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Improved electron emission properties of screen-printed carbon nanotube film by hydrogen plasma surface treatment

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1. Introduction

Since the initial discovery carbon nanotubes (CNTs) [1], it has attracted many engineers and scientists attention and becomes a potential candidate as field emission emitter, because of its excellent field emission properties [2]. Most of the experiment work on field emission from CNTs focuses on application in field emission displays (FEDs), which often use a well-aligned patterned array of CNT prepared by chemical vapor disposition (CVD) or other methods as a cathode. In comparison with this CNT array emitters, a CNT film emitter based on the screen-printed technology has been developed, and it owns many advantages, such as higher yield, lower cost, and larger area etc. Many companies, such as ISE [3], Samsung [4], and ERSO/ITRI [5] etc, have announced the CNT-FED devices. When using CNT film emitter, surface treatment is important to electron emission properties.

In this paper, we report the effect of hydrogen plasma (HP) surface treatment on electron field emission from CNT film. It is shown that HP surface treatment can have a great effect on electron emission properties of CNT film.

2. Experimental detail

The purified CNT powders were mixed with organic binders and screen printed on Ni substrate. Then these samples were dried at 100℃ and annealed at 600℃ in N_2 atmosphere for 10 minutes to burn out of the organic binders. A homemade plasma equipment was used to treat the prepared CNT films in hydrogen plasma. The radio-frequency (RF) source was operated at 13.6MHz with a maximum power of 800W. The HP surface treatment was carried out with the parameters: hydrogen flow rate 10 sccm, operating pressure 150 Pa, RF power 200-300 W and process duration 10-30 min. The treatment was operated at room temperature.

After the HP surface treatment, the CNT films were immediately put into the vacuum chamber for electron field emission test at a pressure of 10^{-5} Pa. Each CNT films was separated by spacer from a phosphorus/ITO/glass anode, which made up a testing diode structure.

To understand the enhanced electron emission properties of CNT film mechanism, the microstructure of CNT film for different treatment time has been studied by field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM).

3. Results and discussion

The electron emission properties of CNT film are improved after HP surface treatment. Figure 1 shows the typical curves of the emission current density versus applied field (J-E) plots for the tested samples. The decreasing of turn on field and the increasing of emission current density after HP surface treatment are found, The Fowler-Nordheim model[16] is used to analyze the obtained data. The insert of Fig.1 illustrates the linear relations of the $\ln(I/V^2)\sim(1/V)$ which indicates that the measured current is indeed the result of field emission.

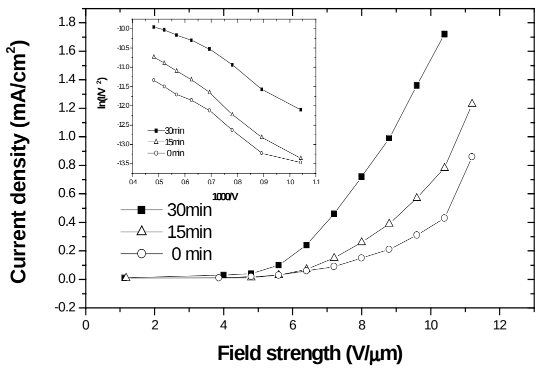

Figure 1. The typical curves of the emission current density versus applied field for CNT films with different duration of HP treatment. The inset is the corresponding F-N plots.

Figure 2 are photos of fluorescent display at a field of 6.84 V/μm for samples A (untreated), B(treated for 15min) and C (treated for 30min), respectively. The last sample C is most uniform and has the largest emission site density

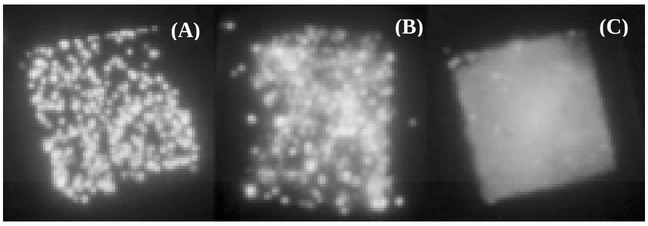

Figure 2. Fluorescent displays of field emission from the CNT films: (A) untreated, (B) treated for 15 min, and (C) treated for 30 min, respectively. The applied field is 6.84 V/μm.

(ESD) about $10^6/cm^2$, which is more than three orders of magnitude over that of the sample A.

The observation with FESEM shows that the surface configuration of CNT film is totally changed after HP surface treatment. Figure 3(a) and 3(b) are the FESEM images of sample A and C which indicate that the CNTs on the film surface are gradually covered by nano-particles. TEM images (Fig.3(c)) prove that the nano-particles are multilayered fullerenes. With the help of HP surface treatment the "multi-tip" CNTs are obtained.

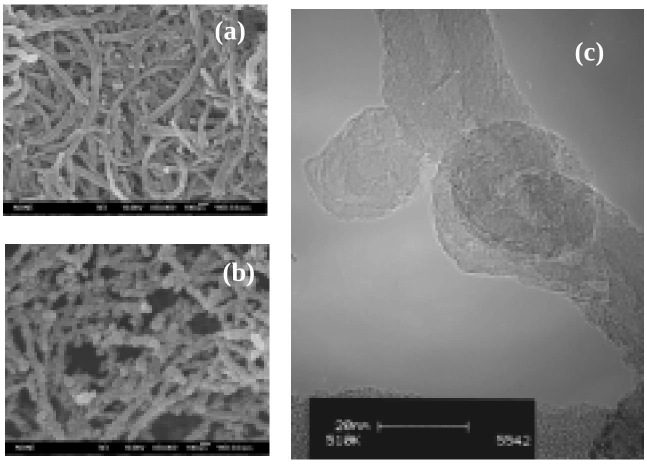

Figure 3. FESEM and TEM images of samples. (a) and (b) are FESEM images of sample A and C, which shows the CNTs on the film surface were gradually covered by nano-particles with the increasing of treatment duration. (c) is TEM image of typical nano-particles, which can be identified multilayered fullerenes.

Both the experiments[2,7] and theoretical studies [8-10] have showed that the tip as well as defects has predominant effects on field emission of CNTs, and the field emission properties of CNTs are sensitively dependent on the electronic and geometrical structures of the tip and defects. Carroll *et al.*[8] found the presence of sharp resonant states in the local density of states (LDOS) near the ends of capped CNTs results in weak acceptor states in field emission. G.Zhou *et al.* [10] showed that for the local emission regions at the tip, the LDOS peaks at the both sides of the Fermi level, corresponding to the donor and acceptor states, remarkably shift to the Fermi level in comparison with those at the body, due to the presence of conventional topology defect (i.e. pentagons). For those "multi-tip" CNTs, the increasing of the tip defects induce the increasing of the electrons emission probabilities in CNTs, because electrons at the "tip" are easily emitted in virtue of these yielding donor or acceptor states under the electric field. Besides the effects of tip electronic structure, the effects of tip geometrical structure are very important for field emission properties of CNTs. Calculation [11] showed that the field enhancement factor of the body is about 1/125 of that of the tip with the same radius. Therefore, the emission probability of electrons at the tip should be much larger than those at the body due to geometrical effects. Consequently, we can deduce that, by changing the electronic and geometrical structure of the CNTs, the emission probability of electrons in the "multi-tip" CNTs could be drastically enhanced which improved the electron emission properties of CNT film.

4. Conclusions

The electron emission properties of screen-printed CNT film are greatly improved by HP surface treatment. The enhancement mechanism is studied based on the microstructure information from FESEM and TEM. After HP surface treatment, the CNTs on the film surface were completely covered by nano-particles which have been proven to be multilayered fullerenes. Owing to the increasing of the "tip" defects and the field enhancement effect at the "tip", the electron emission probabilities of those "multi-tip" CNTs is increased. It is believed that the emission probability of electrons in the "multi-tip" CNTs could be drastically enhanced which induced the electron emission properties of CNT film dramatically enhanced. These results indicate that the HP surface treatment is an effective method to improve the electron emission properties of CNT film.

5. Acknowledgements

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