Selective Growth of Carbon Nanotubes and Its Electron Emission Properties

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Abstract

We have grown well-aligned carbon nanotube arrays on the selective areas by plasma enhanced chemical vapor deposition at the substrate temperature of 580 °C. The selective areas for CNTs growth can be defined by photo lithography technology. The CNTs are uniformly grown on the areas regardless of island diameters. Electron emission currents were measured in a vacuum with a diode structure at room temperature. Uniform electron emission currents were achieved with 40 μm island spacing with 5μm island diameter.

1. Introduction

Carbon nanotube (CNT) has been highlighted as a candidate of field-emission emitters and vacuum nanoelectronic devices.[1,2] Since the discovery of carbon nanotubes, the structural, electrical, mechanical, electromechanical, and chemical properties have been investigated to explore the applications of the materials.[3]

On the other hand, various methods of CNT growth have been proposed to improve its electron emission property[4]. In this work, we report a novel selective growth technique to control the position and density of CNTs. We can control the position of CNT growth and its area. The results show good uniformity over large area with various island pattern dimension, such as from micrometer to millimeter scale.

Figure 1 shows the process flow of selective growth of CNTs using the protection layer. Previously, we have reported the controlled density and vertically aligned growth of CNTs on substrate with barrier layer by using a triode dc-PECVD system.5 In this work, we reported the selective growth method with a protection layer. The protection layer was used to protect CNTs growth on unselected areas. To make selective area, the protection layer was coated and patterned by photolithography process. After then, the substrate was formed under vacuum with high temperature condition. The Table 1 summarized the forming condition of protection layer and growth condition of CNTs

Table 1. Process parameters for protection layer forming and CNTs growth

Forming condition	
Substrate temperature	580 ℃
Flow rate	50 sccm
Time	30 min

Growth condition	
Substrate temperature	580 ℃
Feed gas	C_2H_2 / NH_3
Pressure	2 Torr
Growth time	15 min

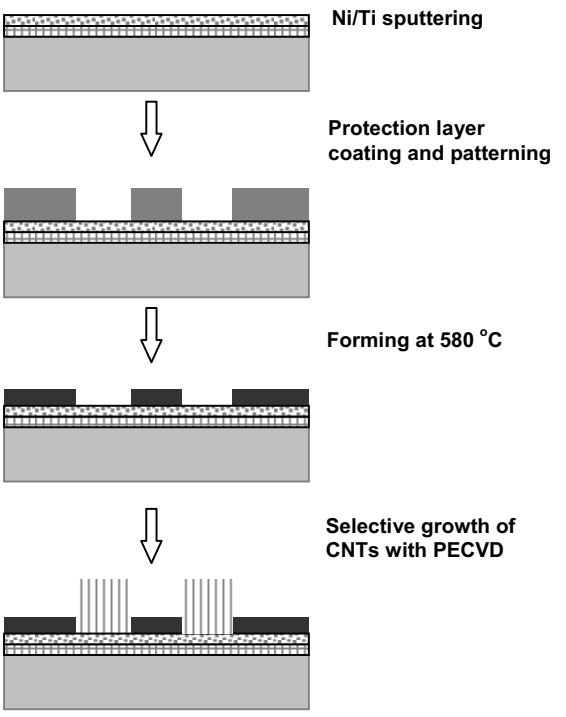

Figure 1. Process flow of selective growth of CNTs using the protection layer

The growth of CNTs was carried out with a triode dc-PECVD, with a mesh grid being placed 10 mm above the substrate holder electrode with +300 V bias.[6,7]. The substrate electrode was maintained at -600 V with the top electrode grounded, and the spacing between the two electrodes was 30 mm. The Ti barrier metal of 30 nm and the Ni catalyst of 30 nm were deposited by RF magnetron sputtering. The growth area was opened by photolithography of protection layer. The NH_3 plasma pretreatment time was 3 min for the granulation of the Ni catalyst layer prior to CNT growth. Acetylene (C_2H_2) and ammonia (NH_3) gases were used for CNT growth. The total gas pressure during the growth was kept to be 2 Torr and the CNT growth time was 15 min. The growth temperature was maintained at 580°C.

A field-emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM) was used to characterize the CNTs. Electron emission currents and light emission were measured in a vacuum of 1 x 10^{-6} Torr with a green-phosphor-coated indium-tin-oxide (ITO) anode placed 150 μm above the cathode electrode.

2. Results

Figure 2 shows the SEM images of the CNTs grown with various patterns by using selective growth technology. The SEM images show the array of CNT line with regular pattern (a), rectangular (b to d), some characters (e) and disc-shape (f). The CNTs show vertically aligned and very good selectivities.

Some CNT samples were removed from the substrate and positioned directly on a TEM copper grid for TEM analysis. The TEM image of the CNTs are shown in Figure 3. TEM revealed a multiwalled structure of the CNTs and can find holes inside of the tube. The diameter of the CNTs are around 70 nm to 120 nm. The Ni catalysts can be seen on the top of tubes.

The electron emission properties of the CNTs were measure with a diode structure device. The CNT arrays for 5 μm disc-shape island pattern with various island pitches were grown. The electron emission

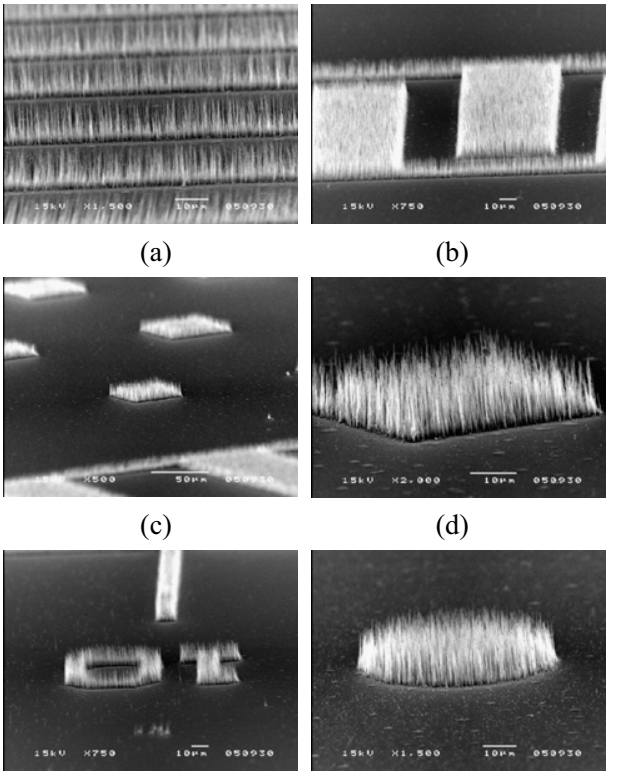

Figure 2. Scanning electron microscope images of CNTs grown with various patterns of (a) line, (b) and (c) rectangle, (d) magnified image of (c), (e) text, (f) disc-shape.

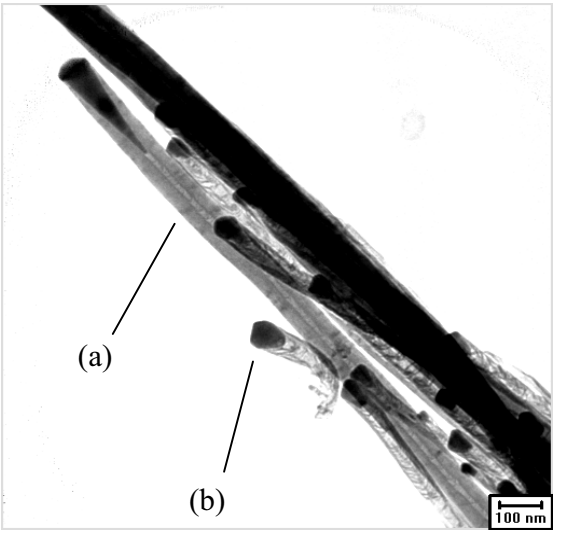

Figure 3. Transmission electron microscopy image showing, (a) hole in the tube and (b) catalyst Ni particles on the tube tip.

current density and its Fowler-Nordheim plot with various disc-shape island pitch are measured.

Figure 4 shows electron emission characteristics of selectively grown CNT arrays with pitches of 10, 20, 30, and 40 μm. The electron emission currents increase with increasing island spacing up to 30 μm. The electron emission current of 40 μm pitch sample is similar with 30 μm one. The increase of electron emission current appears to reduce screen effects[8,9]. The length of CNTs are around 10 μm. A neighbor CNTs within 20 μm distance will be affected by screen field, result in reduced electron emission of the shorter distance pitch. The electron emission current of 40 μm island spacing sample showed a current density of 1.33 mA/cm^2 at 11 V/μm field, and turn on field of 7 V/μm at 1 μA emission current. The turn on field of 7 V/μm is higher than that (~ 3 V/μm) for conventional CNTs. It should be studied on the origin of the turn on field.

Figure 5 shows the Fowler-Nordheim plot of the emission current for various island pitch distance. The plot indicates the emission current is governed by a tunneling process. The field enhancement factors of 40 μm spacing sample shows 2.5 x 10^6. For the calculation, the work function of the CNT was assumed to be 4.5 eV.

Figure 6 show the light emission images from the phosphors using the CNT emitters with 10 μm island pitch (a) and 40 μm island pitch (b). The emission site density of the 40 μm spacing CNTs is much higher than 10 μm and uniform light emission.

3. Conclusion

Selective positioning of CNTs is one of the key points for FED application. The positing and area of the CNTs can be controlled by protection layer

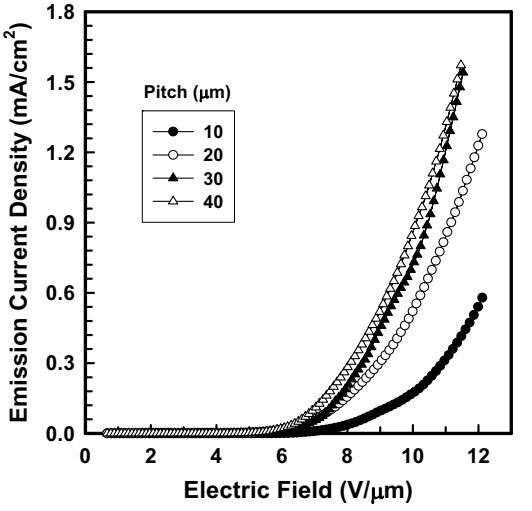

Figure 4. Electron emission characteristics of selectively grown CNT arrays with island pitch of 10, 20, 30, and 40 μm.

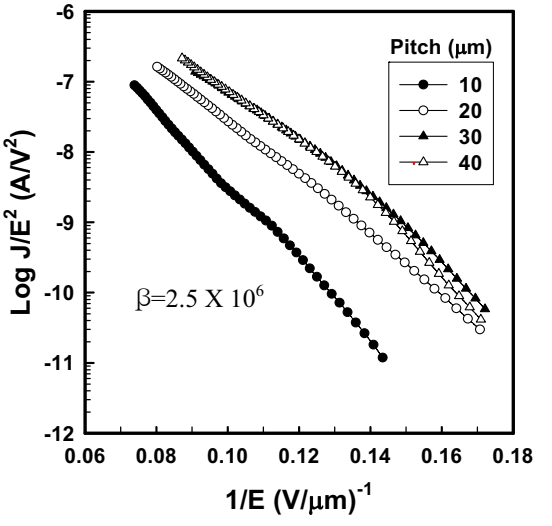

Figure 5. Fowler-Nordheim plots with island pitch of 10, 20, 30, and 40 μm.

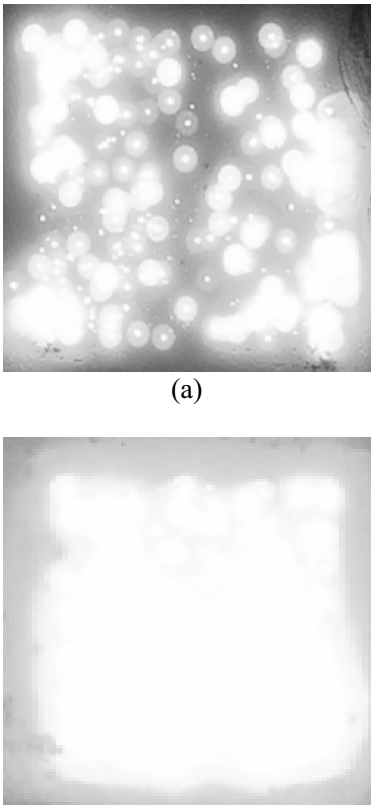

Figure 6. Light emission images of the diode-type devices of CNT emitters using disc-shape pattern. The pattern pitch between 5 μm disc is 10 μm (a) and 40 μm (b).

patterning and forming. The proposed method is very simple and can be applied to make large area CNT arrays on glass. The uniform electron emission can be achieved by controlling the island pattern pitch to 40 μm for 10 μm length CNTs on 5 μm disc-shape island patterns.

The electron emission current of 40 μm island pitch sample showed a current density of 1.33 mA/cm^2 at E = 11 V/μm, and turn on field of 7 V/μm at 1 μA emission current. The novel CNTs grown technique can be applicable to electron emitters for nano-electronics devices.

4. Acknowledgements

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