High-Density Short-Height Directly Grown CNT Patterned Emitter on Glass

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Vertically aligned, high-density (4×10^9 /cm^2) carbon nanotubes (CNTs) with an average short height of 1.5 µm were grown directly on a Cr electrode patterned on a glass substrate at a substrate temperature below 550 °C by water-assisted chemical vapor deposition (CVD). Threshold field of the emission of the patterned grown CNT could be tuned with the pattern shape, and it was 1.8 V/µm at 1 µA/cm^2 for the emitter with a hole spacing parameter of S = 20 µm. The stability of field emission of the patterned CNT emitter on glass was confirmed with continuously working more than 24 hours at a pulse current density of 70 µA/cm^2 with the duty ratio of 7.5 %.

Keywords: Carbon nanotube; Field emission; Field emission measurements; Surface structure; Photo lithography; Patterned emitter; Field enhancement effect

I. INTRODUCTION

Carbon nanotubes (CNTs) [1] have attracted considerable attention as a field emitter material for high efficient electron source for field emission devices such as displays and lamps due to their excellent field emission characteristics, chemical stability, and high electrical and thermal conductivities. CNT emitters are generally formed by screen printing method, or directly grown on cathode electrode by CVD process. The screen printing CNT emitters have been investigated by many researchers because they have advantages of low cost and large-area fabrication. Up to date, surface treatments of the screen printing CNT emitters have been attempted to improve the uniformity of emitting points and to obtain high density of emitting standing CNTs [2]. Even if many improvements for screen printing CNT emitters have been attempted, some issues such as inhomogeneity of emitting point caused by agglomeration of CNT paste still remained for screen printing CNT emitters. Plasma or thermal CVD growth [3, 4] of CNTs at low temperatures are possible methods to form emitters directly on cathode electrode on glass substrate.

It is well known that density control of CNTs is quite important to achieve high current density and stable emitters because the high-density CNTs cause shielding effect, so that the electric field and the emission current will be reduced on the tips of high density CNTs [5]. Katayama et al. reported [6] that long (> 100 µm) CNT pillars consisted of high density (>10^10 CNTs/cm^2) with a spacing to height aspect ratio of 2 could reduce the threshold field of the field emission drastically to below 0.4 V/µm at 1 µA/cm^2 in which the electric fields were enhanced on the edges of the CNT pillars [7, 8]. But it is difficult to form these long CNT pillars on glass substrate because the growth temperature should be higher than 700 °C for the CNT pillars. And also it is difficult to form triode structure for the control of emission current using such a tall pillar shape emitter.

To overcome these issues and to achieve highly-stable high efficient emitters, following features are considered required. (1) Low temperature formation of short-height CNTs utilizing glass substrates, (2) direct growth of uniform and high-density CNTs without agglomeration, (3) pattern shapes of cathode electrode to avoid shielding effect of the high density CNTs. In this report, patterned emitters were fabricated using directly grown, high-density and short-height CNTs on patterned cathode electrodes by thermal CVD utilizing glass substrates. The IV characteristics, uniformity and stability of the field emission of the patterned emitters dependent on pattern shapes are discussed.

II. EXPERIMENTAL

CNT emitters on a patterned cathode electrode were fabricated with the following process (Fig. 1). A cathode electrode of Cr metal layer with a thickness of 120 nm was deposited on a 4 inch glass substrate by RF magnetron sputtering method. Fe/Al multi-layer catalyst films were utilized to form the vertically aligned high density CNTs [9, 10]. The glass substrates with the Cr metal layer were set in a magnetron sputtering chamber and the chamber was evacuated to below 4×10^-4 Pa. The Al buffer layer and Fe catalyst layer were deposited continu-

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FIG. 1: Process flow and SEM image of directly grown CNT patterned emitter on Cr electrode utilizing glass substrate.
ously using the RF magnetron sputtering system without substrate heating at an Ar sputtering pressure of 1.8 Pa. The thicknesses of the Al and the Fe catalyst layers were 3 and 2 nm, respectively. The Fe/Al and the Cr metal layers were photo-lithographically patterned onto the cathode with holes using H₂PO₄ based commercial Al etchant and Cl etchant (H₂SO₄:30% + H₂O₂ + HClO₄), respectively. The diameters of the cathode holes were 80 μm. CNT emitters with different pattern shapes were prepared to confirm the pattern shape effects on the field emission properties. The distance between cathode holes (spacing parameter: S) was varied from S = 20 μm to 160 μm. CNT emitters without holes on the cathode were also prepared to compare with the patterned emitters. CNT emitters of patterned shapes of S = 40, 160 μm and a flat CNT emitter were deposited at the same time in the CVD chamber. An additional CNT emitter with a pattern shape of S = 20 μm was prepared under the same conditions described above.

Thermal CVD were carried out at 490, 510, or 550 °C for 30 min using the glass substrate with the Fe/Al catalyst films on the patterned Cr cathode electrode. Carbon source was acetylene (C₂H₂) gas with a flow rate of 200 sccm. A small amount of water vapour is known to reduce the deposition of amorphous carbon on the catalyst particles and to enhance the growth rate of CNTs (Super growth) [11]. During the CNT growth, an additional water vapour was introduced with He bubbling gas into the CVD chamber.

Morphology of CNT emitters grown on electrodes, including growth height and vertically alignment, were observed by a Scanning Electron Microscope (SEM, Hitachi, S-3000N). I-V characteristics and stability of emissions of the directly grown CNT emitters were measured in diode configuration using a series resistor of 100 kΩ in the vacuum pressure below 1×10⁻⁴ Pa. Spatial uniformity of the emitters were observed during the emission characteristic measurements using a commercial available green powder phosphor formed on ITO anode glasses. The electric fields on the pattern shaped carbon nanotube emitters were calculated in diode configuration using a finite element method program (AMAZE, Field Precision LLC.). The simulation parameters for the field calculation are cathode to gate distance of 2 mm, and anode bias voltage of 10 kV.

III. RESULTS AND DISCUSSION

Figure 1 shows SEM images of the CNTs directly grown on the patterned cathode electrode utilizing the glass substrate at a growth temperature of 550 °C. Vertically aligned CNTs with an average short height of 1.5 μm were uniformly formed with a density of 4×10⁹ CNTs/cm² on the patterned cathode electrode area of 65×65 mm². Figure 2 presents the effect of the H₂O vapour flow rate on the CNT growth height at various temperatures of 550, 510 and 490 °C. The addition of H₂O vapour at 0.75 to 1 sccm increased the growth height of the CNTs. Low density and randomly oriented CNTs were observed on the CNTs grown without the addition of H₂O vapour. It is noted that the growth orientation of the CNTs was changed from random to vertical by the addition of H₂O vapour in CNT growth, which is considered caused by the effect of the high density of CNT growth. It was found that the growth temperature of the vertically aligned CNTs decreased to below 510 °C by the addition of H₂O vapour at a flow rate ratio of C₂H₂/H₂O = 200/1. The addition of H₂O vapour was considered to generate OH radicals on the Fe catalyst which removed amorphous carbon components on the Fe catalyst and kept the catalyst surface clean even at a low temperature below 510 °C.

The peak position of the growth height shifted to lower H₂O flow rate for the higher growth temperature of 550 °C. The effect of excess water beyond optimum flow rate on the CNT growth [12] is oxidizing the iron particles resulting in poisoning of the CNT growth. In the temperature range of 490 – 550 °C, higher temperature might easily cause the oxidation of the iron catalysts by the H₂O gas. The growth height of the CNT forest is also affected by both of the density of CNTs and the length of individual CNTs. Further characterizations, such as diameter and density of CNTs, are required to clear the growth mechanism of the water-assisted CNT in the low temperature region of 500 – 600 °C.

I-V characteristics of the field emission were measured for the patterned CNT emitter, grown at 550 °C, with the cathode hole spacing of S = 40 μm using a series resistor of 100 kΩ in the vacuum chamber at a vacuum pressure below 1×10⁻⁴ Pa. The cathode to anode gap was kept at 2 mm. Figure 3 shows an I-E plot and a Fowler-Nordheim plot of the field emission from the patterned emitter. The apparent threshold electric field to obtain field emission

FIG. 2: CNT growth height at various growth temperatures dependent on additional H₂O flow rate during CVD process.

FIG. 3: Emission characteristics and Fowler-Nordheim plot of directly grown patterned CNT emitter of spacing parameter S = 40 μm. The cathode to anode gap was 2 mm.
with a current density of $1 \mu A/cm^2$ was 3.0 V/\mu m for the patterned emitter with $S = 40 \mu m$. The electric field on the patterned emitter with holes of $S = 40 \mu m$ were calculated for the diode structure with cathode to anode gap of 2 mm and applied anode bias voltage of 10 kV. Figure 4 presents the calculated distribution of the electric field on the patterned emitter. The electric field at the flat surface area on the cathode electrode was about 5 V/\mu m. On the other hand, the electric fields exceeded 7.5 V/\mu m at the edges of the cathode holes. The calculation showed that the field enhancement at the edges of the cathode holes could reduce the threshold field of the field emission.

The stability and the uniformity of the field emission current were observed under a diode configuration with phosphor anode plate. The distance between the cathode and the anode was kept at 0.75 mm and the applied pulse bias voltage on the anode electrode was 6 kV at 7.5 % duty ratio. Stable emission current of 70 $\mu A/cm^2$ within 5% fluctuations in current were observed over 24 hours for the patterned CNT emitter as shown in Fig. 5. Cathode luminescence (CL) images observed at 3, 6, and 24 hours were enhanced at the edge of cathode hole.

Electric field enhancement on patterned emitters were calculated for various emitter shapes with the spacing factor $S$ to design high efficiency emitters. Figure 6 shows the distribution of the calculated electric fields on the surface of the CNT patterned emitter and cross-sectional view of the electric fields. The electric fields were enhanced at the edges of the cathode holes. The local electric field increased to 8 V/\mu m with the decrease of the cathode hole spacing to $S = 20 \mu m$.

Figure 7 shows I-V curves of the patterned emitters grown at 550 °C with the cathode hole spacing patterns of $S = 20, 40$, and 160 $\mu m$ comparing with the flat CNT emitter without holes. The flat CNT emitter without cathode shape patterning showed apparent high threshold field of 12 V/\mu m to obtain the anode current density of 1 $\mu A/cm^2$, which was caused by the shield effect of the high density of vertically aligned CNTs ($4 \times 10^9$ CNTs/cm$^2$). On the contrary, the threshold fields decreased with reducing the cathode hole spacing $S$. It was confirmed that the spacing of the cathode holes could reduce the threshold electric field of the emissions. A low threshold field of 1.8 V/\mu m at 1 $\mu A/cm^2$ was achieved for the fine patterned emitter of $S = 20 \mu m$. The uniformity of the emissions was also improved with reducing...
cathode hole spacing. Figure 7(b) shows CL image of the CNT patterned emitter with the cathode hole spacing of $S = 20 \mu$m. The density of the emission point increased as compared with the emitter of larger cathode hole spacing of 40 $\mu$m shown in Fig. 3.

The reason for the low threshold voltage and the long lifetime of the pillar shaped vertically aligned CNT arrays was considered to be that the field enhancement effect on the CNT pillar edges could reduce the threshold voltage and the high density CNTs could reduce the emission current per one CNT tube\[7\]. The fine patterned high-density vertically aligned short-height (< 2 $\mu$m) CNT emitters, directly grown on the cathode electrode on glass substrate, also had the feature of the field enhancement effect on the cathode pattern edges.

IV. CONCLUSION

Short-height (1.5 $\mu$m), vertically aligned, and high-density ($4 \times 10^9$ CNTs/cm$^2$) CNTs were grown directly on cathode electrode utilizing glass substrate below 550 °C by water assisted CVD. Patterned CNT emitters on glass were formed using patterned catalyst on cathode electrodes. The threshold field of the emission of the patterned grown CNTs could be tuned with pattern shape of cathode, and a low threshold field of 1.8 V/µm at 1 $\mu$A/cm$^2$ was achieved for the fine patterned emitter with the hole spacing of $S = 20 \mu$m. The field emission of the patterned CNT emitter on glass was stable over 24 hours within 5% fluctuation at a pulse current density of 70 $\mu$A/cm$^2$ (duty ratio of 7.5 %). The patterned emitter on glass using the short-height, high-density, vertically aligned CNTs will contribute to realize high reliable and high efficient field emitters for various application field.

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