Selective Formation of Carbon Nanotubes and Its Application to Field-Emitter Arrays

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Abstract—At room-temperature ambient, carbon nanotubes (CNTs) were selectively synthesized on each bridge of the microheater array (MHA) formed on a glass substrate. Both multiwalled (MW) and single-walled CNTs could be formed by controlling the MHA temperature, which was confirmed from Raman spectroscopy. By incorporating the selectively grown MW CNTs into the lateral-gated field-emitter arrays, high current density of electron emission was observed with low device leakage.

Index Terms—Carbon nanotubes (CNTs), field-emitter arrays (FEAs), microheater arrays (MHAs), selective synthesis.

I. INTRODUCTION

CARBON nanotubes (CNTs) have achieved noticeable progress over the last decade owing to their unique electrical, mechanical, and optical properties [1]. Many researchers have developed CNT-based electronic devices, such as field emission displays [2]–[4], field-effect transistors [5], and different types of sensors [6]. To realize these applications in large scale, low-temperature synthesis of the high-quality CNTs at the desired locations on a glass substrate is essential. Local synthesis of CNTs by resistive heating of the catalyst on a bridge-type microheater is reported [7], [8]. This method would enable the direct integration of CNTs even at room-temperature ambient. Moreover, depending on the purpose, vertical or lateral growth of the multiwalled (MW) or single-walled (SW) CNTs could be realized. However, all these attempts are limited to or based on a single-level microheater, which is difficult to apply for large-scale devices including flat panel displays.

Recently, we have developed the microheater array (MHA) on a glass substrate, which is consisted of a number of bridge-type heater units connected in series [9]. This letter reports selective synthesis of MW or SW CNTs using the MHA. By incorporating selectively grown MW CNTs to the lateral-gated field-emitter arrays (FEAs), the field emission characteristics are also investigated.

II. EXPERIMENTS AND RESULTS

Fig. 1 shows the fabrication process of the MHA. By plasma-enhanced chemical vapor deposition (PECVD) and sputtering, 3-μm-thick SiO₂ and 1-μm-thick molybdenum (Mo) layers were successively deposited on a glass substrate, respectively [Fig. 1(a)]. The MHA is formed through the “heater pattern,” shown in Fig. 1(b), followed by isotropic wet etching of the SiO₂ to form insulating columns and bridges [Fig. 1(c)]. The MHA consists of a number of microheater units connected in series. A microheater unit is a suspended bridge heater, both ends of which are supported by two insulating columns as marked by dotted rectangle in Fig. 1(c). With serial and parallel extension of the heater pattern, MHA can be readily fabricated in large scale since the fabrication process of the MHA is compatible to that of liquid crystal displays. The length (l) and

Fig. 1. Fabrication process of the MHA. (a) PECVD of SiO₂ and sputtering of Mo and (b) Mo heater patterning, and (c) isotropic wet etching of SiO₂ to form insulating columns and bridges.
the width \((w)\) of the bridge were fixed to be 40 and 10 \(\mu m\), respectively. As a catalyst layer for CNT growth, aluminum and invar (Fe–Ni–Co alloy) were successively deposited by electron beam evaporation with thicknesses of 5 and 2 nm, respectively. The catalyst layer is deliberately not patterned to make it become a temperature indicator during the CNT synthesis.

The synthesis process is basically the same as that of [8]. A glass substrate with the MHAs was placed within a quartz tube and connected to an exterior dc power supply through an electrical feed-through. The quartz tube was evacuated to the base pressure of 7.5 \(\times\) 10^{-3} torr at room temperature, and then the MHA is resistively heated to reach the designated temperature. Finally, a gas mixture of 200 sccm C\(_2\)H\(_2\) and 500 sccm Ar is inserted for 10 min. During the process, the measured substrate temperature by thermocouple was 70 \(\pm\) 80 \(\degree\)C. Current (\(I_{\text{MHA}}\))–voltage (\(V_{\text{MHA}}\)) characteristics of the MHA under various pressures were measured in the same C\(_2\)H\(_2\)/Ar ambient. Glowing from the hot MHA was monitored by charge-coupled device (CCD). This synthesis method can be implemented both to undergated and lateral-gated FEAs, where MHA works as a cathode electrode. The former can be used for display applications including FEDs since \(X\)–\(Y\) matrix addressing is available [4], whereas the latter is applicable to flat-light lamp. Raman spectroscopy with the laser excitation wavelength of 633 nm was performed to estimate whether the synthesized CNTs were SW or MW.

Estimating the temperature on the operating MHA is not straightforward due to its size and inherent temperature nonuniformity. Such micrometer-scale temperature distribution may be measured by detecting the emitted radiation spectra from the MHA. However, this method may be impractical to monitor in situ temperature of MHA (\(T_{\text{MHA}}\)) during the real CNT synthesis since implementing additional optical components to the growth system is not trivial. We obtained in situ \(T_{\text{MHA}}\) using the following method, which is based on the assumption that the resistance of a specific metal is only a function of its temperature. First, \(R_{\text{MHA}}/R_0\) values for various temperatures up to 300 \(\degree\)C are measured on a hot plate, where \(R_{\text{MHA}}\) and \(R_0\) are the resistances of the MHA at the specific temperature and at the reference temperature of 50 \(\degree\)C, respectively. The empirical equation is obtained as

\[
T_{\text{MHA}}(\degree\text{C}) = 536 \times \frac{R_{\text{MHA}}}{R_0} + 95 \times \left(\frac{R_{\text{MHA}}}{R_0}\right)^2 - 581.
\]

Then, the relationships of \(R_{\text{MHA}}\) (= \(V_{\text{MHA}}/I_{\text{MHA}}\)) versus \(I_{\text{MHA}}\) are determined from the \(V_{\text{MHA}}\) versus \(I_{\text{MHA}}\) curves [Fig. 2(a)]. Finally, by putting \(R_{\text{MHA}}\) values into above equation, \(T_{\text{MHA}}\) versus \(V_{\text{MHA}}\) curves are obtained [Fig. 2(a)]. Since this method can only estimate the overall temperature, the local temperature information was supplemented by the corresponding intensity distributions of CCD glow images. A CCD image corresponding to the point “B” marked in Fig. 2(a) is shown as an example. The temperature is the maximum at the center of each bridge, and gradually decreases as going to the region just above each insulating column. This is due to heat transfer by heat conduction. The amount of heat conduction is affected by the heater geometry, particularly, by the diameter of insulating columns. Moreover, heat transfer is occurred by heat convection, which is known to become significant at higher pressure levels. With fixed heater geometry, the power consumption (\(I_{\text{MHA}} \times V_{\text{MHA}}\)) to reach the designated \(T_{\text{MHA}}\) increases with increasing pressure as shown in Fig. 2(a). It should be noted that the overall temperature of the MHA can reach stably up to 1200 \(\degree\)C without any breakage or melting of the glass substrate.

Fig. 2(b) and (c) shows the morphologies of CNTs formed at \(T_{\text{MHA}}\) of 550 \(\degree\)C [the condition “A” in Fig. 2(a)]. It can be seen clearly that CNTs were selectively grown and vertically well aligned on each bridge [Fig. 2(b)]. The height of the CNTs at central regions of the bridges is about 9 \(\mu m\), and gradually decreases near the insulating column [Fig. 2(c)], which is consistent with the temperature distribution. These CNTs were bottom grown [inset of Fig. 2(c)] and identified as MW CNTs by Raman spectroscopy [Fig. 2(d)]. When \(T_{\text{MHA}}\) reaches 850 \(\degree\)C [the condition “B” in Fig. 2(a)], the typical Raman spectrum of SW CNTs was obtained [Fig. 2(e)]. The radial breathing mode (RBM) peaks were clearly detected. In addition, high
peaks intensity ratio of $G$-band relative to $D$-band indicates that purity of the synthesized SW CNTs is quite high. The peak analysis of RBM under the excitation wavelength suggests that metallic and semiconducting nanotubes coexist with an average diameter larger than 1.2 nm. The temperature just on or very near the catalyst seems to determine mainly the growth kinetics of CNTs irrespective of the low-ambient temperature.

Such selectively grown CNTs were incorporated into the FEAs with a lateral gate [Fig. 3(a)], where the MHA work as a cathode electrode. In Fig. 3(b), the emission current ($I_e$) was 1 mA at the gate voltage ($V_g$) of 180 V, which corresponds to high current density of 1.8 A/cm$^2$. For calculating the emission current density, the used area value was the total bridge area. The bridge shape cathode might be desirable form for high-current density device. Using a plot of $\ln(I_e/V_g^2)$ versus $1/V_g$ (left inset of Fig. 3(b)) and Fowler–Noordheim formula, the field-enhancement factor is calculated as 360 on the values of $1/V_g$ between 0.006 and 0.0075 which were determined by procedure in [10]. Right inset of Fig. 3(b) shows that the light emission pattern on the phosphor is reproduced following the line-shaped emitters. Nonetheless, brightness uniformity still needs to be improved. We assume uniform temperature distribution of MHA is crucial to obtain uniform CNTs [Fig. 3(c)], which, in turn, possibly determines the eventual display uniformity with the help of resistive layer.

Considering the highly dense CNT morphologies [Fig. 3(d)], and [11], it is assumed the aforementioned calculated value of field-enhancement factor seems to be reasonable. The gate leakage current was measured as less than 1 μA even after the CNT synthesis. This triode-type field emission device might also be used as an electron source for the backward-wave oscillators requiring high current density.

### III. Conclusion

CNTs were selectively formed at room-temperature ambient using MHA. The overall temperature of the MHA can reach stably up to 1200 °C without any breakage of the glass substrate. The relevant growth temperatures of the MHA were 550 °C and 850 °C for MW and SW CNTs, respectively. The MW CNTs were incorporated to the lateral-gated FEAs, and emission current density of 1.8 A/cm$^2$ was obtained. We expect the MHA devices might be utilized for other nanoelectronic devices on large-scale glass substrates which require high-temperature processes including gallium nitride nanowire synthesis.

### REFERENCES


