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Improvement of Electron Field Emission in Patterned Carbon Nanotubes by High Temperature Hydrogen Plasma Treatment

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Abstract

In this paper, we report a significant improvement of electron field emission property in patterned carbon nanotubes films by using a high temperature (650 °C) hydrogen plasma treatment. This treatment was found to greatly increase the emission current, emission uniformity and stability. The mechanism study showed that these enhanced properties are attributed to the lowering of the potential barrier and the creation of geometrical features through the removal of amorphous carbon, catalyst particles and the saturation of dangling bonds after such a hydrogen plasma treatment.

Keywords

Patterned carbon nanotubes; electron field emission; hydrogen plasma treatment; vacuum microelectronic devices

1. INTRODUCTION

Carbon nanotubes (CNTs) have become one of the most promising candidates for electron field emitters [1,2] to be used in future generations of various vacuum microelectronic devices [3–5]. This is due to their high aspect ratios, small tip radii of curvature, and high chemical and thermal stability. Chemical vapor deposition (CVD) is a good technique for CNT growth [6–8], where a transition metal catalyst is essential to the growth of CNTs. However, employment of this technique was also commonly found to produce some by-products on the CNT surface, e.g., encapsulated catalyst particles, adsorbates and amorphous carbon that can degrade the electron field emission property, and in particular adversely affecting the emission uniformity and stability. Hydrogen plasma treatment has previously been demonstrated to enhance the electron field emission property of cold cathode emitters. Schwoebel *et al.* [9] experimentally found that low-pressure hydrogen glow discharge can clean the surface contaminants in both microfabricated single molybdenum tips and arrays which resulted in a decrease of ~1 eV in the work function. Zhu *et al.* [10] achieved a low-field electron emission in undoped nanostructured diamond by employing a hydrogen plasma heat treatment. Hydrogen plasma treatment was also found to decrease the threshold electric field in CNTs [11,12]. However, to date, little systematic work has been reported on the enhancement of the emission stability and uniformity by hydrogen plasma post-treatment, which is extremely important in practical

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emitter applications. In this paper, we report a high temperature hydrogen plasma simple process subsequently applied to patterned CNT samples after the nanotube growth in the same microwave chamber, which produces a significant enhancement in the field emission properties especially in the emission current, emission uniformity and stability. A possible mechanism is also discussed, based on the characterization results of the CNTs.

2. EXPERIMENTAL DETAILS

The CNTs were selectively grown on a n-type (100) silicon substrate (resistivity of 0.001~0.005 $\Omega\cdot\text{cm}$) in an ASTeX microwave plasma enhanced chemical vapor deposition (MPEC VD) system, equipped with a 2.45 GHz microwave source. Prior to CNT growth, nickel catalyst pads with thickness of 5 nm were fabricated using a conventional lift-off process. During the CNT growth, the substrate temperature, deposition pressure and microwave power were maintained at 720 $^{\circ}\text{C}$, 20 Torr and 1.5 kW, respectively. A mixture of N_2 and CH_4 was used as the gas source and the flow rates were computer controlled precisely at 60 and 25 sccm, respectively. In order to examine the effect of high temperature hydrogen plasma treatment on the electron field emission property of the patterned CNTs, some of the samples were subsequently subjected to a hydrogen plasma treatment at 650 $^{\circ}\text{C}$ for 15 min in the same microwave chamber, where the microwave power and total pressure were controlled at 500 W and 20 Torr, respectively.

The surface morphology and microstructure of the CNTs were examined by a FEI Quanta 200 F scanning electron microscope (SEM) and a JEM-2010 transmission electron microscope (TEM) with an acceleration voltage of 200 kV. Raman spectra of CNTs were collected using a Renishaw micro-Raman spectrometer. The Raman scattering signal is excited by an Ar^+ laser (514.5 nm line) and scanned from 500 to 2000 cm^{-1} .

The electron field emission characteristics of CNTs were studied using a parallel plate diode structure, which was situated with an anode-to-cathode spacing of 300 μm . The CNT films acted as the cathode, whilst an indium-tin-oxide (ITO) coated glass plate acted as the anode. A Keithley (Model 248) high voltage supply was used to apply the voltage up to 5 kV to the cathode. Current-voltage (I - V) measurements were computer-controlled and performed in an automatic mode at room temperature in a high vacuum chamber of 10^{-7} Pa, which was evacuated by a rotary pump and a turbo-molecular pump. Emission site images were captured at home-made phosphor screen on ITO glass during I - V measurement using a microscopy-attached charge coupled device camera system.

3. RESULTS AND DISCUSSION

Nickel catalyst pads with thickness of 5 nm were fabricated on a n-type (100) silicon substrate (resistivity of 0.001~0.005 $\Omega\cdot\text{cm}$) using a conventional lift-off process. Fig. (1a) shows a SEM image of the nickel pads (patterned as “N” and “T”, which stands for “nano-technology”). It can be seen that the edges of the catalyst pads are sharp and smooth, indicating a high quality lithography. Fig. (1b) shows the top-view SEM image of the as-grown CNTs. Uniform growth of the CNTs was only observed on the prefabricated catalyst pads, indicating a well controlled selective growth of CNT patterns. The inset of Fig. (1c) shows a transmission electron microscopy (TEM) image. It can be seen that the average diameter of the CNTs was around 20 nm, and that a residual nickel catalyst particle is encapsulated at the tube top. This suggests that the CNT growth is via a tip-growth mode. On the other hand, in Fig. (1b), it can be seen that there are some absorbates present at the nanotube surfaces, which are identified as some bright dots in the images.

Fig. (1c) shows the TEM image after hydrogen plasma treatment; it can be seen that the nickel catalyst particle at the CNT top was removed. This results in producing two or more sharp tips

at the top of each individual CNT, which will increase the geometrical enhancement factor of CNTs in electron field emission.

Fig. (2) shows the Raman spectra of the CNT patterns. The Raman scattering signal is excited by an Ar⁺ laser (514.5 nm line) and scanned from 500 to 2000 cm⁻¹. Two strong peaks located at 1350.6 (D-line) and 1585.1 cm⁻¹ (G-line) were detected for both untreated and hydrogen treated CNT samples. The D-line is usually attributed to the presence of disordered carbon, and in the case of nanotubes it is generally attributed to the presence of amorphous carbon [13]. The D-line in nanotubes is also thought to originate from defects in the curved graphene layers and tube ends, and the residual particles in nanotubes [14]. Whereas the G-line near 1580 cm⁻¹, observed in high oriented pyrolytic graphite (HOPG), is attributed to sharply curved and closed graphitic structures of CNTs [15]. Interestingly, it can be seen that the ratio of the peak intensities I_D/I_G decreases from 1.09 to 0.83 after the hydrogen plasma treatment. At the same time, the full width at half maximum (FWHM) of both the D-band and the G-band reduces, while the FWHM of the D-band decreases from 90.7 to 53.3 cm⁻¹. The noticeable changes in the Raman spectrum after the hydrogen plasma treatment probably resulted from the following effects: i), the etching of amorphous carbon and the cleaning of surface absorbates and impurities; ii), the saturation of the dangling bonds, and iii), the removal of nickel catalyst particles.

Fig. (3) presents the typical electron field emission I - V characteristics of the CNT patterns. It can be seen that average threshold electric field, defined as a field at which $J=10 \mu\text{A}/\text{cm}^2$, is 1.2 and 2.0 V/ μm for the hydrogen treated and untreated CNT samples, respectively. Interestingly, the treated CNT sample has a much higher emission current density than the untreated sample at the same applied voltage. On the other hand, among the 5 cycle data, it can be seen that the I - V curves are roughly coincident with increasing and decreasing applied voltage for the treated CNT sample, see Fig. (3b). Whilst for the untreated sample, the up-cycle and down-cycle of the I - V curves are not very coincident, on reducing the electric field, the emission I - V characteristic shows a weak hysteresis, see Fig. (3a). It is found that the emission current slightly increases with increasing the cycle number. This reflects that the hydrogen plasma treated sample has better emission reproducibility than the untreated sample [16]. The corresponding $\ln(J/E^2)$ versus $1/E$ plots according to the Fowler-Nordheim (F - N) equation, $J=A(\beta E)^2 \exp(-B\phi_e^{3/2}/\beta E)$ [17], where ϕ_e the effective work function, β the dimensionless local field enhancement factor, A and B the constants for the CNT films, are shown in the inset of Fig. (3). The $\ln(J/E^2)$ versus $1/E$ follows a roughly linear relationship over the measured range, indicating a conventional tunneling mechanism. The field enhancement factor β of treated sample, which was extracted from the F/N plots by assuming a work function of 5.0 eV for graphite, was found to be 1.8 times higher than that of untreated sample. The increase in enhancement factor of the treated sample is consistent with the observation in Fig. (1c).

Fig. (4) shows the emission images of both the untreated and treated samples at an electric field of 2.6 V/ μm during the up-cycle. It can be clearly seen that the treated sample shows a much brighter and more uniform emission image with a denser distribution of emission sites compared to the untreated sample. This indicates that the treated sample has much more efficient emission sites and hence leads to a higher emission uniformity and emission current.

The emission stability of the CNT patterns was also tested for the untreated and treated samples, respectively. Fig. (5) shows the typical emission current versus time for the untreated and hydrogen treated CNT samples at an electric field of 2.6 V/ μm at room temperature. It can be seen that the treated sample yields a much higher emission current than that of the untreated sample. More interestingly, the emitted current of the treated sample shows only a slight variation over the period of 48 h. The slight variation might be caused by the adsorbed gas. In contrast, the emitted current of the untreated sample increases at the initial 5 hours, and then

decreases. The data indicate that the treated sample has a higher emission stability than the untreated sample.

High emission current and low threshold electric field are expected for cold cathode emitters for high brightness electron sources. Besides, uniform and stable emission is also highly desired for practical application of the electron emitters [16]. Figs. (3–5) demonstrate that the high temperature hydrogen plasma treatment is a more effective process in enhancing the electron field emission property of CNTs than the previously reported hydrogen treatment [11,12]. This would be attributed to the following effects: on the one hand, Fig. (2) suggests that the high temperature hydrogen plasma can remove the by-products; e.g., amorphous carbon, which were deposited on the surface due to the decomposition of the hydrocarbon gases used during the growth process. Amorphous carbon is a dielectric which can modify the effective local work function and conductivity at the top surface of CNTs. This will broaden the width of the energy barrier, making electrons emission difficult to tunnel through the amorphous carbon dielectric layer [18]. The effective etching of the amorphous carbon layer can lead to the decrease in work function and thus the potential barrier, resulting in a significant increase in the emission current and a decrease in the threshold electric field. On the other hand, the hydrogen plasma can remove the adsorbates and impurities, and saturate the dangling bonds on the CNT surface. This can greatly increase the emission reproducibility and stability. Meanwhile, the hydrogen plasma can remove the nickel catalyst particles in the top of the CNTs which produced sharper tips on the CNT tops (see Fig. (1c)) that might have provided a local field enhancement, resulting in an increase in effective emission sites and so making the electron emission denser and more uniform. However, the detailed mechanism needs to be further studied.

4. CONCLUSIONS

In conclusion, we demonstrated a high temperature hydrogen plasma post-deposition simple process to treat the as-grown CNT patterns. A significant enhancement of the electron field emission properties was observed, especially in the emission current, emission uniformity and stability of the patterned CNTs. The removal of amorphous carbon, adsorbates, nickel catalyst particles, and the saturation of dangling bonds on the CNTs was thought to be responsible for the lowering of the potential barrier at the surface and creating geometrical features in CNTs, which result in an effective improvement of the electron field emission property.

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Fig. 1. SEM images of (a) nickel catalyst pads, (b) as-grown CNT patterns, (c) TEM image after hydrogen plasma treatment, inset: TEM image of the as-grown CNTs.

Fig. 2.
Raman spectra of (a) untreated and (b) hydrogen treated CNT samples.

Fig. 3. Emission current density versus applied electric field (5 cycles) for (a) untreated and (b) hydrogen treated CNT samples. Inset: the corresponding F-N plots.

Fig. 4. Typical emission images of **(a)** untreated and **(b)** hydrogen treated CNT samples captured at an electric field of $2.6 \text{ V}/\mu\text{m}$ in the up-cycle, respectively.

Fig. 5. Emission current density versus emission time for (a) untreated and (b) hydrogen treated CNT samples at an electric field of 2.6 V/ μm , respectively.