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低溫一維奈米材料之製作及熱場發射特性之研究(1/3)

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計畫主持人：陳家富

計畫參與人員：徐振航，陳光中，洪淙琦，陳宜輝，莊方慈

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國科會專題研究計畫成果報告

NSC Project Reports

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研究內容

在場發射的應用上，奈米碳管具有許多優異的性質，例如能提供高的電流密度，與相對低的起使電場。然而由於屏蔽的效應，致使奈米碳管優異的性質無法完全發揮。研究中利用印刷的方式製備電極何觸媒，並利用化學氣相沈積法在低於 500℃的條件下成長奈米碳管。由實驗結果可得到均勻分佈的碳管。實際的場發射量測也可證明具有良好地場發射性質。

除此之外，利用微波電漿話學氣相沉積系統，進一步開合成出相較於奈米碳管有著更好場發射效能的奈米碳結構材料；基於低電子親和力，其寬能帶的特性已證實是適合作為場發射的材料。實驗當中也針對不同組成的奈米碳尖錐材料進行相關的量測並做比較。

Abstract

Carbon nanotubes (CNTs) have superior properties such as high current density and relative low threshold field in the field emission applications, however, the potential was not totally elaborated due to screening effect. In this report, in order to combine advantages of screen printing processes and CVD processes, both catalyst and electrodes were screen printed; while CNTs emitters were uniformly grown on electrodes below 500℃ by CVD.

Also, the chromium carbide on top of carbon nanotips forms a new kind of high aspect ratio nanomaterial which may be suitable for field emission application. The wide band gap nature of chromium carbide greatly affects the field emission properties. Wide band gap materials have been identified suitable for field emission due to their low electron affinities, as well as their thermal chemical and mechanical stability. In this report, field emission characteristics of the two kinds of nanotips are presented and electron emission process is discussed.

A. Low-temperature CVD growth of carbon nanotube for Field Emission Application

Introduction

At present, using CNTs paste by screen-printing technology has a relatively low resolution and needs a surface rubbing technology or other activated steps to enhance field emission properties [9]. For CVD method, it can directly grow CNTs on the predefined catalyst layer without the following activated steps and has high yield and uniformity. However, the CNTs growth temperature is limited below 550℃ to avoid glass substrate deformation. In the previous works [10-12], semiconductor processes, such as sputtering or thermal evaporating are commonly used to pattern catalyst metals on cathode electrodes. It is well-known that the cost of the semiconductor processes is much higher than screen-printing processes. Therefore, development of the direct CNTs growth on glass substrates at low temperature by a low cost technology will play an important role in practical FED applications. In order to combine advantages of screen printing processes and CVD processes, both catalyst and electrodes were screen printed; while CNTs emitters were uniformly grown on electrodes below 500℃ by CVD.

Experimental details

For preparing the catalysts, two solutions were prepared individually and then well-mixed. The first solution was 100 ml anhydrous alcohol (Ethyl alcohol) with 29g $Ni(NO_3)_2 \cdot 6H_2O$, while the second solution was made by mixing 50 ml TEOS and 50 ml anhydrous alcohol. Next, the above two solutions were mixed to be Ni/TEOS alcohol solution under stirring for 24 hr.

The Ni/TEOS alcohol solution was then well-mixed with conductive Ag powders, frit ,and organic vehicles by using ball mill and three-roller mill to make a printable paste. Then the paste was printed on the soda-lime glass substrate as a cathode. Another commercial Ag paste was printed next to the cathode line as a gate. After printing the Ag electrode, we removed organic solvents at 400℃ for 2 hr and sintered frit at 560℃ for 15 min. The geometric sizes of cathode and gate lines were ~130 μm width with ~5 µm thickness, and the space between the cathode and gate line was ~90 µm.

After sintering, the sample was etched by 0.7 wt% HNO_3 for 20 min to clean the surface impurities and glass/oxide covered on Ni. Then the sample was loaded into a thermal CVD quartz chamber and heated to a synthesis temperature in the range of 420-480℃. The reduction step proceeded under H_2 and Ar atmospheres for 20 min, followed by the CNTs growth step under H_2 (100 sccm), Ar (500 sccm), and acetylene (C_2H_2) (25 sccm) atmospheres for 10 min.

The morphologies and structures of CNTs were observed by scanning electron microscope (SEM, Hitachi S-4000) and optical microscope (OM). The field emission behavior of CNTs was characterized in the diode and triode method, with a phosphor-coated ITO glass as anode. The spacer thickness is 100μm for diode measurement and 4.8 mm for triode measurement, respectively. The current-voltage characteristics were measured using Keithley 237 under 10^{-6} Torr.

Results and Discussion

The surface morphologies of catalyst-Ni after hydrogen reducing treatment is illustrated in **Fig. 1**, showing that Ni nanoparticles were formed after 20 min treatment. It is well known that H_2 provides a reducing and activating environment for the catalytic nanoparticles and such catalytic seeds are suitable for CNTs growing at low temperature [13,14].

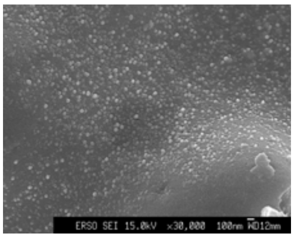

Figure 1. Surface morphologies of catalyst-Ni after hydrogen reducing treatment

Figs. 2 show the SEM images of CNTs grown at four different temperatures (420, 440, 460, 480℃). It can be seen that the lengths of CNTs increased with the increasing of the growth temperature. Compared to the 440℃ grown CNTs, the 420℃ grown CNTs appear shorter and thinner, and there are also carbonaceous particles on the Ag surface. The CNTs do not form in our system when the growth temperature is lower than 420℃. This is attributed to insufficient growth kinetic energy at the lower growth temperature [15]. The CNTs grown over 440℃ appear longer and denser relatively and the average lengths are over 3µm, as shown in **Fig. 2b** to **2d**. The CNTs synthesized in this study seemed to be curly and highly defective [12,16,17]. This is suggested that the growth temperature is below 500℃, which is relatively lower than other researches such as arc discharge or CVD methods [1, 18].

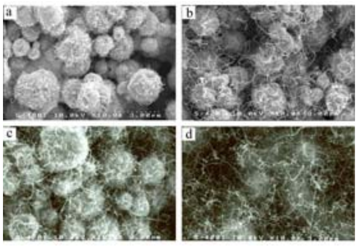

Figure 2. Surface morphologies of CNTs grown at (a) 420, (b) 440, (c) 460, and (d) 480℃ for 10min with a C_2H_2 flow rate at 25 sccm, H_2 flow rate at 100 sccm, and Ar flow rate at 500 sccm

The emission current was measured in the vacuum chamber under 10^{-6} Torr. Fig. 3 shows the emission curves for CNTs growing at (a) 420℃, (b) 440℃, (c) 460℃, and (d) 480℃. A turn-on field is defined as the applied electric field to drive an emission current density of 10 μA/cm^2. The field values for these four samples were (a) 9.86, (b) 5.71, (c) 4.70, and (d) 3.85 V/μm. It can be seen that the turn-on field value decreased with the increasing of the growth temperature. The CNTs grown at 480℃ begin to emit electrons at a lower electric field than other CNTs grown at lower growth temperature, indicating that the emission properties of CNTs depends on the growth temperature. At higher temperature, carbon atoms have enough driving force to diffuse, and thus formed more perfect structure and longer tube, which would eventually affect the emission properties of nanotube. It can be also observed that the CNTs grown at 480℃ show longer and "clean" surfaces relatively, as shown in **Fig. 2d**. Compared to the emission current density of 440℃ grown CNTs, the 420℃ grown CNTs was detected a little emission current at the same electric field which was due to a small amount and higher defective nanotubes, relatively, as shown in **Fig. 3** [19]. The inset in **Fig.3** shows Fowler-Nordheim (F-N) plot of the CNTs grown at 480℃ which indicates that field electron emission was intrinsically driven by electric field [20]. The extremely uniform and bright diode emitting image (over 500 nits) of the anode (coated by the green phosphor) for the CNTs grown at 480℃ at the electric field of 5.5 V/μm was shown in **Fig. 4**.

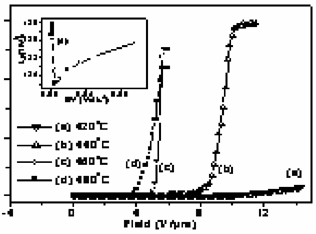

Figure 3. Field emission curves for CNTs growing at different temperatures (The insert is the Fowler-Nordheim plot at 480℃ growth temperature)

Figure 4. Emission image at applied field 5.5 V/μm for diode testing

Fig. 5 shows the obtained current-gate voltage characteristics of the planar triode device [21] (the CNTs grown at 480℃) under a constant anode voltage of 1100 V. The cathode and gate lines were ~130 μm width, and the space between the cathode and gate line was ~90 μm, as shown in Fig. 6. Most of electric current was introduced toward the anode at gate voltage over 300 V. The ratio of anode and gate current was much lower than that expected at the gate voltage 400 V. It is resulted from non-uniform emission behaviors of the CNTs on cathode. The CNTs at the edge of the cathode get stronger electric field (originating from the cathode geometric effect) than those on the top of cathode.

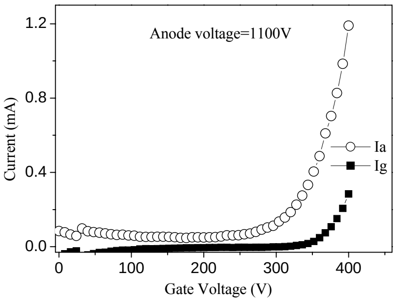

Figure 5. Current-gate voltage characteristics of the planar triode device under a constant anode voltage of 1100 V

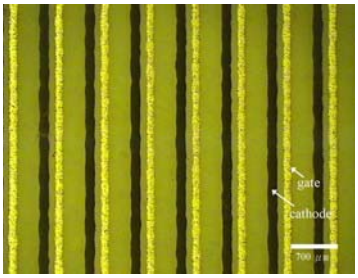

Figure 6. OM image of cathode electrodes with growing CNTs and gate electrodes

High electric field introduces the leakage current from cathode to gate for this planar triode structure. Even though the leakage current was occurred, the planar triode emission image of the anode (coated by the white phosphor) for the CNTs grown at 480℃ was observed with uniform electron emission current and high brightness (no less than 500 nits), as shown in **Fig. 7**.

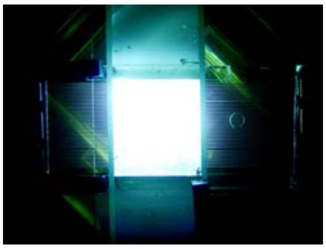

Figure 7. Emission image at anode voltage of 1100 V and gate voltage of 400 V for triode testing

Conclusion

In conclusion, CNTs with superior field emission properties (uniform emission and high brightness) are synthesized under 500℃ by CVD growth on the thick-film constructed cathode structures. Although gate current leakage phenomenon can not be avoided in this work, the field emission results of diode and triode measurements demonstrate the successful application of CNTs emitters incorporated into thick-film cathode structure. It is suggested that preventing of gate current leakage by cathode structure design can reinforce the field emission performance future more.

B. Field Emission Characteristics of Chromium Carbide Capped Carbon Nanotips

Introduction

Developments of cold emitters have been considered the key issue of the field emission device (FED) applications. An ideal emitter should meet the requirements of low threshold field with high emission current and a long lifetime. For the favor of varieties bonding nature of carbon, diverse crystal structures and surface appearance have been synthesized [1-3]. These nanostructures of carbon showed interesting characters. Among them, carbon nanotube, known for its superior field emission ability with high current density, have been studied over years [4-6]. However, to make the commercial applications of field emission displays possible, there are still challenges including uniformity and durability to be overcome. Instead of carbon nanotubes, recently we have synthesized new carbon structures that exhibit even better field emission performances than carbon nanotubes [7,8]. The growth mechanism was also discussed [9].

The chromium carbide on top of carbon nanotips forms a new kind of high aspect ratio nanomaterial which may be suitable for field emission application. The wide band gap nature of chromium carbide greatly affects the field emission properties. Wide band gap materials have been identified suitable for field emission due to their low electron affinities, as well as their thermal chemical and mechanical stability [10-12]. In this report, field emission characteristics of the two kinds of nanotips are presented and electron emission process is discussed.

Experimental details

Samples started with mirror-polished n-type, (100) oriented Si wafers with resistivity of 4.5~5.5 Ω/cm. For chromium carbide capped carbon nanotips, Cr film with thickness of 20 nm deposited by physical vapor deposition was used as a catalyst. The substrates (Cr coated and bare silicon) then underwent bias-assisted microwave plasma chemical vapor deposition to grow the nanotips.

The microwave power was maintained at 400W with an external negative DC voltage supplied to the substrate. The bias system was isolated to the chamber and the polarity was defined as the voltage applied to the substrate. A two-step process was carried out for the synthesis of chromium carbide capped carbon nanotips. The substrates were pretreated under hydrogen plasma for 10 min in order to clean the surface or also activated the deposited catalyst film. Total pressure in the chamber was kept at 2000 Pascal and the hydrogen flow rate was 200 SCCM. After the pretreatment, methane and hydrogen mixture was admitted to the quartz chamber to begin the growth process. The substrate temperature during pretreatment was about 650℃ and the temperature during growth process was about 700℃, measured with an IR thermometer. The brief experimental parameters were shown in table 1.

After deposition, the synthesized nanotips were observed using scanning electron microscope (SEM) with accelerate voltage of 25kV to observe the surface morphology. Field emission measurements were carried out utilizing high voltage system under pressure of 1 x 10^{-4} Pa. Indium tin oxide coated glass was used as an anode and sodalime glass was equipped as a separator between the sample and the anode.

Results and Discussion

Figure 1 (a) and (b) show the surface morphology of the carbon nanotips and chromium carbide capped carbon nanotips by SEM observation, respectively. The growth parameters were chosen to grow the two kinds of nanotips to about 0.5μm in their length, as to ensure the similar conditions for field emission measurements. The tip end of the carbon nanotips consist of several graphene layers which were less than 0.1 nm [3]. The chromium carbide capped carbon nanotips ends with crystalline nanoparticles which was about 40nm and the diameter of the graphite right beyond the chromium carbide was a few nanometers smaller than the chromium carbide. The chromium film deposited for the growth of the capped carbon nanotip was used as catalyst and was carburized into chromium carbide which was gradually lifted-off during growth. The diameter of the two kinds of nanotips gradually increased toward the substrate via vapor-solid growth and may reach to about a hundred nanometers. The graphene layers of the nanotips body were perpendicular to the silicon substrate for both nanotips and were important to electron conduction.

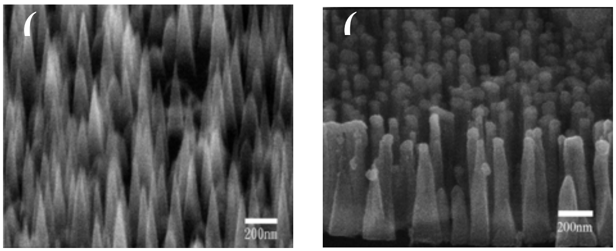

Figure 1. SEM images of surface morphology of (a) carbon nanotips, and (b) chromium carbide capped carbon nanotips.

The composition of the chromium carbide was most likely to be Cr_7C_3, which was identified from x-ray diffraction technique and diffraction patterns by transmission electron microscopy (TEM) [8]. However, weak peaks in the x-ray spectrum and visible diffuse rings could also be found in further analysis. According to the database, it suggested that the chromium carbide nanostructure may consist of Cr_3C_2, $Cr_{23}C_6$ or CrC, incorporated with large amount of defects.

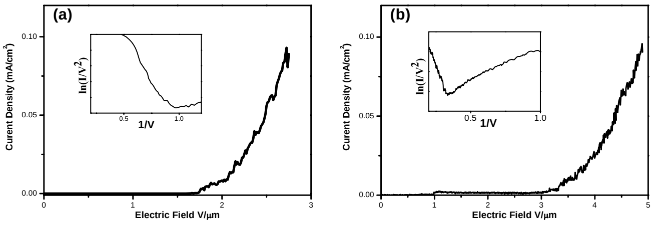

Figure 2. The emission current density as a function of the electric field for (a) carbon nanotips and (b) chromium carbide capped carbon nanotips. The insets show the Fowler-Nordheim plot for each material.

Relationship between field emission current density with electric field of the as grown materials was shown in figure 2. Due to the ultra-sharpness of the bare carbon nanotips, a low turn-on field (defined as the field required to emit a current density of 10μA/cm^2) of 1.4V/μm can be reached. With chromium carbide, the tip structure exhibited a much higher turn-on field of 3.5V/μm. Basically, the results differed from the surface appearances of which the field enhancement factor was greatly affected by the geometrical distribution. The sharpness and less dense of the carbon nanotips also comparatively reduced screening effect [13,14] due to a larger tip-to-tip spacing. The insertions of figure 2 (a) and (b) shows respectively the Fowler-Nordheim (FN) relations which suggest the behavior of FN tunneling of the electron emission process.

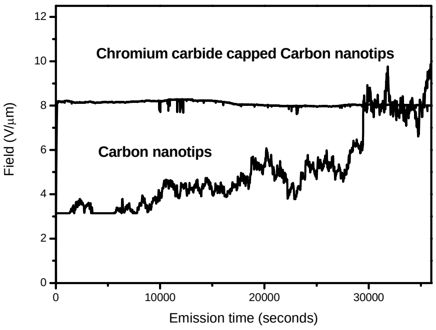

Figure 3. Plot of electric field with emission time for carbon nanotips and chromium carbide capped carbon nanotips. The current was set to a constant value of 1mA.

Figure 3 shows the plot of applied field versus emission time under constant current density which was set to 1 mA. Total emission time was 36,000 seconds, which was 10 hours. The degree of stability of field emission was obviously quite different. The mean electric field for chromium carbide capped carbon nanotips was 8.02 V/μm with fluctuation less than 5 percent can be achieved. On the contrary, although the carbon nanotips showed a superior turn-on and thresholds field on the beginning of the test, the situation became chaotic after about ten thousand seconds. The oscillation was mainly due to the physical damage of the tip, which was confirmed by post observation of SEM. Instead, the chromium carbide capped carbon nanotips showed a smoother surface after the test without distinguishable major change. This phenomenon suggests that chromium carbide, known for its excellent oxidation resistance and hardness, effectively shield the carbon nanotips from destruction, which may mainly due to ion bombardment, heating and oxidation. On the other hand, the extremely sharp of the carbon nanotips would cause a great amount of current density arise over the tip and generate a lot of heat due to ohmic heating. The uniformity of the capped carbon nanotips also benefited to the lifetime experiment while the disorderliness of the uncapped nanotips causes un-equivalent current contribution and as a result of breakdown sequentially.

Chromium carbide has been synthesized and used for long period of time, but were focus on the bulk applications such as hard coatings for tribological use. So far the electric properties have not been totally explored yet. Even though the existence of the chromium carbide was unfavorable for current density performance, the steady emission was more important for practical application.

Conclusion

Field emission characteristics of carbon nanotips and chromium carbide capped carbon nanotips were investigated through I-V measurements and discussed theoretically. The electrical measurements showed a turn-on field of the bare carbon nanotips (1.4V/μm) lower than the chromium carbide capped carbon nanotips (3.5V/μm) for the as-grown sample. However, the bare carbon nanotips shows very unstable field emission behavior while chromium carbide capped carbon nanotips reveal stable emission of fluctuation less than 5%. The chromium carbide acts as shield for the graphite to resist decay due to heating, oxidation or ion-bombardment.

行政院國家科學委員會補助專題研究計畫 **□成果報告**
■期中進度報告

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成果報告類型(依經費核定清單規定繳交)：■精簡報告　□完整報告

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中　華　民　國　94　年　5　月　31　日