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Structural transformation and field emission enhancement of carbon nanofibers by energetic argon plasma post-treatment

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Vertically aligned carbon nanofibers (CNFs) grown by plasma enhanced chemical vapor deposition (PECVD) were transformed into cone-shaped nanostructures after treatment by argon (Ar) plasma. Significant enhancement of field emission characteristics of the post-treated CNFs has been achieved. Analysis by electron microscopy and energy dispersive spectroscopy (EDS) suggests that the structural transformation is a result of a cosputtering/deposition process by energetic plasma ions. The enhancements can be attributed to the combining effects of an additional Si/C layer coverage, catalytic nanoparticles removal and the sharpening of CNFs tips. The argon plasma post-treatment processes developed here can be easily extended to in situ PECVD processes for fabricating CNFs based emitters. © 2004 American Institute of Physics. [DOI: 10.1063/1.1815062]

Carbon nanotubes (CNTs) or carbon nanofibers (CNFs) have been considered one of the most promising materials for field emission (FE) applications due to their high aspect ratio geometry, small radius of curvature at tips, and high physical/chemical stability.¹⁻³ CNTs/CNFs based electron emitters thus potentially allow low turn-on voltage operation, large emission current density, and long-time stability at large current loading.^{4,5} Their FE properties at device level, however, are often affected by additional factors, such as the alignments and density/length/diameter of the tubes/fibers, absorbents on the tube/fiber surface, conductivity between CNTs/CNFs and substrates, etc.^{3,6–8} In order to optimize the FE properties, it is highly desirable to produce vertically aligned CNTs/CNFs with optimal combinations of density, length, and diameter on substrates. Therefore, direct synthesis of CNTs/CNFs on catalytic transition metal patterned substrates by chemical vapor deposition (CVD) have been widely employed for better control of those properties of CNTs/CNFs.^{2,9} In particular, synthesizing by plasmaenhanced CVD (PECVD) provides further benefits of producing isolated and better vertically aligned CNTs/CNFs at much lower substrate temperatures.¹⁰ This feature is essential for fabricating FE devices on large-area glass substrates in the field emission displays (FEDs) application.^{10–12} However, impurities produced during CNTs/CNFs growth by CVD/ PECVD methods, for example, the catalytic nanoparticles at tips^{13,14} or amorphous phase carbons,^{5,14} are believed to hamper the FE characteristics. Post-treatment techniques, such as ultraviolate laser irradiation,¹⁵ hydrogen (H_2) ,¹⁶ or argon (Ar)¹⁷ plasma treatments, and oxidation by oxygen or ozone gases,¹⁸ etc., have been developed to process the as-grown CNTs. Significant enhancement of FE has been obtained as a result of one or combination of the following mechanisms: catalytic nanoparticles removal or caps opening of CNTs,^{13–18} purifications of CNTs,^{13–15,17} or C–H dipole layer formation on CNTs surface,¹⁶ etc.

In this study, an Ar plasma post-treatment process was developed for CNFs grown by high density inductively coupled plasma CVD (ICP-CVD). In contrast to previous studies,¹⁷ regimes of more energetic ions were chosen for post-treatments. Mechanisms for enhancement of field emission characteristics and the structural transformation of asgrown CNFs resulting from Ar plasma treatments were investigated.

The CNFs growth and post-treatment processes were both carried out in a home-built ICP-CVD system.¹² Two separate 13.56 MHz radio-frequency (rf) power generators were used for high density plasma generation and substrate stage bias, respectively. The graphite substrate stage was temperature controlled in an operating temperature in the range of 400-900 °C. For CNFs growth, the chamber was fed with a gas mixture of acetylene (C₂H₂), H₂ and Ar at a total pressure typically below 50 mTorr. For the results shown in this letter, p-type Si (100) wafers with squarepatterned (10 μ m \times 10 μ m) Ni film of thickness 10 nm deposited by electron beam evaporation were used as substrates. Figure 1(a) shows the scanning electron microscopy (SEM) image of the vertically aligned CNFs grown in this ICP-CVD reactor with the following process conditions: flow rates $C_2H_2/H_2/Ar=8/24/0.5$ sccm, total pressure 20 mTorr, substrate temperature 580 °C, ICP power 1000 W, bias power 300 W, and growth time 10 min. The resulting CNFs have an average diameter of 60-80 nm, a length of $1-2 \mu m$, and a density of $\sim 10^9 - 10^{10} \text{ cm}^{-2}$.¹² Catalytic Ni nanoparticles are found encapsulated at CNFs tips, indicating the tip-growth mode for CNFs growth.¹¹ Good uniformity of CNFs was obtained in terms of their morphology, density and Raman spectroscopy analysis (intensity ratio of D-G-band modes). The as-grown CNFs samples were then further treated separately in the same reactor by Ar plasma under various process conditions.

Figures 1(b)-1(e) show the SEM images of CNFs posttreated by Ar plasma for different treatment time. The process conditions are ICP power 1000 W, rf bias power 300 W (self-bias voltage \sim 410 V), and total pressure 20 mTorr. Post-treated CNFs became more like cone shaped as the treatment time was increased. In addition, catalytic nanoparticles encapsulated at CNF tips were gradually removed by Ar plasma and almost disappeared after 5 min treatment.

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FIG. 1. SEM images of the CNFs: (a) as-grown CNFs, and after treatment time of (b) 2 min, (c) 5 min, (d) 10 min, and (e) 20 min, respectively. The insets show the images of CNT tips at higher magnification.

Figure 2 shows the transmission electron microscopy (TEM) images of the as-grown and the post-treated CNFs, revealing the evolution of catalytic Ni nanoparticles and the morphological transformation. The TEM images, Figs. 2(c) and 2(d), also show that CNFs surfaces were covered by a thin amorphous layer of thickness 10–50 nm, dependent on the treatment time. The layer coverage was identified to be composed of Si and/or C atoms by qualitative energy-dispersive spectroscopy (EDS) analysis auxiliary to TEM, as shown in Fig.



FIG. 2. TEM images of the CNFs, and the EDS analysis: (a) as-grown CNFs, and after treatment time of (b) 2 min, (c) 10 min, (d) 20 min, where the black arrow indicated the buried particle, and (e) EDS analysis obtained by directly focusing the electron beam on the post-treated CNFs body of (c) as depicted. The copper (Cu) signal was from the TEM sample grids; (f) tip part of (b) at higher magnification. The insets of (c) and (d) show the thin amorphous layers by white double-headed arrows.



FIG. 3. Raman spectra of the CNFs. Peaks at \sim 520 and \sim 950 cm⁻¹ were from the Si substrates: (a) as-grown CNFs, and after treatment time of (b) 2 min, (c) 5 min, (d) 10 min, and (e) 20 min, respectively.

2(e). Furthermore, additional EDS analysis (not shown) showed that Ni nanoparticles of size ~ 20 nm were buried inside cone-shaped CNFs. The residual nanoparticles may be attributed to the incomplete removal of large nanoparticles by Ar ion bombardments. Due to the smaller size reshaped by Ar ion sputtering, nanoparticles might be melted as a result of heating by ion bombardments, and eventually be buried inside the deposited layer of Si/C atoms which were not able to be observed by SEM.

From the electron microscopic and EDS analysis, we propose that the transformation procedure into cone-shaped nanostructures is to follow a simultaneously "sputtering" and "deposition" process. The Si and/or C atoms (from the substrate and CNFs, respectively) were first sputtered off by energetic Ar ions and then deposited back on CNF surfaces to form the amorphous layer coverage. This process occurred repeatedly during the entire post-treatment period. The morphological change into cone shaped is suggested to be originated from the different sputtering yields of Ni nanoparticles and graphitic layers, as indicated in Fig. 2(f), where the black-dash arrows represent the incidence of Ar ions. The lengths of the arrows correspond to the sputtering yields with typical dependence of the incident angles of ions. It can be observed that the graphitic layers over CNF tip were more easily removed than the encapsulated Ni particle. In addition, the white-curved arrows stand for the amorphous layer deposition over the entire surface, which might also be sputtered off simultaneously.

The CNFs were also characterized by micro-Raman spectroscopy where a He-Ne laser of wavelength 632.8 nm was employed to induce the spectra, as depicted in Figure 3. The spectrum of as-grown CNFs, as shown in Fig. 3(a), exhibited the normal spectra of carbonaceous materials.¹⁹ The intensity ratio of D to G-band modes, which represents the amorphous phase content or the degree of crystallinity of carbonaceous materials,²⁰ of the as-grown and the 2 min treated CNFs is ~ 1.3 and ~ 1.2 , respectively. The decrease of this value indicates that Ar plasma sputtered off the amorphous phase carbons and random-oriented CNFs at the beginning stage of post-treatment [see Fig. 1(a) and 1(b)]. However, for CNFs with longer treatment durations, an extra photoluminescence-like (PL-like) background signal was found in addition to the normal Raman spectrum. Qualitatively, it is believed that the PL-like background signals provided an indirect evidence for certain structural transformation from the spectroscopic point of view.

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FIG. 4. Field emission measurements of the CNFs: (a) Typical J-E curves, while the insets are the corresponding F–N plots and (b) the dependence of turn-on field (open-circle) and threshold field (solid-square) on the treatment time.

FE measurements were carried out in the sphere-to-plate configuration.^{4,16,21} Figure 4(a) shows the typical emission current density–electric field (J-E) curves and the corresponding Fowler–Nordheim (F-N) plots.²² The experiment results show that FE characteristics were significantly enhanced after the treatments of Ar plasma. Even for the case of 2 min treatment, where the catalytic nanoparticles were not completely removed [see Figs. 1(b) and 2(b)], the enhancement was also evident. The dependence of turn-on fields (electric field for emission current density of 10 μ A/cm²) and threshold fields (the electric field for emission current density of 10 mA/cm²) on the treatment time is shown as Fig. 4(b). The results show that the turn-on fields decreased from 10.3 V/ μ m to ~5 V/ μ m, which demonstrates a remarkable FE enhancement of post-treated CNFs.

The FE behaviors of Ar plasma treated CNFs are extraordinary. Three factors are believed to contribute to the enhancements of FE characteristics. The first factor may be due to the additional thin Si/C layer deposited on CNFs surface. It has been shown that FE could be improved by an additional thin layer coating of specific materials on CNTs such as a low work function material (Cs),²¹ or a wide band-gap material $(MgO,SiO_2)^{23}$ where the thin layer coating serves as a tunneling window for electrons emitting into vacuum space.²⁴ Second, energetic Ar plasma ions removed the catalytic nanoparticles on the emission tips as shown in Fig. 4. The last factor is a result of the changes of CNFs density and morphology of individual CNFs. It has been shown that the field enhancement effect will be maximized for CNTs emitters with optimal combinations of diameter, length, and spacing.^{3,7} Overlong period of treatment reduces the density, shortens the length, thickens the coatings, and makes the tips blunt; each would influence the resulting FE characteristics.^{3,6,7} However, what must be emphasized is that all post-treated samples exhibited far better FE characteristics than the untreated one, regardless the final CNFs morphology, length, density, or the appearance of catalytic nanoparticles [see Fig. 1(b)]. Therefore, it is believed that the first factor, an additional layer coverage, plays a dominate role in the FE enhancement of post-treated CNFs.

In conclusion, we have demonstrated an effective method for FE characteristics enhancement of as-grown CNFs by energetic Ar plasma post-treatment. The Ar plasma treatment process and mechanisms described in this work could also be applied to other types of field emitters having a vertically aligned and rod/tube like geometry to improve FE properties, but special care must be taken to avoid extensive structure damage by the energetic plasma ions. Further studies, such as *in situ* post-treatment process integration, as well as other FE characterizations, e.g., long-time stability of emission current and large-area uniformity of luminance, are required to demonstrate the viability of this approach.

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