Stable Field Emitters for a Miniature X-ray Tube Using Carbon Nanotube Drop Drying on a Flat Metal Tip

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Abstract Stable carbon nanotube (CNT) field emitters for a vacuum-sealed miniature X-ray tube have been fabricated. The field emitters with a uniform CNT coating are prepared by a simple drop drying of a CNT mixture solution that is composed of chemically modified multi-walled CNTs, silver nanoparticles, and isopropyl alcohol on flat tungsten tips. A highly thermal- and electrical-conductive silver layer strongly attaches CNTs to the tungsten tips. Consequently, the field emitters exhibit good electron emission stability: continuous electron emission of around $100\mu A$ at 2.3 V/\( \mu \)m has stably lasted over 40 h even at non-high vacuum ambient ($\sim 10^{-3}$ Pa).

Keywords Carbon nanotube · Field emission · Drop drying · Miniature X-ray tube

Introduction

Carbon nanotube (CNT) as a cold field emitter emits high brightness of electron owing to their high aspect ratio, small radius of curvature, high electric and thermal conductivity, and structural robustness [1, 2]. Recently, CNT emitters have been intensively developed for electron sources of several devices, such as field emission displays (FED) [3–5], high-resolution X-ray microscopes [6–9], and miniature X-ray devices [10, 11]. A miniature X-ray tube [12–15] that normally consists of an electron emitter, an electron beam optical system, and an X-ray target has been applied to a cavity-inserted X-ray imaging [12] and a radiation source of brachytherapy for human body [13] with the help of its needle-like shape. However, since the inside of the tube is narrow and long, the electron emitter should be also miniaturized, and additional use of an electrostatic or magnetic lens for electron beam focusing is limited.

Recently, a thermionic filament-based miniature X-ray tube with the diameter of 2.25 mm and the dose rate of a 15 Gy/min (at 1 cm water depth) is commercialized for an X-ray source of electric brachytherapy [13, 14]. However, total operating time has been not guaranteed higher than 2.5 h. In such a thermionic filament-based X-ray tube, high temperature operation of the filament is necessary to increase X-ray dose rate, reducing the lifetime of the filament especially in non-high vacuum environment. CNT field emitters, particularly of a sharp tip shape, have been developed for high-resolution electron and X-ray devices [6, 7, 16–18]. CNT tip emitters can provide high-brightness electron beams due to their point-like electron emission sites. However, a sharp tip emitter has limited number of CNTs and thus each CNT must supply high electron emission current for the application to a high-power X-ray tube. As a result, CNTs can be easily damaged by high joule heating as well as ion particle adsorption [19]. In addition, an electron beam that is produced from a sharp tip is diverged because the electric field generated near the sharp exerts outward forces on the electrons generated from the tip. This diverged beam might be lost during the transport to an X-ray target in a miniature X-ray tube, which prevents the stable operation of the X-ray tube. One of the methods to overcome these properties of CNT tip emitters is to use a flat-tip CNTs, in which many CNTs are attached on a comparatively large area of flat metal substrate. In comparison with a sharp tip emitters, a flat-tip
CNT emitter reduces the electrical power loading per each CNT and can provide more parallel electron beam.

Generally, CNT field emitters have been fabricated using chemical vapor deposition (CVD) [6, 7, 20, 21], pyrolysis [22], screen printing of CNT paste [3, 4, 23], ion bombardment [24], and dielectrophoresis [25]. CVD techniques are appropriate for a precise control of CNT growth length, pattern, and direction [20]. However, in CVD method, a complicated process with high temperature is required, and moreover, the bonding strength of CNTs on a substrate depends on catalyst particle adhesion, which is generally not so strong. Ion bombardment and dielectrophoresis are comparatively simple processes, but the electron emission current of a CNT emitter fabricated by these technique is normally less than that prepared by CVD technique. In screen printing method, a mixture of CNT, inorganic binder, and solvent are printed on a substrate, and this method has the advantages of a simple and cheap process for mass production, stable and uniform electron emission with good CNT adhesion. In this method, an inorganic binder is sintered to form a high electric and thermal conductive layer [26] and tightly bonds CNTs to a substrate. Consequently, electron emitters prepared by this method have stable electron emission property for a longer time [23]. By adopting the advantage of the screen printing method, we fabricated a flat-tip CNT emitter for a miniature X-ray tube using drop drying of CNT solution [27, 28]. The fabricated CNT emitter has shown a high electron emission of \( \sim 0.5 \) mA and a stable electron emission of 100 \( \mu \)A for longer than 40 h in the vacuum ambient of \( 1 \times 10^{-3} \) Pa.

**Experimental**

The fabrication process of the CNT emitter is schematically shown in Fig. 1. The CNT solution has been prepared by mixing a multi-walled CNT (CM-95; Hanwha Nanotech Inc.) with the diameter of 20 nm, silver (Ag) nanoparticles (NPs) (DGH; Advanced Nano Products Co., Ltd.) with the average diameter of \( \sim 60 \) nm, and 99.5% isopropyl alcohol. The CNT has been synthesized by thermal CVD and purified using the hydrothermal treatment [29] with a mixture of nitric acid and sulfuric acid for a better CNT dispersion and cleaning adsorbrates. The Ag NPs are filtered from the diluted Ag NP paste with isopropyl alcohol. The substrate of CNT is a tungsten (W) wire with the diameter of 0.25 mm. One end of the wire has been mechanically polished to have a flat surface with the average roughness of 0.1 \( \mu \)m in height and 0.4 \( \mu \)m in width for uniform coating of the CNT solution and regular electric field on the cathode tip surface. In Fig. 1a, 2 \( \mu l \) of the CNT solution drop dangles from the vertically stood W tip according to the force equilibrium between gravitational force and surface tension originated from the adhesion force between CNT solution and alcohol-philic metal substrate. During drying out of the isopropyl alcohol at atmosphere for 5 min, CNT and Ag NPs mixture is uniformly coated by evaporating sessile drop [30] (Fig. 1b, c). The sintering of the Ag NPs for good adhesion of CNT is processed in \( \sim 10^{-1} \) Pa vacuum ambient at gradually increased temperature of 200\( ^\circ \), 300\( ^\circ \), 400\( ^\circ \), and 500\( ^\circ \)C for 30 min each.

**Results and Discussion**

The uniform coating of the CNT mixture on the metal-tip substrate follows the mechanisms of homogenization of CNT solution and the drop drying on alcohol-philic metal substrate. The chemically modified CNTs are not aggregated during the evaporation due to increased solubility in polar solvent by providing an oxygen-containing group on CNT surface [29]. Since the sessile drop is evaporated quasi-steadily [30], the CNT drop dried uniformly little by little from the outer diameter to the center of the metal tip through the reduction in air–alcohol interface [28] (decreasing contact angle/area). Figure 2 shows the scanning electron microscope (SEM) images of the dried CNT
drop morphology and the fabricated CNT emitter with 4.2 w% multi-walled CNT and 4.2 w% Ag NPs concentration. The CNT mixture layer with the thickness of \( \sim 1.5 \mu m \) hardened to the flat W tip after the sintering (Fig. 2a). The CNTs soared from the layer with height of \( \sim 0.5 \mu m \) and uniformly dispersed on the metal surface except few aggregations. c Drop dried pristine CNT-Ag NP mixture. d Sintered CNT-Ag NP mixture.

down, and few aggregated nanoparticles with the diameter of \( \sim 100 \text{ nm} \) are remained on the CNT surface.

To optimize the uniform CNT coating, the concentration and mixing ratio of the CNT solution have been changed as shown in Fig. 3. In the Fig. 3a, b for the relatively higher concentration of Ag NPs, large amount of Ag particles are not homogeneously mixed with CNT and mutually aggregated as a protrusion on the CNT surface. However, in the
**Table 1**  Field emission properties of the various CNT emitters on sharp substrates

| Substrate       | Production method            | Emission area (cm²) | Best emission | Vacuum ambient (Pa) | Stability       | Refs. |
|-----------------|------------------------------|---------------------|---------------|---------------------|-----------------|-------|
| Conical tip     | Plasma-enhanced CVD          | 1.6 x 10⁻⁶          | 26 µA, 1.2 kV/250 µm | 4 x 10⁻⁷          | 10 µA, >20 h    | [6]   |
|                 | Inductively coupled plasma CVD | ~3 x 10⁻⁸         | 51 µA, 1 kV/250 µm | 1.06 x 10⁻⁵        | 10 µA, >40 h    | [16]  |
|                 | Pyrolysis of ferrocene       | 6.7 x 10⁻⁷          | 1 mA, 16.5 kV/5 cm | 1 x 10⁻⁸          | 100 µA, >180 min| [17]  |
| Flat plate      | Arc                          | ~5.9 x 10⁻⁴         | ~100 µA, 2.7 kV/1 mm | 1 x 10⁻⁸          | 80 µA, >100 h   | [18]  |
|                 | Plasma-enhanced CVD          | ~7.9 x 10⁻⁴ (50 µm φ, 1 mm length) | 7 mA/cm², 6 kV/1 mm | 2.6 x 10⁻⁴        | 2 mA/cm², >15 h | [34]  |
| Flat tip        | CVD/Ag NP paste              | 4.9 x 10⁻⁴          | 465 µA, 6.6 kV/2 mm | ~1 x 10⁻³         | >100 µA, >40 h  | [8]   |
migration of positively charged residual gas particles toward negatively charged CNT emitter and joule heating [19]. The flat-tip-type CNT emitter fabricated with the Ag adhesion layer can provide larger number of CNTs for electron emission, and thus the electric power loading per CNT is decreased. Table 1 shows the field emission properties of various CNT emitters fabricated on sharp substrates, which are recently published [4, 6, 8, 16, 17, 34–36]. The flat-tip substrate can provide an enough electron emission site for high emission current similar to that of a flat plate, and together with the CNT mixture coating can help to stabilize electron emission in a worse vacuum condition. In addition, with the flat-tip substrate, the structural damage to the CNT tips due to ionic collisions will be less likely to occur. Therefore, a fatal emission failure in a bad vacuum condition has been lessened compared to sharp-tip-type CNT emitters [6, 16, 17].

Conclusions

In summary, flat-tip-type CNT field emitters were fabricated by drop drying of a CNT-Ag NP mixture on flat tungsten tips. We observed that the concentration and mixing ratio of the CNT solution were crucial for the performance of CNT field emitters. The fabricated tip-type field emitters exhibited very stable electron emission at high emission current. We believe that the tip-type CNT field emitters are very useful to realize a miniaturized X-ray tube with a high X-ray brightness.

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