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Field emission characteristics of screen-printed carbon nanotubes cold cathode by hydrogen plasma treatment

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ABSTRACT

Selective plasma etching and hydrogen plasma treatment were introduced in turn to improve field emission characteristics of screen-printed carbon nanotubes (CNTs) cold cathode, which was prepared by using slurry of mixture of multi-wall CNTs, organic vehicles and inorganic binder, i.e. silicon dioxide sol. The results show that selective plasma etching process could effectively remove parts of surface inorganic vehicle (SiO_2) layer and expose more smooth and clean CNTs on cathode surface, which could significantly decrease the operating field of CNTs cathode. There are some nanoparticles emerging on the out of CNTs wall after hydrogen plasma treatment, which are equivalent to increase field emission point of cathode. At the same time, these nanoparticles can increase the local electric field of CNTs, which can decrease operating voltage of CNTs cathode and improve uniformity field emission.

1. Introduction

The field-emission display (FED) attracted much attention for its high display quality and low power consumption in flat-panel displays field [1]. Since carbon nanotube (CNT) was first demonstrated as efficient cold electron source in 1995 [2], people have continuously reported its excellent field emission characteristics [3–5] and research results in FED prototypes using CNTs cathodes [6–9]. In CNT-FED cathode patterning techniques, screen printing method has been widely adopted for simplicity, lower cost and mass production feasibility [10–13]. Various CNTs slurries for screen-printing have been reported, which are usually formed by mixing CNTs with organic vehicles and in some cases, metal particles or oxide conductive powders. To solve persistent problems from screen-printed CNTs, e.g. bend or/and buried CNTs and binder-residue-induced emission degradation, various post-treatment methods have been adopted including mechanical rubbing [15], adhesive taping [14,15], plasma treatment [16,17] and laser irradiation [18]. However, mechanisms of these treatments need to be further investigated, and treatment conditions need to be optimized. In this report, screen-printable CNTs slurry consisting of SiO_2 binder was introduced and corresponding post-treatment process by RIE selective etching and hydrogen plasma treatment were researched systematically to improve the field emission characteristics of the CNTs cathode.

2. Experimental

The starting CNTs materials for screen printing were multi-wall CNTs purchased from Nanotech Port Inc. The multi-walled CNTs powders were synthesized by chemical vapor deposition (CVD). Before using, the CNTs powders were filtrated by griddle to remove big metal particles. The starting CNTs powders were characterized by transmission electron microscope (TEM, JEM-2010HR). The CNTs were mixed with organic vehicle and inorganic binder silicon dioxide (SiO_2) sol to form the slurry for screen-printing. The glass coating with indium-tin-oxide (ITO) film (short title is ITO glass) was chosen as substrate of cathode. Because transparency and conductivity of ITO film can be deteriorated in hydrogen atmosphere, and the conductivity of ITO film as cathode electrode can directly affect field emission characteristics, chrome (Cr) film was coated onto ITO by magnetron sputtering. The Cr film has good stability in high temperature and hydrogen atmosphere.

The CNTs slurry was screen-printed onto ITO glass substrate coating with Cr film by using a DEK 248 printer. Point arrays of 16×16 CNTs cathodes were printed. The diameter of each dot emitter is 0.5 mm and space between the dots is 1.25 mm. After drying in air, the cathodes were annealed at the temperature of $\sim$375 °C for 25 min to remove the organic materials and good adhesion to the substrate was achieved. Selective plasma etching was carried out in a reactive ion etching (RIE) system to remove a part of inorganic

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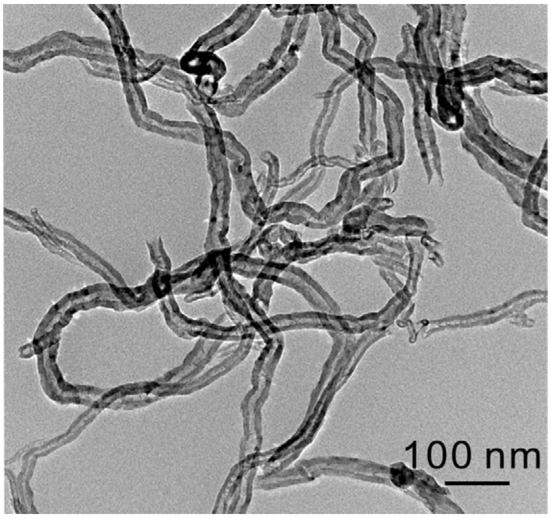

Fig. 1. TEM image of starting CNTs for screen-printing.

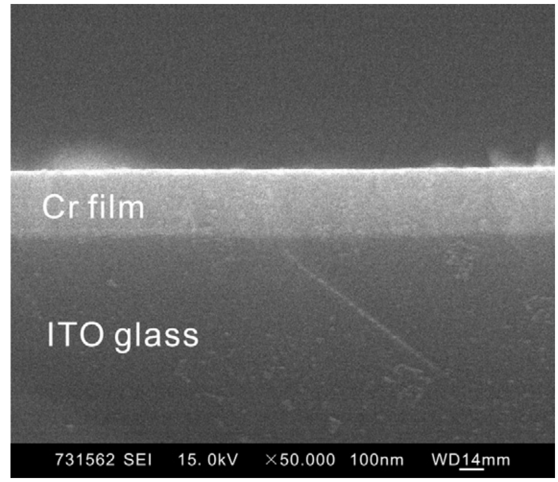

Fig. 2. SEM image of Cr film on ITO glass.

binder silicon dioxide (SiO_2) and expose CNTs buried inside cathode. In the experiment, radio-frequency (RF) source power was 60 W, operating pressure was 25 Pa, and the flow rate of etching gas (SF_6) was 50 sccm, etching time is 15 min. After RIE etching, hydrogen plasma treatment was introduced to the cathode, and the flow rate of H_2 was 40 sccm. Seven H_2 treatment durations were used, i.e. 0, 5, 10, 20, 30, 40 and 60 min. The morphological of screen-printed CNTs cathodes before and after treatment were examined by field emission scanning electron microscope (FESEM, JSM-6330F). The field emission characteristics of CNTs cathodes were studied using a diode structure with green-phosphor-coated ITO glass as the anode. The distance between cathode and anode was 250 μm and all measurements were carried out under pressure less than 10^{-7} Torr. The emission site distribution was recorded by a charge-coupled device (CCD). The applied field was calculated by dividing the applied voltage by the distance between the anode and cathode and the current density is obtained by dividing the total current by emitter area. To obtain a statistical result, at least seven cathodes in one group were prepared at one time for each post treatment experiment or field emission measurement.

3. Results and discussion

Fig. 1 shows the TEM image of CNTs powers after filtration for screen-printing, which indicates the diameter of the CNTs is around 30–40 nm. Fig. 2 shows the Cr film on ITO glass is smooth, and the thickness of Cr film is about 250 μm.

The surface morphologies of cathodes before and after different hydrogen plasma treatment time are shown in Fig. 3. It is found the cathode surface without any post treatment (see Fig. 3a) has few CNTs, a large number of CNTs were buried inside cathode by inorganic binder silicon dioxide (SiO_2). And more smooth and clean CNTs were exposed after RIE etching in SF_6 atmosphere (see Fig. 3b), which is good for field emission. Then, hydrogen plasma treatment was introduced to the cathode etched by RIE. It is showed the cathode surface became rougher with increasing hydrogen plasma treatment time. After short time hydrogen plasma treatment (≤10 min, see Fig. 3c and d), the cathode surface showed micro-porous structure, at the same time, morphology of CNTs exposed to cathode surface changed, for example the length of CNTs were shorter than before, the wall of CNTs became rougher, and there are numbers of nanoparticles emerged on CNTs outer-wall. With the increasing of hydrogen plasma treatment time (≥20 min, see Fig. 3e–g), the number of CNTs on the cathode surface became less, which is due to high-energy ions from hydrogen plasma resulting in the destruction of parts of CNTs. At the same time, the remaining CNTs without destruction were almost completely coated with nanoparticles. When treatment time increased to 60 min (see Fig. 3h), the CNTs and nanoparticles were destroyed badly and even disappeared. Through TEM examination (Fig. 4a and b), it can be observed very clearly the nanoparticles originate from the smooth and clean CNTs after RIE etching. And EDX analysis (Fig. 4c) further shows the nanoparticles are C element, which may be related to the reconstruction of the carbon atoms of carbon nanotube during hydrogen plasma treatment [19].

Fig. 5 shows the typical *J–E* plots of cathodes with different hydrogen plasma treatment time and the corresponding *F–N* plots. Table 1 is the comparisons of the field for obtain current density of 1 and 2 mA/cm^2 from cathodes with different hydrogen plasma time. It is found the cathode without any treatment has lower field for current density of 1 mA/cm^2 than the cathode after RIE etching (i.e. 0 min hydrogen plasma treatment), which was due to the temporary priority eclectic emission of CNTs with high aspect ratio from local area of cathode. As voltage increasing, these priorities (or hot points) were burned, and the field for high current density (i.e. 2 mA/cm^2) of cathode decreased.

Effect of hydrogen plasma treatment on cathode field emission characteristics was fluctuant (see Table 1). Short-term treatment (i.e. 5 min, 10 min) can obviously decreased the field for current density of 1 and 2 mA/cm^2. The field for 1 and 2 mA/cm^2 current density from the cathode after 5 min hydrogen plasma treatment is respectively 6.45 MV/m and 7.2 MV/m. Furthermore, the emission site image results (Fig. 6a) show the cathode after 5 min hydrogen plasma treatment has better uniformity and stable field emission, which is due to C nanoparticles on CNTs outer-wall. These C nanoparticles are equivalent to localized states of CNTs and can provide electric channels for electrons to travel trough, which leads to emission point increase of CNTs cathode, so field emission uniformity is improved. Furthermore, these C nanoparticles also play the role of micro-tip, the local electric field of CNTs increases and the operating field of cathode decrease. However, when the hydrogen treatment time is too long (i.e. ≥20 min), the field emission characteristics of cathode is getting worse. Relating to the surface morphology observed by FESEM (see Fig. 3e–h), it is owing to the CNTs number reduction and cathode surface become rough for high-energy ions destruction, which is also reflected in the emission site image results (Fig. 6b–f).