Carbon-nanotube cathode modified by femtosecond laser ablation

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Abstract

Femtosecond laser ablation of carbon nanotube (CNT) cathode was demonstrated in the laser fluence range of 0.05-2 J/cm². It was shown that the CNT ablated by femtosecond laser were aligned perpendicular to the cathode surface. The emission characteristics of the CNT cathode were measured using a diode system. The modified CNT cathode had a turn-on field of 1.8 V/µm, which was approximately half that of the original CNT cathode. As the laser fluence decreased, the turn-on field also decreased.

1. Introduction

Carbon nanotube (CNT) is the ideal material for a cathode emitter of a Field Emission Display (FED) [1]-[3]. However, CNT cathode prepared by the printing method has far from ideal emission characteristics, because the CNTs lie flat in the cathode and have random orientation. To utilize the characteristics of CNTs for FED, the CNTs should be highly oriented perpendicular to the surface. Thus additional processing is required to produce CNTs having ideal characteristics for FED. A variety of different processing methods, including peeling, scratching, ion bombardment [4], and nanosecond laser ablation [3], have been proposed and investigated. However, it has not been possible to obtain sufficient emission uniformity at low applied electric fields using these methods. Recently, a periodic nano-structure formation produced by femtosecond laser ablation [5][6] has been demonstrated for various materials such as metals [7], dielectrics [8][9], and semiconductors [10]. The periodic formation originates from the interference between the incident laser and the scattered wave (or plasma wave) along the surface. Controlled nano-structure formation could improve the characteristics of material surfaces [11]-[13]. Thus femtosecond laser ablation could be a promising additional processing method for a CNT cathode. Additionally, the ablation threshold decreases for shorter pulses when the laser pulse is shorter than that of characteristic time for the electron-phonon interaction (~ps). In this paper, the turn on field, surface structure and a Raman spectrum for a CNT cathode modified by femtosecond laser ablation are reported.

2. Experimental

The CNT cathodes were fabricated using multiwall CNT mixed with an organic binder of cellulose and printed on a glass substrate. The CNT cathode had an area of 2 × 2 mm² and a thickness of ~3 µm. Laser ablation was performed on the CNT cathode with a Gaussian laser beam (800 nm wavelength, 180 fs pulse duration, 10 Hz repetition rate) produced by a Ti:sapphire laser system. The laser beam was focused on the CNT cathode surface with a lens (f=10 cm) at normal incidence. At the focal position, the laser beam was nearly circular, with a diameter of 38 µm at the 1/e intensity. The laser pulse energy was varied from 0.7 µJ to 15.0 µJ by an energy attenuator. The CNTs were irradiated by laser pulses at a distance of 50 µm for single-shot and 10 µm for multi-shot. The CNT cathodes modified by laser ablation were measured with a
scanning electron microscope (SEM) and Raman spectroscopy. The emission current was dependent on the applied field, which was measured by a diode system (Fig. 1). The distance between the CNT cathode to the anode was 60 μm and the pressure was maintained at ~ 10⁻⁷ Torr. Prior to femtosecond laser irradiation of the CNT cathode, the ablation threshold of the CNT cathode was measured using the crater diameter dependence on laser fluence. Using this method it was found that the ablation threshold of the CNT cathode was 0.046 J/cm².

Figure 1. A diode system for the field emission current measurements.

3. Results and discussion

The emission current density as a function of the applied electric field for modified CNTs for two different laser fluences is shown in Fig.2(a). The current-field curves were relatively smooth and reproducible for the modified CNTs irradiated at a laser fluence of 0.068 J/cm². The turn-on field represents the applied electric field at which the emission current measured by the diode system exceeded 0.3 μA (7.5 μA/cm²). The turn-on fields were 1.9 V/μm and 2.3 V/μm for laser fluences of 0.068 J/cm² and 1.4 J/cm², respectively. In order to discuss the modified turn-on field, Fowler-Nordheim (F-N) model is used. The current density from the material surface can be express as

\[ J = \frac{A\beta E^3}{\phi} \exp \left( -\frac{B\phi}{\beta E} \right), \]

where \( A = 1.5 \times 10^6 \), \( B = 6.83 \times 10^7 \), \( \beta \) is field enhancement factor, \( \phi \) is work function, \( E \) is the applied electric field. F-N plot is shown in Fig.2(b). The lines of Fig.2(b) were determined by the method of the least square fitting applied to the results obtained for each current density dependence. Fitting lines show that the field enhancement factors are \( \beta = 2500 \) and 3700 for the laser fluence of 1.4 and 0.068 J/cm², respectively. At the laser fluence of 0.068 J/cm², the field enhancement factor is 2.5 times higher than that of original surface.

The dependence of the turn-on field on the laser fluence is shown in Fig.3. As the laser fluence decreased, the turn-on field decreased. The modified CNT cathode irradiated at the lowest laser fluence had a turn-on field of 1.8 V/μm for a single shot. The observed turn-on field was approximately half of that of the original CNT cathode (4 V/μm). The dependence of the turn-on field on the laser fluence followed a similar trend for both single-shot and multi-shot irradiation.

Cross-sectional SEM images of a CNT cathode are shown in Fig. 4. The images clearly show that the CNTs in Fig. 4(c) were aligned perpendicular to the substrate as a result of laser ablation. Femtosecond laser irradiation of the solid produces a standing wave, the electric field of which is oriented perpendicular to the surface. The standing wave originates from interference between the incident laser beam and the scattered wave (or plasma wave) along the surface. The standing wave may contribute to the driving force that produces the CNTs’ orientation.

The average heights of the CNTs tips were 3 μm and 8 μm for laser fluences of 0.068 J/cm² and 0.74 J/cm², respectively. The height of the CNTs tips was dependent on the laser fluence as shown in Fig. 5. The height of the tip was averaged over five different positions where the laser was irradiated. The maximum height of the CNTs tip was observed at a laser fluence of 0.7 J/cm² and the height changed rapidly near the fluence of 0.35 J/cm². Below the laser fluence of 0.2 J/cm², the turn-on field decreased as the height of the CNTs tips also decreased.
The minimum applied field for electron emission is roughly estimated from \( E_{\text{min}} = \frac{\phi}{(e h)} \) [14], where \( \phi \) is the work function, \( e \) is the charge of an electron, and \( h \) is the height of the field-enhancing structure. This simple equation suggests that the turn-on field should decrease as the height of the CNTs tips increases. However, the experimental results showed that there was no correlation between the turn-on field and the height of the CNTs tips in the fluence range from 0.06 - 0.35 J/cm².

A Raman spectrum of the modified CNTs is shown in Fig. 6. The Raman spectrum exhibits the G line at 1590 cm\(^{-1}\) [15][16], which originates from vibrations of the carbon sheet, and is characteristic of CNTs generally. The D line at 1335 cm\(^{-1}\) indicates the existence of defective graphite layers. As the laser fluence decreased, the intensity ratio of the G to D lines increased to 2.3, while that for a non-ablated CNT cathode was 1.7. The results of our work suggest that the height dependence of the turn-on field might be explained by the purification of CNTs.

In conclusion, the modified CNTs had a turn-on field of 1.8 V/\( \mu \)m (for an applied voltage of 108 V), which was approximately half that of the original, unmodified CNT cathode. The dependence of the turn-on field on the laser fluence was measured over the range of 0.05 – 2 J/cm². As the laser fluence decreased, the turn-on field also decreased. The CNTs on the cathode were aligned perpendicular to the substrate as a result of laser ablation. The Raman spectrum results for the modified CNT cathode suggest that the achieved turn-on field might be due to purification of the CNTs.

**Figure 2.** Field emission current density vs. the applied electric field for two different laser fluences.

**Figure 3.** Turn-on field vs. the laser fluence for modified CNT cathode.
Figure 4. SEM images of a CNT cathode before laser ablation (a) and after laser ablation at 0.7 J/cm² (b) and 0.068 J/cm² (c).

Figure 5. Average height of CNTs tips vs. the laser fluence.

Figure 6. Raman spectrum of the CNT cathode before laser ablation and after laser ablation at 0.068 J/cm².

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