Field Emission Stability of Carbon Nanotubes Grown by Thermal Chemical Vapor Deposition

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Abstract

Multi-walled carbon nanotubes (CNTs) were synthesized on glass substrates in the different ramp-up heating ambient of vacuum, He, Ar, and N_2 by thermal chemical vapor deposition. CNTs with higher crystallinity were developed in the buffer gases with faster growth rates than in vacuum. Field emission characteristics were strongly related to the relative position of CNT emitters to the cathode electrodes. The areal-spread emission and instability were overcome by locating the emitters far away from the edges of cathode electrodes. The electrical conditioning of emitters improved their emission uniformity over a large area although it decreased the emission current. This study also discussed the long-term stability of CNT emitters.

1. Introduction

Since demonstrating the carbon nanotubes (CNTs) as excellent field emitters,[1] in particular, for flat panel display applications, much effort has been made to find inexpensive and efficient ways for controlled deposition of CNTs on large-area substrates.[2]-[5] With the advances in the application field of CNTs, technological aspects of the field emission (FE) including lifetime, emitter degradation or stability become more relevant.[6]-[8] In the CNT field emitters, such characteristics seem to be key parameters to be controlled. Despite their importance for the practical application, there have been few investigations of the FE stability of CNTs as a function of operating conditions.

This study not only investigated the effect of the geometry of CNT emitters and cathode electrodes on the FE characteristics of CNT emitters, but also the electrical conditioning for the better FE uniformity as well as stability. For these purposes, the catalyst layers were patterned to have different geometries and the CNT growth was optimized in terms of the ramp-up heating ambient in thermal chemical vapor deposition (CVD).

2. Experimental

CNTs were synthesized on glass substrates by thermal CVD. The 100 nm-thick Cr layer served as cathode electrodes and the 10nm-thick layer of 52Fe-42Ni-6Co as a catalyst for CNT synthesis. All metallic thin films were deposited by electron beam evaporation. The cathode electrodes were line-patterned by photolithography. The catalyst layer was also patterned to have several different shapes: (1) the catalyst lines patterned with the same geometry as the Cr cathode lines (so-called, simple line pattern); (2) the catalyst lines patterned to be located along the central area of the cathode lines (central line pattern); (3) the catalyst dots patterned on the Cr lines (dot pattern). The substrates were heated up to the growth temperature of 580°C by infrared lamps through a quartz window, and the CNTs were grown for 30min. During the ramp-up heating, the chamber was maintained to be under the vacuum, He, Ar, or N_2 ambient. As soon as the temperature was reached, a gas mixture of CO (0.08slm) and H_2 (1.27slm) was fed into the chamber for the growth of CNTs. The ramp-up heating ambient of vacuum or buffer gases had a great effect on the morphologies of as-grown CNTs, even though all the other growth conditions were kept to be the same but the ramp-up ambient.

FE characteristics of CNTs were measured in a diode configuration in a vacuum of ~$3x10^{-6}$ torr. The ITO glass coated with phosphors was used for the anode. The cathode-to-anode gap of 400μm was kept by glass spacers. The voltages were applied to the anode while the cathode was grounded. The duty ratios of voltage pulses were changed to estimate the FE stability. FE characteristics were analyzed by the Fowler-Nordheim relationship.

3. Results and discussion

Fig. 1 shows the CNTs grown in the different ramp-up heating ambient of vacuum, He, Ar, and N_2, which are 2, 7, 12, and 15μm thick, respectively. The CNTs are grown to be vertically aligned, probably due to the steric hindrance between CNTs. In TEM, the CNTs appear as long tubular products with the diameters of 10~60nm. While the herringborne structure of graphene sheets was observed in vacuum, the graphene sheets with high crystallinity were developed parallel to the tube axis in the buffer gases. *In-situ* monitoring of substrate temperatures during the ramp-up heating in vacuum showed a sharp drop of ~40°C at the instant of introducing the precursor gases of CO and H_2 at 580°C for the growth. The higher growth rates and higher crystallinity in the buffer gases seem to be attributed to more vigorous decomposition of the precursor gases since the additional kinetic energy transfer would occur by collision of the precursor gases with the hot buffer gases. The kinetic energy transfer in the gas collision may depend upon the heat capacity and molecular weight of the buffer gases.

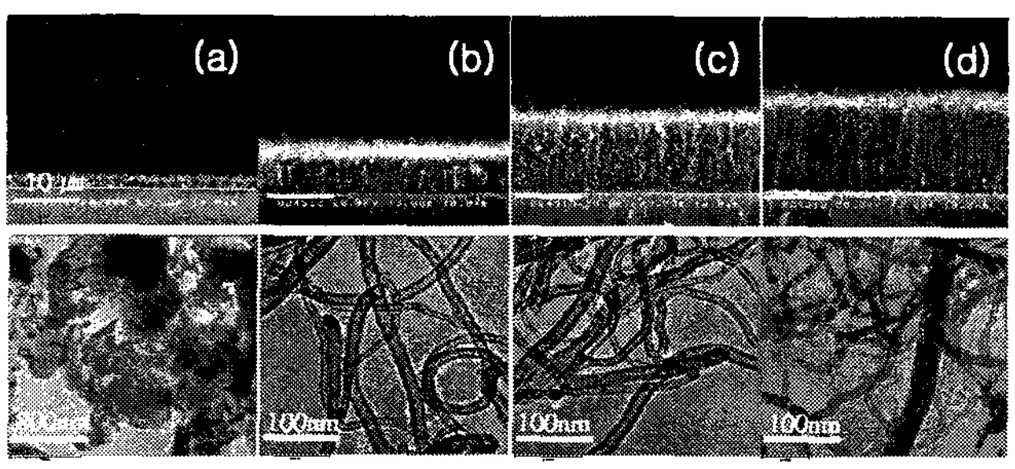

Fig.1. SEM (upper) and TEM images (lower) of CNTs grown at 550°C to which the substrates were heated up in (a) a vacuum, (b) He, (c) Ar, and (d) N_2, prior to the growth.

Fig. 2 gives the CNTs grown for the different patterns of catalyst. The CNTs are grown with the similar morphologies, but emission characteristics are considerably different for the catalyst patterns. In Fig. 3(a), the threshold electric fields for an onset of FE are approximately 2.3, 2.8, and 3.5V/μm, for the simple line, central line, and dot patterns of catalyst, respectively. Using the Fowler-Nordheim relationship, we estimated the field amplification factors β from the I-V curves.[9] The β value in principle depends only on the geometrical shape of the emitter for a given work function. The β is defined as E= $\beta V/d$, where E is the electric field just above the surface of the emitter tip, V the applied voltage, and d the cathode-to-anode distance. Given 5.0eV as the work function, the β values are calculated to be 1380, 1451, and 889, for the simple line, central line, and dot patterns, respectively. Simply from the FE curves, the simple line-patterned sample seems to be better than the others. In the observation of FE images using phosphors, phenomena of delayed and gradually expanded emission occurred in the CNTs grown on the simple line-patterned catalyst, as seen in Fig. 3(b).

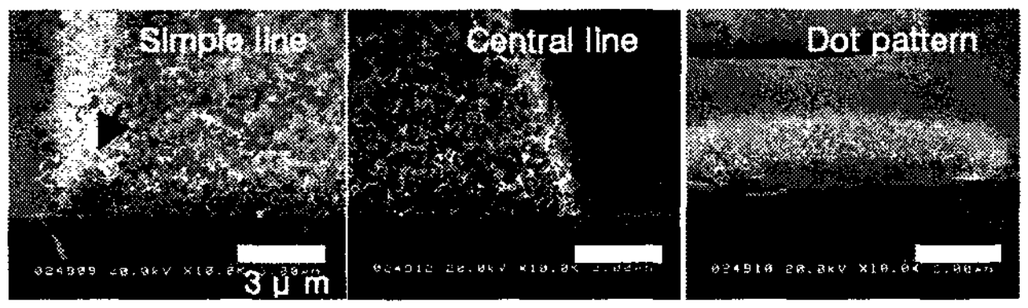

Fig. 2 SEM images of CNT films grown on the different geometries of catalyst patterns: simple line, central line, and dot patterns

For the simple line pattern, the emission area spreads out gradually to the neighbors upon the application of voltages to the anode. In some cases, the emission was extinguished in some area at instant and then resumed slowly again. For such samples, the emission was not instantly turned on even over an area of 2×2cm^2. The areal-spread, delayed emission and FE instability were not observed for the CNTs grown on the central line- or dot-patterned samples. Such phenomena seem to occur due to the edge emission in the simple line-patterned sample. We calculated electric field strength around the CNT emitters for the simple line and central line patterns of catalyst, as given in Fig. 4. It is shown that equipotential lines are densely distributed at the edge in case of the simple line pattern. Such a concentration of electric fields would give rise to larger FE on the edges than in other area, likely leading to the emission at lower voltages. When only one line of cathode electrodes is turned on, two lines are actually lit up on the phosphor plate. It is implied that electrons are emitted only from both edges of

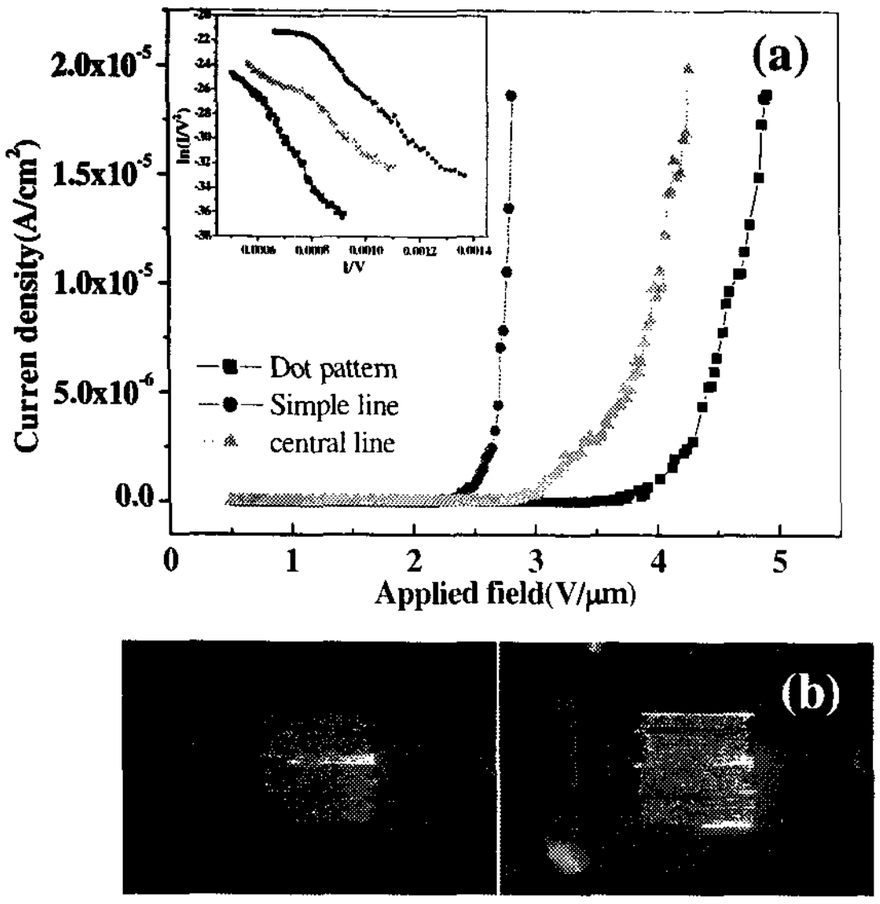

Fig. 3 (a) I-V characteristics of CNTs grown on the catalysts with the simple line, central line, and dot patterns, with the corresponding Fowler-Nordheim plots in insets. (b) phosphor emission images of the simple line-patterned CNTs (operation: 50% duty, 1kHz).

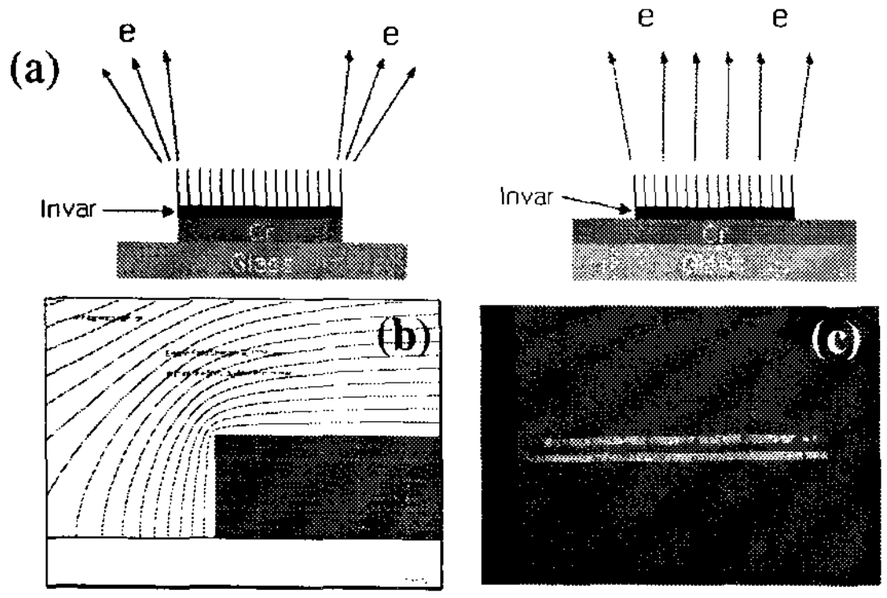

Fig. 4 (a) Geometry of simple line- and central line-patterned samples, (b) distribution of equipotential lines in the simple line-patterned sample, and (c) two line emission image upon turning-on one line of cathode electrodes.

CNT film. It seems that such localization of FE on the edges decreases the emission site density, resultantly increasing the load of emission current per emitter. In case of the simple line-patterned sample, the emission capability of emitters would be degraded with a faster speed due to the larger structural damage. The structural damage of CNTs during FE was observed at high electric fields.[10] The delayed emission and FE instability for the simple line-patterned case may be related to the electric charging on the insulating surface around the edges of the CNT film, but it is not yet clearly understood. For the central line and dot patterns of catalyst, however, stable FE was observed with instant turn-on and –off. The long-term emission stability of CNTs with the different geometry of catalyst is now under progress.

Electrical conditioning of CNT emitters was carried out at the constant DC voltages. In many samples, the emission current monotonically decreased with time during the conditioning, but the current increased, saturated for a while, and then slowly decreased with time for a few samples. Such behaviors strongly depended upon the voltage levels and emission site densities. The lower voltages and the higher emission site densities resulted in the slower decrease of the currents. The I-V curves of the very same sample measured before and after the conditioning indicated that the field amplification factors of emitters decreased from 1075 to 918 by the conditioning in Fig. 5(b), implying that the electrical conditioning damaged the CNT tips to probably shorten their lengths, although the conditioning improved the emission uniformity. The effective emission area α increased $8.35\times10^{-5}cm^{-2}$ to $9.44\times10^{-4}cm^{-2}$ by conditioning. Such a problem may be overcome by controlling the emission site densities.

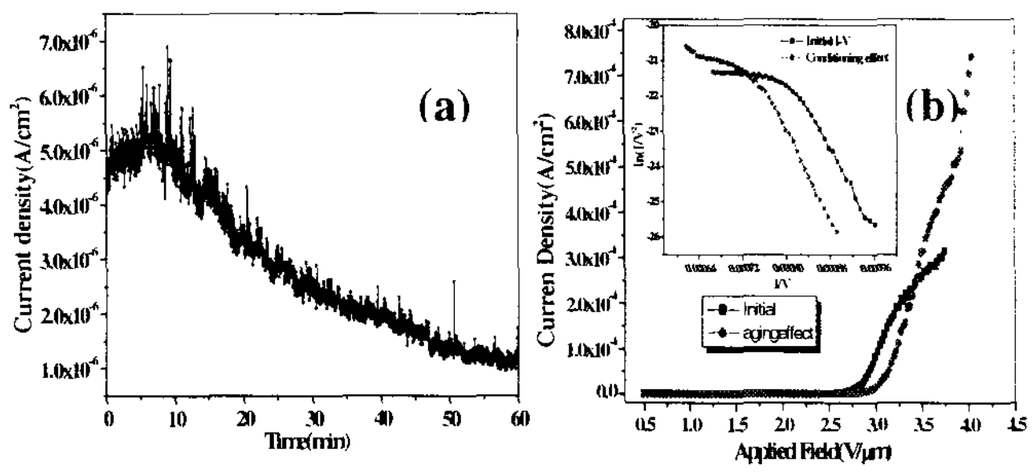

Fig. 5 (a) Electrical conditioning for 60min at 1100V and (b) I-V curves before and after conditioning. The inset in (b) shows the F-N plots of the corresponding I-V curves.

As a preliminary investigation of the long-term stability of CNT emitters, we measured the dependency of emission currents upon the duty ratios. The emission currents linearly increased with the duty ratios in the range of 1% to 100%(DC). In the pulse operation, the emission current level can be changed by adjusting the applied voltages and duty ratios. For the same level of emission current to be achieved, which one of increasing the voltages and increasing the duty ratios is more fatal to the degradation of emitters? Fig. 6 shows the short-term stability at the

constant initial current of ~70μA for the duty ratios of 1, 10, 50% under the fixed frequency of 60Hz. In this experiment, the voltage was set for a given duty ratio to maintain the constant the initial current. The voltage increase seems to degrade the emitters at a faster rate than an increase of the duty ratios.

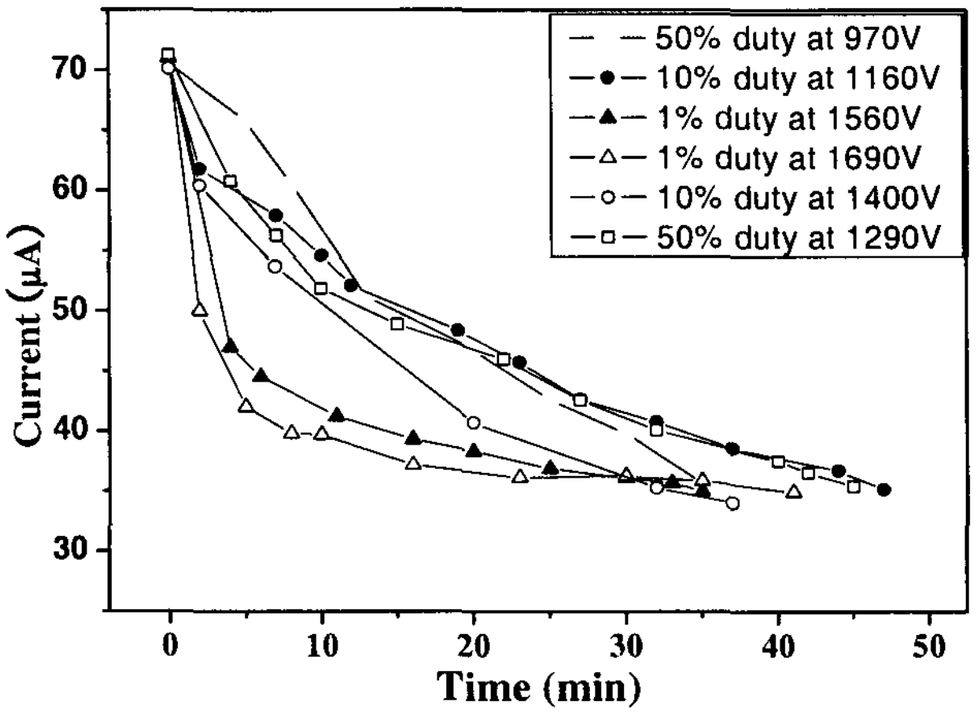

Fig. 6 Emission currents with time for different duty ratios and voltages at the frequency of 60Hz.

4. Conclusion

We studied controlled growth of CNTs with high crystallinity and their FE characteristics. The growth rates of CNTs increased in order of the ramp-up heating ambient of vacuum, He, Ar, N_2. The crystallity of CNTs was considerably enhanced in the ramp-up heating in gases. It was shown that FE characteristics were strongly related to the relative position of CNT emitters to the cathode electrodes. For the simple line pattern of catalyst, the areal-spread, delayed emission, and FE instability were observed, but such phenomena were overcome by locating the emitters far away from the edges of cathode electrodes. Such FE behavior in the simple line-patterned sample seems to be attributed to the concentration of electric fields on the edges of the CNT films. The electrical conditioning decreased the field enhancement factors, but increased the effective emission areas, thereby giving rise to lower emission currents and better emission uniformity. Simultaneous variation of applied voltages and duty ratios showed that the voltage increase was more fatal to the degradation of CNT emitters than the increase of duty ratios.

5. References

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