Edge effect on the field emission properties from vertically aligned carbon nanotube arrays

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Carbon nanotubes (CNTs) have been considered as one of the best field emitters due to their unique properties of high aspect ratio, chemical inertness, high mechanical strength, and high electrical conductivity. For an application to the field emission displays (FEDs), the CNT emitters have been fabricated using various practical methods such as the suspension-filtering [1], screen printing [2], and electrophoresis [3]. In addition to these practically tractable methods of the preparation, a novel approach of direct chemical vapor deposition (CVD) growth has been also adopted [4].

One important issue in the CVD approach is the controllability of the stable and high emission currents over the large area. It has been suggested that the patterned CVD growth could lead to high emission currents due to the edge effect [4]. This is related to the nanotube density which may not be easily controlled in the CVD growth. A high CNT density was usually obtained, in which a significant field-screening effect was presumably involved due to the proximate presence of nanotubes. It have been known that the field emission current could be maximized, when the tube-tube separation distance was comparable to the tube length [5].

In this report, we investigated the change of the emission current from the center to the edge of the patterned carbon nanotubes. We found that the emission current and the field enhancement factor were significantly improved at the edge compared those at the center. We also found that the dot-dot separation distance needs to be tuned up in order to obtain the high and stable emission currents.

A nickel catalyst was deposited with a thickness of 120 nm by the radio-frequency (RF) sputtering method [6]. Conventional nickel grid mask was mounted on a TiN-deposited Si substrate in order to fabricate the patterned Ni catalysts. A magnet was attached on the reverse side of the substrate to hold a tight contact between the nickel mask and substrate. The multiwalled CNT emitters were synthesized at 650 °C for 40 min using C₂H₂ gases as a carbon source by the thermal CVD. We installed two nanomanipulators inside the field-emission scanning electron microscope (FESEM) for the field emission measurements [7].

The square shaped-CNT arrays grown selectively on the Ni catalysts are clearly shown in Fig. 1(a). Fig. 1(b) and (c) show the vertically aligned CNTs grown at the central part and the edge part of one of the

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square-patterned CNTs, respectively. We can observe CNTs with high density, uniform length of 13.5 μm, and diameter of about 30 nm at the central part in Fig. 1(b). Contrary to this, CNTs grown at the edge part show relatively short tube length, low density, and poor uniformity. The diameters of CNTs at the edge part were also larger and less uniform than those at the central part. This suggests that the growth rate of CNTs is quite different for both parts. It is well known that the CNT growth rate and the diameter are strongly dependent on the size of the catalyst particles. Ni atoms could be deposited more severely at the edge part than at the central part during the Ni sputtering owing to the high plasma density at the edge. This resulted in the Ni grain formation with larger diameter and smaller density, giving rise to slower growth rate and larger diameters of CNTs compared to the center.

The sample was moved into the FESEM chamber where the nanopositioner was installed [7]. The tungsten tip with very high aspect ratio as an anode was installed at the end of the nanopositioner. The nanopositioner was moved from the center to the edge to see the change in the emission currents, while the height with respect to the bottom of the nanotube arrays was maintained at 20 μm. Fig. 2(a) shows the FESEM image of the tungsten tip that is located near at the center of the CNT pattern. Fig. 2(b) shows the $I-V$ characteristics in Fowler–Nordheim (FN) plot in terms of various tip positions. The emission currents near the center, indicated by triangles and diamonds, are relatively low, whereas the currents near the edge, indicated by circles and
pentagons, are very large. We note that the emission current from the region between two CNT arrays that no nanotube was present, shows the maximum values especially at high field region. It is generally known that the field emission from the CNT films is dominated by the few exceptionally long nanotubes [8]. However, as can be seen from the high resolution SEM image, it is very unlikely to see the field emission from such a long individual nanotube. In fact, the edge-to-edge spacing was 25 μm in this case, which was still quite close to have a strong emission. Fig. 2(c) shows the turn-on voltage (the starting voltage of the linear region at the FN plot) and the field enhancement factor as a function of the tip position extracted from the FN plot. We note that the turn-on voltage decreased at the edge, whereas the field enhancement factor was increased at the edge oppositely. This suggests that the screening effect from the high dense CNTs degrades the field emission currents very seriously. Therefore, an optimum pattern design with an appropriate edge-to-edge spacing and the size of CNT arrays, is necessary to maximize the edge emission currents.

Fig. 3(a) shows the height dependence of the tip nanopositioner on the emission currents. The tip position was fixed on top of the edge. The tip height was first maintained at 33 μm. With decreasing the tip height, the emission currents were increased as expected. At a height of 17 μm, however, the current was suddenly dropped. We note that the turn-on field (the starting field of the linear region at the FN plot) remained almost constant up to 22 μm and showed a sharp increase at very close distance of 17 μm, as shown in Fig. 3(b). The inset shows the FESEM images of the CNTs after completion of the \( I-V \) measurements at a height of 17 μm. Some of the protruded CNTs were plucked out by the strong electric fields. The maximum field strength became higher with reducing heights, since the maximum voltage was kept almost constant. The maximum field strength reached about 47 V/μm with a height of 17 μm. At high fields, considerable amount of charges could be accumulated at the ends of each nanotube. Some of the protruded CNTs will feel stronger electrostatic forces by the high fields such that they could be plucked out more easily than other CNTs. This suggests that some protruded CNTs could be a source of the unstable emission. This effect could be reduced by maintaining the anode position far from the cathode.

In conclusion, we have investigated the edge effect of the field emission properties from patterned CNT arrays using a nanomanipulator installed inside the FESEM. We found that both the edge current and the field enhancement factor were significantly improved due to the less screening effect compared to those at the center. We also found that the separation distance between anode and cathode is an important factor in determining the stability and uniformity of the emission current. Our works propose that a high emission current could be obtained by the optimization of edge-to-edge spacing and the size of square arrays at the patterned CNTs, and furthermore, the uniformity could also be obtained by controlling the cathode-anode separation distance.

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References

Calorimetric study of the effect of carbon fillers on the curing of epoxy

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Epoxy is widely used in industrial applications in relation to adhesives, coatings, electronics and aerospace structures. Due to its attractive mechanical and chemical properties, such as excellent bonding ability, high tensile and compressive strengths, good chemical resistance and high heat distortion temperature, epoxy is the dominant matrix material for lightweight polymer–matrix structural composites, such as carbon fiber composites. The superior mechanical and chemical properties of epoxy are due to the three-dimensional network structure that results from the curing process, in which a low molecular weight resin is transformed into a high molecular weight polymer. The interfacial strength between carbon fillers and epoxy resin varies with the surface structure of fillers [1–3]. As a result, the surface structure affects numerous properties, such as the interlaminar shear strength and the impact resistance.

Studies have been reported on the curing behavior of epoxy/carbon filler systems, particularly systems involving carbon nanotubes [4,7], carbon fiber [5,6] and carbon black [4]. It was shown by differential scanning calorimetry (DSC) that the heat of the epoxy curing reaction was higher in the presence of carbon nanotubes than in the presence of carbon black [4], and that the rate of the reaction was increased by surface treatment of carbon black [4–7]. However, DSC also showed that carbon fiber had very small effect on the curing kinetics [5]. Little attention was given to the comparison of the effects of different carbon fillers and different carbon fiber surface treatments on the curing of epoxy. Therefore, this work provides a comparative study of carbon fillers, including carbon fiber, carbon nanofiber and carbon black. In addition, this work addresses the effect of filler surface treatment on the curing process. Understanding the effect of fillers on the curing reactions is valuable for improving and/or optimizing the manufacturing process of epoxy–matrix composites.

Epoxy resin filled with various carbons (carbon fiber, carbon nanofiber and carbon black) was studied. The epoxy resin system consisted of a diglycidyl ether of bisphenol F (DGEBF) (epoxy resin, EPON 862, Shell Chemical Company, Troy, MI) and triethylene tetramine curing agent (EPI-CURE curing agent 3234, Shell Chemical Company, Troy, MI). The molecular structures of the resin and the curing agent are shown in Fig. 1. The resin and curing agent were used in the weight ratio of 100:15.4.

The carbon fiber was obtained by manual chopping of Thornel P-25 continuous pitch-based carbon fiber, which was obtained from BP Amoco Polymers, Alpharetta, GA. The carbon fiber had a density of 1.90 g/cm³, a specific surface area of 0.70 m²/g and a diameter of 11 μm. The length of the chopped carbon fiber was in the range from 2 to 4 mm. As-received and two types of surface-treated fibers were used. The surface treatments were ozone-treatment and activation. The ozone-treatment involved exposure of the carbon fiber to O₃ gas (0.6 vol.% in O₂) at 150 °C for 10 min. Prior to O₃ exposure, the fibers had been washed with acetone and dried at 90 °C for 24 h. The activation of the chopped carbon fiber in CO₂ involved (i) maintaining the carbon fiber