

# Carbon Nano-structured Films on Chrome Electrodes with Excellent Electron Emission Characteristics

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## ABSTRACT

We report the fabrication of carbon nanostucture films with excellent electron-emission characteristics on chrome electrodes using a pre-deposited transition metal catalyst layer. The emission current densities of  $1 \mu\text{A}/\text{cm}^2$  and  $1 \text{mA}/\text{cm}^2$  were measured at the electric field of 2.5 and 4.8  $\text{V}/\mu\text{m}$ , respectively, and the current fluctuation of less than 2.5% was observed at the average current density 211  $\mu\text{A}/\text{cm}^2$  for the measurement duration of 20 minutes. We counted more than  $\sim 10^4$  emission sites per  $\text{cm}^2$  from the emission images, and also noticed good mechanical stability. Moreover, we were able to fabricate good electron-emitting carbon films on chrome electrodes on Corning glass substrates at the nominal temperature below 650  $^\circ\text{C}$ .

## INTRODUCTION

Carbon nanotubes have attracted a great deal of attention as promising electron-emitting materials due to their unique structural and electronic properties. In particular, nanotubes grown by using a metal catalyst such as Co, Fe, Ni, or their alloys have been vigorously studied lately since they do not require a post-growth treatment. Another advantage of the catalytic growth-method is the potential for the fabrication of patterned nanotube field emitters. However, from the practical point of view, it is essential to deposit the electron-emitting carbon films on the cathode electrodes to make practical display devices. Also it is important to have a low growth temperature so that glass substrates can be used.

In this work, we report the successful fabrication of nano-structured carbon films using a Ni/Fe-alloy catalyst layer on chrome electrodes, which are commonly used as cathode feed-lines. Adoption of the hot-filament-chemical-vapor-deposition (HFCVD) method allowed us to deposit nano-structured carbon films at temperatures lower than the typical thermal CVD conditions, and eventually we were able to fabricate decent emitting films on the chrome electrodes sputtered on Corning glass substrates.

## EXPERIMENTAL

Carbon films were grown on either silicon or Corning glass substrates with sputter-deposited chrome electrodes by using the HFCVD method. Before the substrates were introduced into the HFCVD chamber, catalyst layers of Ni/Fe alloy were sputter deposited on the substrates. Mixture gases of  $\text{CH}_4$  and  $\text{H}_2$  were used as a precursor.

Field emission measurements were carried out using a diode configuration consisting of a cathode (sample) and a parallel plate anode in a vacuum chamber maintained at a pressure of  $10^{-7}$  torr with an oil-free turbomolecular pump. An indium tin oxide (ITO) glass or a phosphor-coated ITO glass was used as the anode plate, and a Kapton foil was used as a spacer between the anode and the cathode. The emission current density was estimated by averaging the measured current over the entire area of a 3- or 6-mm diameter hole in the spacer, through which the current was collected, and the site density was estimated from the actual emitting images.

## RESULTS AND DISCUSSION

Fig. 1 shows the emission I-V curve of the carbon film deposited

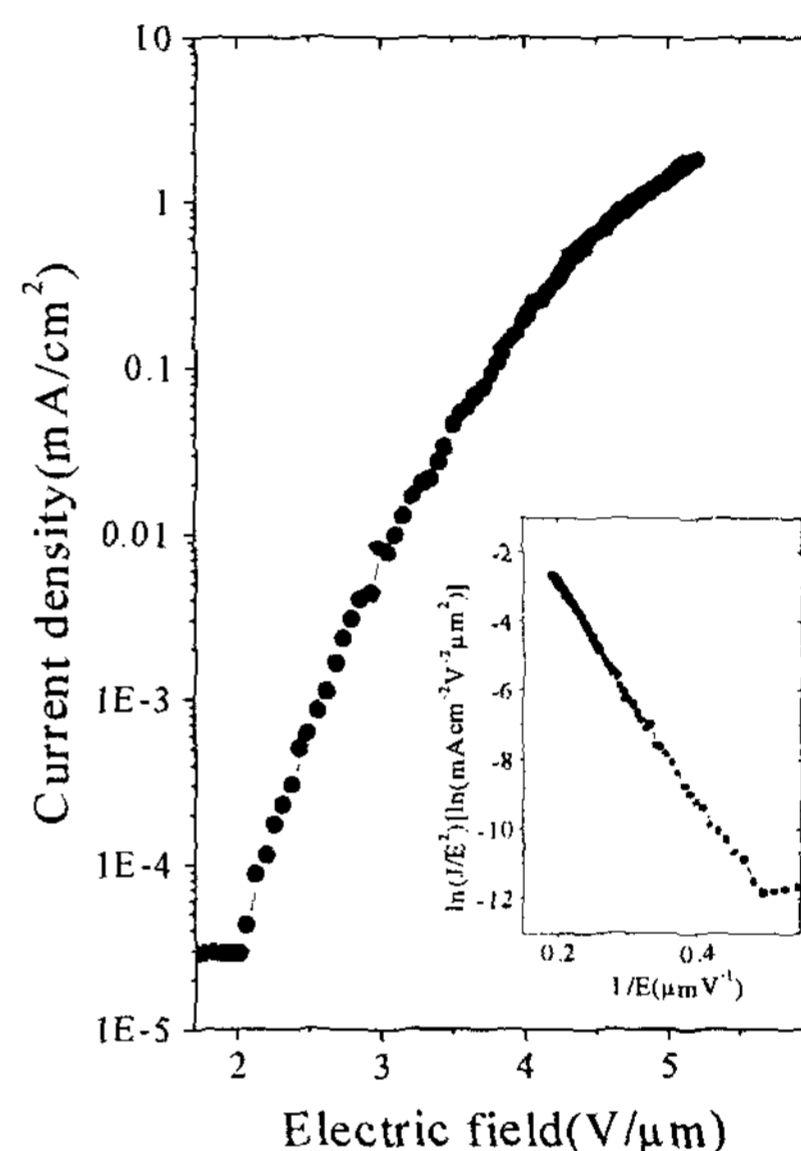


Fig. 1. Emission current density versus electric field of the carbon film deposited on silicon substrate. Corresponding F-N plot is shown in the inset.

on the chrome electrodes on a Si substrate. This film was fabricated with the 35-nm-thick Ni/Fe-alloy catalytic layer. This figure clearly illustrate the excellent field emission characteristics; the emission current densities of  $1 \mu\text{A}/\text{cm}^2$  and  $1 \text{mA}/\text{cm}^2$  were measured at the electric field of 2.5 and 4.8  $\text{V}/\mu\text{m}$ , respectively. The Fowler-Nordheim (F-N) plots corresponding to the measured I-V curve is shown in the inset. The linear F-N plot is indicative of the standard field emission. However, unlike the typical F-N plot of other carbon-based emitters, there is no change in the slope of this F-N plot even at the high emission-current range, which implies that these are very stable emitters indeed.

Fig. 2 shows the test results for the stability of the emission current at two different emission current densities. At the emission current density of  $\sim 70 \mu\text{A}/\text{cm}^2$ , a slight increase was recorded after the initiation of emission. However, at higher emission current densities, a better temporal stability was observed; at the current density of  $\sim 211 \mu\text{A}/\text{cm}^2$  less than 2.5% current fluctuation was observed during the 1200-second measurement.

Emission images of 3mm diameter through a phosphor-coated ITO glass presented in Fig. 3 demonstrate the good emission uniformity. In Fig. 4, all the RGB patterned phosphors were lighted even though there are a few not so bright pixels. Only  $\sim 4 \times 3 \text{ mm}^2$  are shown for the clear distinction of each color component. However, we were able to achieve comparable emission image from the area of  $1 \text{ cm}^2$ . The emitting-site density was estimated from the emission images. Because of the rather high emission site density together with the bright spots overwhelming less bright spots, we were able to estimate only the low limit of the emission site density:  $\sim 10^4$  sites/ $\text{cm}^2$ .

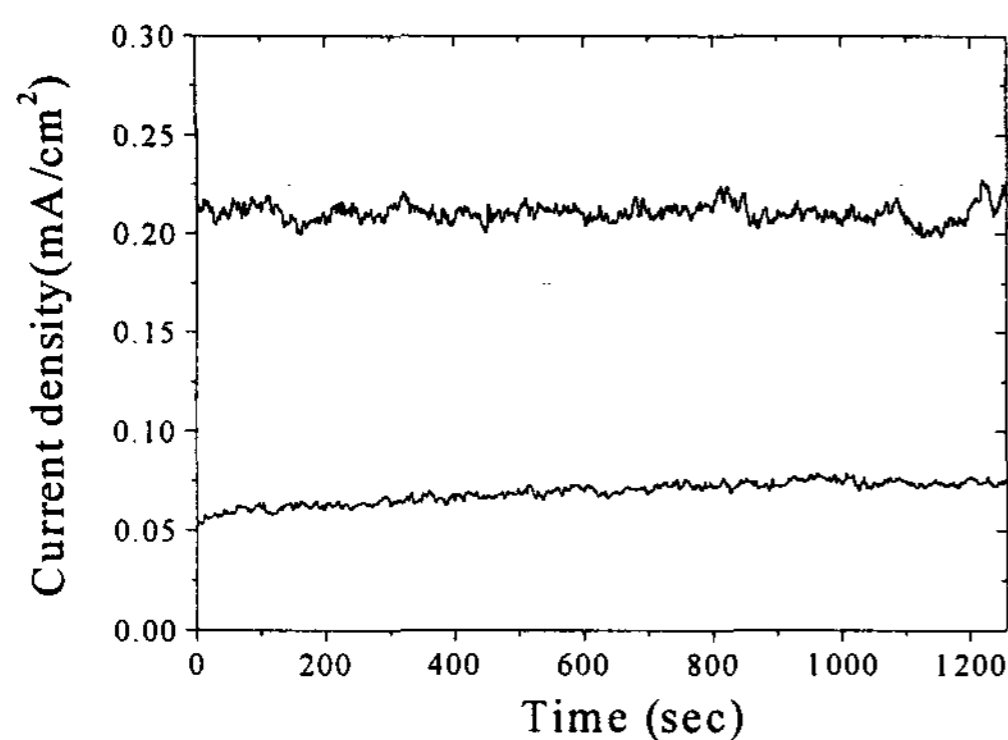


Fig. 2. Temporal variation of emission current density; at 70 and 211  $\mu\text{A}/\text{cm}^2$ , respectively. This film was deposited on silicon substrate.

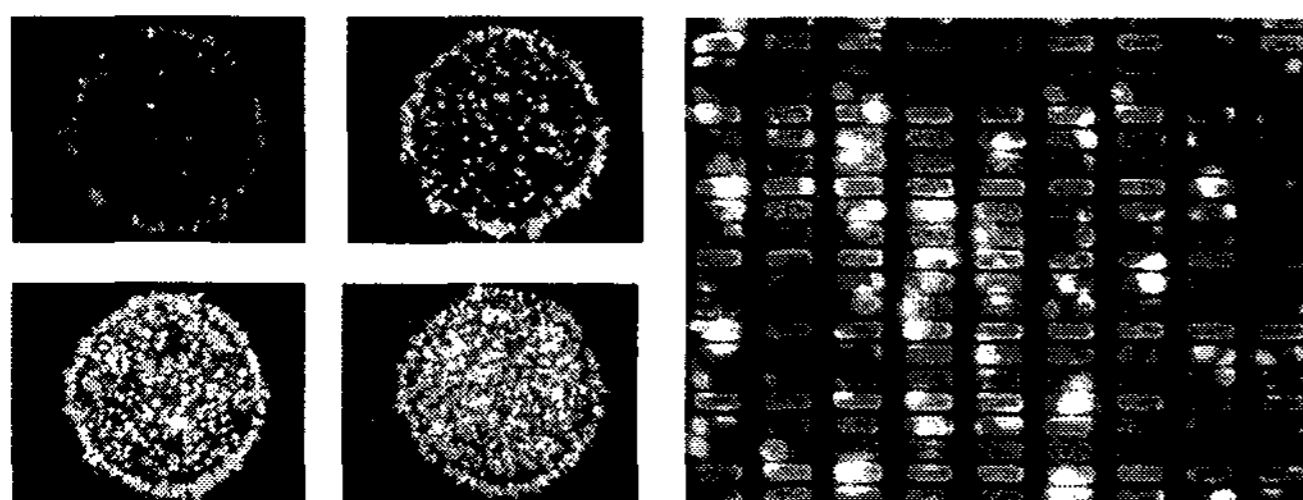


Fig 3. Emission images; clockwise from upper left, 3.3 V/ $\mu\text{m}$ , 4.6 V/ $\mu\text{m}$ , 6.0 V/ $\mu\text{m}$ , 7.3 V/ $\mu\text{m}$ .  
Fig. 4. A patterned RGB image. Each dot represents  $90 \times 300 \mu\text{m}$

One additional advantage of the fabrication of the carbon emitters on chrome electrodes is the great improvement of the mechanical stability. In the case of the nano-structured carbon emitters fabricated directly on either Si or glass substrates using metal catalysts, the poor adhesion of carbon films to substrates and the susceptibility of carbon films to the mechanical damage were observed. However, when the carbon emitters were fabricated on chrome electrodes, due to the strong adhesion the nano-structured carbon films could not be cleanly separated from the substrates. Moreover, we found that the hardness of the films was greatly improved.

Another advantage of using HFCVD, instead of thermal CVD, is the possibility of the low-temperature deposition of good electron-emitting carbon films. Since the independent control of the hydrocarbon-precursor decomposition is possible by adjusting the filament temperature, we were able to fabricate carbon emitters at successively lower substrate temperatures. Fig. 5 shows the I-V curve of the carbon emitters fabricated on the chrome electrodes sputter-deposited on a Corning glass substrate. Both the nominal

substrate temperature measured by thermocouple and the fact that the integrity of the chrome electrode was maintained throughout the deposition indicate that the deposition temperature was below  $650^\circ\text{C}$ . Since the low-temperature deposition conditions were not fully optimized, the emission characteristics of the carbon films deposited on Corning glass substrates are inferior to those of the films deposited on Si substrates. However, the preliminary I-V result presented in Fig. 5 is promising. Moreover, the carbon films on Corning glass substrates showed reasonably good temporal stability of current densities. For example, the current density depicted in Fig. 6 showed about 10% temporal variation over 1 hour except the initial drop.

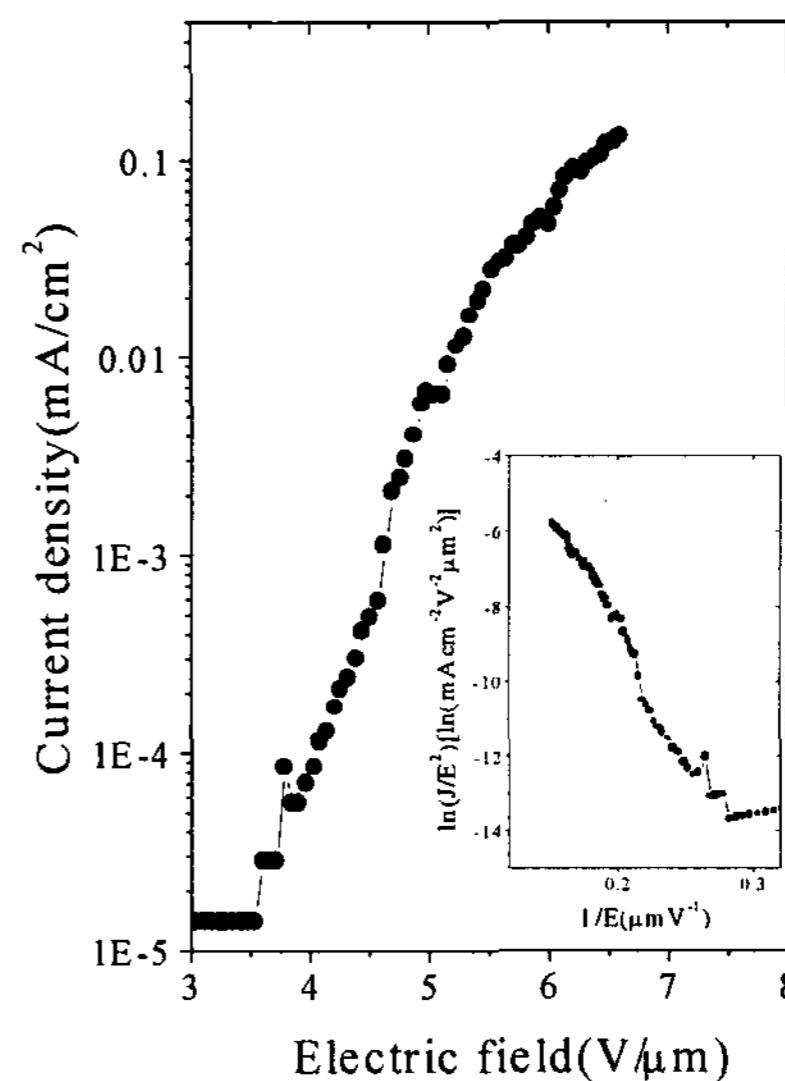


Fig 5. Emission current density versus electric field for the carbon film deposited on Corning glass substrate at the temperature below  $650^\circ\text{C}$ . Corresponding F-N plot is shown in the inset.

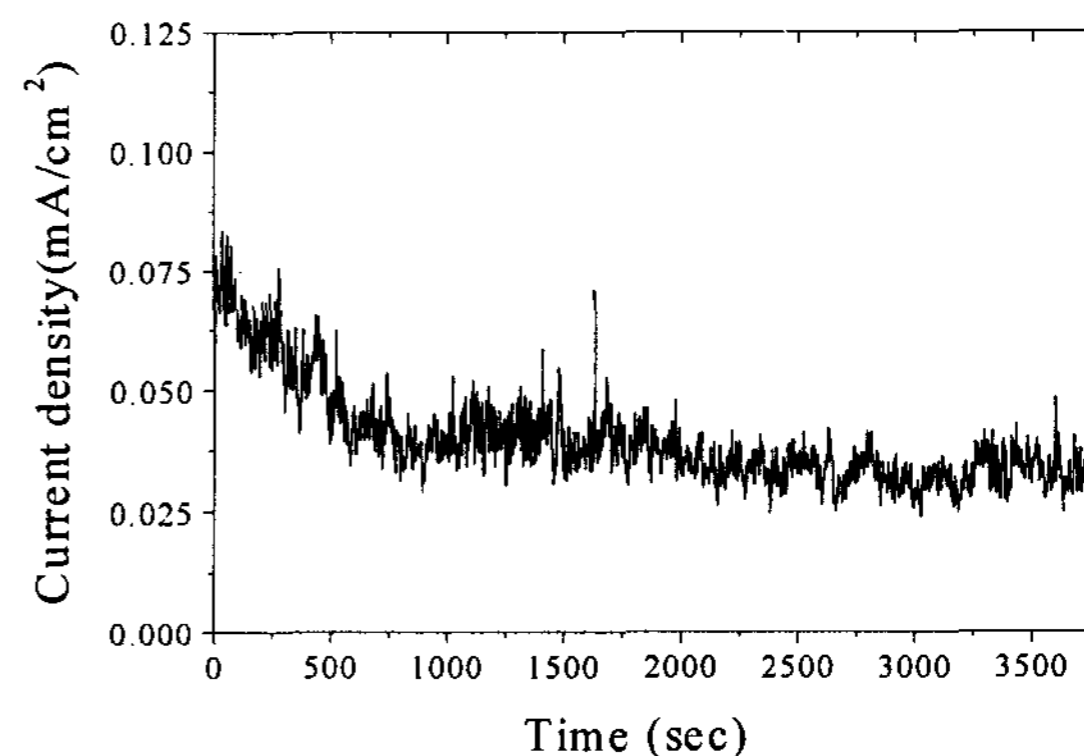


Fig. 6. Temporal variation of the emission current density of the film deposited on Corning glass.

## SUMMARY

We demonstrated that carbon emitters with excellent emission characteristics could be fabricated on chrome electrodes by HFCVD method using metal catalyst layers. Moreover, the preliminary result of the low-temperature fabrication of carbon emitters on Corning glass substrates was presented.