when it was compared with the random state of untreated CNTFs demonstrated in Fig. 2a and b.

(1) The surfaces of five sample groups are featured by the protruding and bundling of CNTs. They are groups A, B, D, E, and H, which were treated by the plasmas of Ar, O₂, CHF₃, Ar + O₂, and CHF₃ + SF₆, respectively. In these samples, the CNTs are protruding out of the surface, but their tips tend to twist with each other into some bundle-like morphology. As indicated in the corresponding micrographs in Figs. 2 and 3, the morphology of these samples is similar. However, it is shown that the CNTs protruding height, density, and bundle size are different in each case. Although it is difficult to be quantified, the FESEM analysis supports that the O₂ plasma can produce the lowest protruding height and the shortest bundles’ spacing; additionally, CHF₃ and Ar + O₂ plasmas can produce the largest bundle size and the largest protruding height, respectively.

(2) The feature of CNTs morphology is difficult to be found in the surfaces of sample groups C, F, G, and I, which
were treated by SF₆, Ar + CHF₃ + SF₆, 40 mTorr O₂ + SF₆, and 80 mTorr O₂ + SF₆, respectively. On the contrary, the surface morphology of these samples is featured by various newly formed nanostructures. In detail, in sample group C, the morphology is difficult to be characterized by the FESEM because it is very smooth, as indicated in Fig. 2g and h. In sample group I, it is featured by an array of nano-tower-like nanostructures with vertical orientation, as indicated in Fig. 3c and d.

In sample groups F and G, the morphology is featured by some spherical nano-tip morphology, as indicated in Fig. 3g-j. Compared with the sample group G, there are many contaminating particles (<10 nm) attached on group F samples as shown in Fig. 4i and j. It is possibly because those particles can be etched off by O₂ plasma, however, the lower working pressure reduces the etching effect of O₂ plasma on the amorphous substance [35].

(3) Needle-like tips can be observed in sample groups J and K, which were treated by sequential method. In Fig. 5a and b, the tips are randomly distributed and very short (<30 nm). However, Fig. 5c and d exhibits more regular array-like distribution with inter-distance and protruding height of about 70–110 and 150–200 nm, respectively. This surface condition is achieved based on the low-cost screen-printing technique, and it is close to the optimized morphology suggested by Jo et al. [36].

Besides the gas species, the impact of the working pressure on the surface morphology changes has also been carefully examined in the samples treated by plasmas of single component gas feed. However, no significant differences were observed. So did the case of gas flow rate. These two factors are more influential to the etch rate as indicated in Table 1.

3.1.2. Microstructure examinations
Secondly, the results of the TEM examination would be presented. Fig. 5 has shown the TEM micrographs before and after the plasma treatments. Compared with the original samples shown in Fig. 5a and b, the tips are randomly distributed and very short (<30 nm). However, Fig. 5c and d exhibits more regular array-like distribution with inter-distance and protruding height of about 70–110 and 150–200 nm, respectively. This surface condition is achieved based on the low-cost screen-printing technique, and it is close to the optimized morphology suggested by Jo et al. [36].

Fig. 3 – FESEM images of CNTF surface morphology after plasma treatment with multiple etchant. (a) and (b) are of sample H using Ar + O₂; (c) and (d) are of sample I using Ar + CHF₃ + SF₆; (e) and (f) are of sample E using CHF₃ + SF₆; (g) and (h) are of sample G using O₂ + SF₆ (80 mTorr); (i) and (j) are of sample F using O₂ + SF₆ (40 mTorr). The insets of (f), (h), and (i) are of 20,000×. The insets are the corresponding enlarged images, where the length of the scale bars is 200 nm. The right-hand side figures are the enlarged version of their counterparts on the left and taken from the same area.

Fig. 4 – FESEM images of CNTF surface morphology after sequential plasma treatment. (a) and (b) are of sample K using Ar + CHF₃ + SF₆ (90 s)–Ar (90 s); (c) and (d) are of sample J using O₂ (90 s)–Ar (90 s). The insets are the corresponding enlarged images, where the length of the scale bars is 200 nm. The right-hand side figures are the enlarged version of their counterparts on the left and taken from the same area.
typical amorphous structure, which may be resulted from coating effect. However, for the O2/Ar plasma sequentially treated samples, Fig. 5c demonstrates a very sharp tip structure that cannot be found in sample groups A and E. The inset of Fig. 5c represents the electron diffraction pattern, which also reflects an amorphous state. As a conclusion, the TEM examination has provided some evidences of bundle formation, lattice rupture, and amorphous coating effects resulting from plasma treatments.

3.1.3. Composition examinations

Thirdly, the elemental analysis using the energy dispersive X-ray diffraction spectrum (EDX) supports that the plasma treatments of samples A, B, C, and J can introduce new substances, as indicated in Table 2; this may be considered as the evidence of functionalization and/or coating effects. The introduction of lattice defects induced by the ion irradiation can be responsible for the increase in the oxygen content after the Ar and SF6 plasma treatments [29]. The increase of oxygen and fluorine content in sample groups B, C and J should be the consequence of the plasma induced functionalization effect.

3.2. Modeling of the CNTFs’ plasma treatments

In this section, a model is discussed as an interpretation of the results shown in Section 3.1, as illustrated in the diagram of Fig. 6. Fundamentally, the microscopic or macroscopic changes in CNTFs resulted from plasma treatments are determined by two interactional and synchronous processes, viz. etching and coating. Phenomenally, they can produce three effects that can reshape the surface morphology into certain character, i.e., CNTs’ protruding, bundle forming, and neo-nanostructure forming. The combination of those competing effects can interpret the results observed in our experiments.

3.2.1. Two opposing processes in plasma–CNTFs interactions

Firstly, a physical etching process is featured by CNT erosion that resulted from ion bombardment, while a chemical etching process is induced by surface reaction between reactive ions and CNTs. Chemical processes are limited in those non-inert plasma gases. However, in the energetic plasmas with highly orientated ion flow, such as those generated from a RIE system, both inert and reactive plasma gases can produce the physical effect.

Secondly, the inverse process is surface coating including the functionalization of CNTs. The coating process results from deposition physically or chemically from the complex
plasma environment induced by the etching process. One of its possible mechanisms is sputter deposition induced by plasma bombardment, which is widely believed in the literature, e.g., Refs. [24,25] where Raman spectra method was utilized to find out the significant increase of amorphous carbon after reactive and inert plasma gas treatment. However, another mechanism, viz., plasma enhanced chemical deposition (PECVD) is also possible in a reactive plasma because the etchant particles and the plasma may form a PECVD environment [14]. The latter mechanism may be responsible for the organic coating on the surface of CNTs during plasma treatments. Besides the surface coating, in microscope, the other inverse process is the functionalization, which is confirmed experimentally by several reports in reactive plasmas [20,24, 25,28-34], except for the equivocal case of H plasma treatments [13,26]. However, for the inert gas feeding, Gohel et al. proved that no chemical reactions occur by measuring the work function of CNTs before and after the Ar plasma treatment [25].

Thirdly, for the interaction between these two processes, surface coating can retard the etching process while etching can enhance or remove the surface coating depending on the plasma gas chemistry. Besides, irradiations in plasmas can induce microstructure changes [37,38] that can lead to neo-nanostructure (such as new nanoscale particles and tips) formation on the CNTF surface. The most important cause in these two contrary processes in a treatment depends on the plasma property that resulted from some complex factors. However, the results in this paper support that plasma gas chemistry including the gas feeding species methods is the most fundamental factor.

3.2.2. Three competing effects in plasma modification of CNTFs’ surfaces

First, the CNT protruding effect can produce erecting morphology and may be dominantly caused by the etching process by the plasma with ion flows of considerable orientation. The CNTs can be selectively etched off based on their geometry configuration, i.e., vertical protruding CNTs can last longer while decumbent ones can be etched off firstly if the etch rates are similar in both cases. The authors of Ref. [18] believed that the etch rate is higher at the tip than at the wall, but it is possibly limited for those aligned CNTs, because no proofs are available for those randomly oriented CNTs, such as in the case of screen-printed CNTFs. As indirect information, in the case of another irradiation, laser irradiation, the decumbent CNTs can be selectively etched off based on the difference in the microstructure, however, no evidence was provided for the etching rate different at the tip and the wall [39]. The other possible mechanism can be the impacts around the wall of a CNT due to the lateral fluent of plasmas, where the low energy ions’ impact may ‘virtually’ straighten the CNTs. This mechanism can interpret the protruding effect of the sparsely distributed CNTs in screen-printed CNTFs [12], under the condition of weak etching effect. Consequently, the former mechanism is possibly dominant in our experiments because the CNTs in the CNTFs utilized here are of very high density. In addition, the latter process is not possible in a plasma environment with intense etching effect as indicated in Table 1.

Second, bundle forming is another conspicuous effect, which can modify the CNTs’ density distribution on the surface. During the plasma treatment, the surface energy of CNTs can be increased by the defects introduced by ion bombardment physically [26] and/or by the functional radicals introduced by reactive ion reactions chemically [25]; this can cause the CNTs’ upper parts coalescent and form into CNT bundles as a method of reducing the surface energy. Consequently, almost all of the vertical oriented surface morphology after plasma treatment (sample A, B, D, E, and H) exhibit obvious bundle morphology to some degree except for group J. The other possible mechanism is that the distribution fluctuation of substances (ions or radicals) and energy in the plasma may deposit on some accidental areas on the surface to retard the etching effect there. That is to say, localized plasma coatings protect the CNTs in those areas from being etched off, while in other areas they have been etched. As a result, the CNT bundles with deposited substances can be formed.

Third, neo-nanostructure forming may act as another major effect of plasma modification. In our experiments, it is dominant in the cases of all SF6 containing processes except for CHF3 + SF6, where it may be overwhelmed by the intense protruding effect induced by the CHF3 gas chemistry. Given the fact that the highly reactive and abundant fluorine containing ions or radicals in SF6 plasmas [40,41] are difficult to produce oriented etching effect, then, homogeneous etching effect can trimmer down the erected CNTs and enhance neo-nanostructure formation as demonstrated in those FES-EM images in Figs. 2 and 3 for sample groups D, F, G, and I.

Fourth, another case is the sequential plasma treatment, which can reflect the accumulative effects of the plasmas on the CNTFs with different gas feeds. In our experiments, followed by the Ar plasma that can produce intense protruding effect, the inheritance of the former plasma treatments (Ar + CHF3 + SF6 or O3) greatly influence the final features of the morphology. In the case of Ar + CHF3 + SF6/Ar treatment, given the fact that the former Ar + CHF3 + SF6 treatment can produce neo-nanostructures on the surface of CNTFs, the subsequent Ar plasma cannot effectively generate protruding morphology because selective etching mechanism is not valid for those neo-nanostructures. In fact, there are very short CNT tips protruding out of the surface based on the FES-EM observation, as demonstrated in Fig. 4a and b. In the other case of O3/Ar treatment, selective etching mechanism is still valid for the O3 plasma treated samples, because CNT bundling is the featured morphology for such treatment. As a result, the Ar plasma conspicuously straightens the CNTs out of the sparse CNT bundles’ array that resulted from the former treatment (O3), as indicated in Fig. 4c and d. In a conclusion, the authors suggest that the difference in those two processes resulted from some kind of inheritance effect which determines the feature of the accumulative modifications. The sequential treatment should be considered as another methodology in the plasma treatments of CNTFs.

3.3. CNTF electrode performance

To compare and demonstrate the results of field emission and gas ionization experiments quantitatively, the onset voltages (voltage needed to extract current of 1 nA in FE [42] and to generate external current of 1 µA in gas discharge) of these two phenomena have been summarized in Fig. 7. It is shown...
that: (1) all plasma treated samples exhibit an enhanced property of lowering the onset voltage both in the application of breakdown gases and field emission electrons. (2) The impact degree of the same plasma treatment on the gas ionization and field emission is different, e.g., for gas ionization, O2/Ar sequential treatment can achieve the lowest onset voltage, which is lower than the aligned sample prepared by CVD method. However, the same technique cannot produce the similar degree of impact in the field emission test.

To interpret these results, firstly, it should be noticed that the field enhancement factor ($\beta$) is basically determined by the property of CNTFs being applied as electrodes. Furthermore, those that determine $\beta$ are mainly the CNTFs' surface morphology, the microstructure, and the work function of CNTs. The optimization of $\beta$ is mainly based on vertical alignment, moderate density, moderate protruding height, sharpness of the tips, as well as small diameter of the tubes. Otherwise, it can be greatly limited by the field screen effect and large ratio of curvature in electric field convergence. Consequently, as demonstrated in the results of Section 3.1, compared with the original statues of intricately distributed screen-printed CNTFs, plasma treatment can trim the surface morphology into the state of quasi-alignment with improved density and protruding height. The different degree of these effects caused by different plasma gases should be considered as the experimental facts in the first place, because it is difficult to quantify such differences in the screen-printed CNTFs.

Secondly, the different results between field emission and gas ionization application of the same sample group treated by the same technique reflect that different physical processes are involved in these two phenomena, which require different optimized conditions of the CNTFs. For this issue, the most interesting result is probably the O2/Ar sequential plasma treatment. The reason for it to achieve the lowest gaseous breakdown voltage is that such resulted morphology and microstructure can enhance field convergence best. However, as the TEM micrograph of Fig. 5c revealed, the surface of these samples may be covered by some amorphous dots that deteriorate the field emission property of the CNTFs [16]. That is to say, the gas ionization process in an electrode system with CNTFs, or more generally, with one dimensional electrode materials, is dominantly determined by the applied field intensity [2] generated from this system rather than the quantity of electrons emitted from the electrodes [43]. Consequently, samples of group I that can emit largest amount of electrons at lowest applied voltage cannot breakdown the gas molecules at lowest applied voltage because it cannot generate the most intense field among all those sample groups. Those results provide a new insight into the different physics in field emission and gas discharge in the electrode systems using CNTs-like electrode.

4. Conclusion

The modification effect of the plasma treatments on the surface morphology, microstructure, composition, and electrode performance of the screen-printed CNTFs have been carefully studied in this paper. The experiments examined four representative plasma gases of Ar, O2, CHF3, and SF6, additionally; the accumulative effect of different gases and the main process parameters (working pressure and gas flow rate) have also been considered. The abundant but complicated results have been treated systematically by: (1) correlating the gas ionization test with the field emission test; (2) correlating the material characterization with the electrode performance test. As a result, the authors would like to conclude that
• Serving as the electrode in field emission and gaseous ionization, screen printed CNTFs performance can be significantly improved by the plasma treatment in respect of lowering the onset voltage. Furthermore, the preferred electrode material state in field emission and gaseous electronics is different, the property of CNTFs in field convergence is more important in the latter case. In terms of the electric field convergence property's improvement of CNTFs, the surface morphology is the most influential factor; this conclusion may be limited in the range of slurry-based CNTFs, where CNTs are originally randomly distributed. Further, plasma treatments can significantly modify CNTFs in that respect.

The plasma gas chemistry including the gas-feeding species and methods is the most fundamental factor to produce certain expected macroscopic and microscopic modifications. In the range of this paper, Ar + CHF3 + SF6 and O2/Ar treatments are the best choices for the improvement in the field emission and gas ionization, respectively. Furthermore, in the case of single component gas feeding, most of the process parameters are not influential, whereas, in the case of multiple component gas feeding, the apparatus parameters should be considered cautiously. In addition, the sequential gas feeding should be further investigated because it can reflect some important cumulative inheritance effect of different plasmas.

We model the underlying mechanisms by two opposite processes, viz., etching and coating, which can produce three effects to modify the surface morphology, i.e., CNT protruding induced by oriented plasma etching, bundle forming induced by surface defects and functionalization, and neo-nanostructure forming resulting from deposition and microstructure transition. The changes in CNTFs after plasma treatments are the outcome of those three interactional and competing effects. Among those effects, CNT protruding and neo-structure forming produce the most severe but irreconcilable morphology modifications. Those effects are determined by the plasma–CNTs interaction processes chemically or physically, which should be analyzed and predicted in view of plasma induced etching and coating. The correct behavior of this model offers somewhat a comprehensive insight into the plasma–CNTs interaction and a reference of the process design.

Acknowledgments

This work was supported by National Basic Research Program of China under Grant Nos. 2006CB300406, Shanghai Municipal Commission for Science and Technology under Grant Nos. 03DZ14025, and Developing Foundation of Shanghai Science and Technology under Grant Nos. 0452nm056.

References


