行政院國家科學委員會補助專題研究計畫成果報告

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※　低工作電壓奈米碳管場發射電子源之製程研究　※

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計畫類別：▨個別型計畫　　□整合型計畫
計畫編號：NSC 90－2215－E－009－074－
執行期間：90 年 8 月 1 日至 91 年 7 月 31 日

計畫主持人：鄭晃忠教授　國立交通大學電子工程學系
共同主持人：
計畫參與人員：洪偉凱、陳國基、林家彬

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行政院國家科學委員會專題研究計畫成果報告
低工作電壓奈米碳管場發射電子源之製程研究
Fabrication on Low Turn-On Voltage Field Emission Electron Source with Carbon Nanotube

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中文摘要

藉由微波電漿化學氣象沈積的奈米碳管，因其過高的碳管密度容易造成電場屏蔽現象。利用準分子雷射處理能降低碳管密度進而增進場發射特性。掃瞄式電子顯微鏡觀察與電特性量測皆指出在適當的準分子雷射處理條件下，碳管的場發射性質有明顯的改善。起始電場由 3 V/μm 降到 2.1 V/μm，且在 5 V/μm 的電場作用下，電流密度由 5.73 mA/cm^2 增加到 87.13 mA/cm^2。

Abstract

The density of carbon nanotubes (CNTs) deposited by microwave plasma chemical vapor deposition (MPCVD) is extremely high, which results in screening effect in the electric field. To achieve excellent field emission characteristics, an excimer laser treatment (ELT) was introduced to reduce the density of CNTs. Scanning electron microscopy (SEM) micrographs showed reduced densities of the CNTs, and the measurement of electrical characteristics results revealed the improved field emission properties under suitable ELT conditions. The turn-on field decreased from 3 V/μm to 2.1 V/μm, and the emission current density increased from 5.73 mA/cm^2 to 87.13 mA/cm^2 at the applied field of 5 V/μm.

Introduction

Carbon nanotubes (CNTs) have attracted increasing attention owing to their promising applications in vacuum microelectronics. Several groups have demonstrated the low turn-on electric field properties and extremely high emission current of CNT field emission diodes. In most works, arc-produced CNTs[1] and screen-printing techniques were used to fabricate low-cost CNT field emission diodes for field emission displays. However, specific purification processes for arc-produced CNTs are required, and the uniformity of screen-printed CNT field emitter arrays is so poor that it results in a non-uniform emission current. Selective growth of CNTs by chemical vapor deposition (CVD) processes is sufficient for fabricating field emission devices with excellent uniformity when no purification or screen-printing process is required. However, the density of the CNTs, which is an important parameter dominating the field emission property, cannot be controlled well by chemical vapor deposition processes such as laser ablation[2], thermal chemical vapor deposition[3-4], and microwave plasma enhanced chemical vapor deposition (MPCVD)[5]. The screening of the electric field by the dense arrangement of CNTs has been reported by several groups[6-7]. The electric field is screened out for the closely spaced CNTs, which results in a reduced effective electric field near the CNT emitters. As a result, the turn-on electric field is increased and the emission current density is decreased　To obtain better field emission properties, the density of CNTs should be optimized. However, the density of CNTs synthesized by MPCVD is too high and is difficult to control. In this study, a novel process using excimer laser treatment (ELT) was proposed to modify the density of CNTs grown by MPCVD. Different laser energy densities and laser beam overlaps were utilized to obtain various arrangements of CNTs. The experimental results reveal that high emission current density and low turn-on field of CNTs can be achieved under suitable ELT conditions.

Results and Discussion

Figure 1 shows the scan electron microscopy (SEM) micrographs of CNTs treated under ELT condition of 50% laser beam overlap with different excimer laser energy densities: (a) untreated, (b) 100 mJ/cm^2, and (c) 200 mJ/cm^2. The density of the CNTs decreases as the laser energy density of the ELT increases, which results from the destruction of CNTs during ELT. The corresponding cross-sectional views of CNTs are illustrated in Fig. 2. For the energy density of 100 mJ/cm^2, parts of the CNTs were destroyed after ELT and the length variation of CNTs increased. For the higher laser energy density of 200 mJ/cm^2, more CNTs were broken and they are shorter than the previous ones.

The SEM micrographs of the CNTs treated by ELT with the laser beam overlap of 99% are presented in Fig. 3. Significant destruction of CNTs occurred at this laser beam overlap. The corresponding cross-sectional views of CNTs are shown in Fig. 4. For the laser energy density of 100 mJ/cm^2, the CNT length was reduced to 5 μm and the CNT density did not changed markedly, as shown in Fig. 4 (a). Most of the CNTs were destroyed after ELT with the laser energy density of 200 mJ/cm^2, and the average length of the CNTs decreased to 2 μm, as shown in Fig. 4 (b).

Figure 5 (a) shows a high-resolution SEM micrograph of the CNT films treated with a laser energy density of 200 mJ/cm^2 and laser beam overlap of 99%. The tops of the CNTs are open ended, which differs from the case of as-grown CNTs, demonstratingthat CNTs can be broken effectively by ELT.

Based on the SEM results, a mechanism for ELT of CNTs was proposed, as depicted in Fig. 5 (b). With the lower laser beam overlap, some CNTs were destroyed by the laser; and the variation of CNT length increased which enhanced the electric field distribution. With higher laser beam overlap, serious destruction of CNTs occurred and the CNT density did not changed markedly as compared to that of as-grown CNTs. The emission characteristics of the CNTs for different ELT conditions are shown in Fig. 6. With an applied electric field of 5 V/μm, the emission current densities were 5.73 mA/cm^2 and 87.1 mA/cm^2, respectively, for the untreated CNTs and the CNTs treated under the ELT conditions of laser energy of 100 mJ/cm^2 with the laser beam overlap of 50%. The emission current densities were 3.71 μA/cm^2 and 2.51μA/cm^2 for the CNTs treated under ELT conditions of laser energy density of 200 mJ/cm^2 with 50% laser beam overlap and the CNTs treated under ELT conditions of laser energy density of 100 mJ/cm^2 with 99% laser beam overlap, respectively. The corresponding Fowler-Nordheim plots for CNTs with different ELT conditions are depicted in Fig. 6 (b). The linearity of the plots confirms the field emission phenomena. The turn-on field of the CNTs field emission diode, which was defined as the field at which F-N plot becomes linear, decreases from 2.3 V/μm to 1.3 V/μm for the untreated CNTs and the ELT-CNTs with laser energy density of 100 mJ/cm^2 and 50% laser beam overlap. Table I shows the relationship between different ELT conditions and the field emission properties. However, the turn-on field increased for other ELT conditions.

Conclusions

The density reduction of CNTs achieved by excimer laser treatment was proposed. The SEM micrographs revealed the surface distribution of CNTs after ELT. For the laser beam overlap of 50%, parts of CNTs were shortened and the remaining CNTs protruded from the surface of CNTs films. When the laser beam overlap increased to 99%, most of the CNTs were shortened and no protruding CNTs were observed. The field emission characteristics confirmed the improvement of field emission properties under suitable ELT conditions, the field emission current density increased from 5.73 mA/cm^2 to 87.13 mA/cm^2 at the electric field of 5 V/μm and the turn-on electric field decreased from 2.3 V/μm untreated to 1.3 V/μm for ELT conditions of a laser energy density of 100 mJ/cm^2 and 50% laser beam overlap. The experimental results reveal that improved emission properties can be achieved by optimizing the density and the length of CNTs under proper excimer laser treatment conditions.

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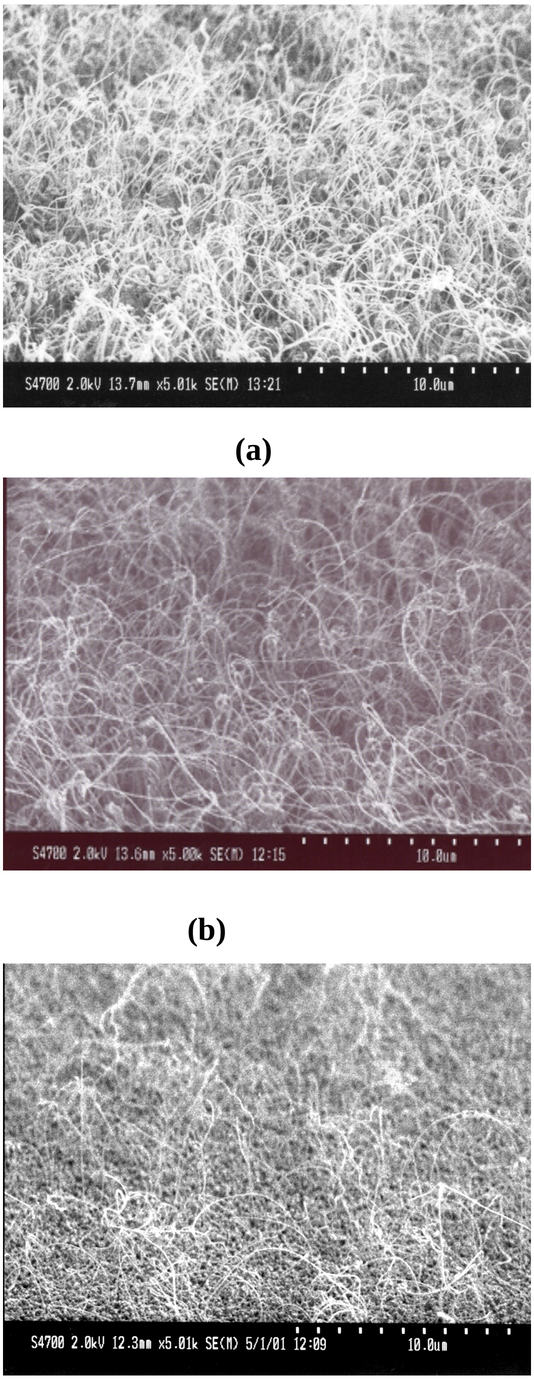
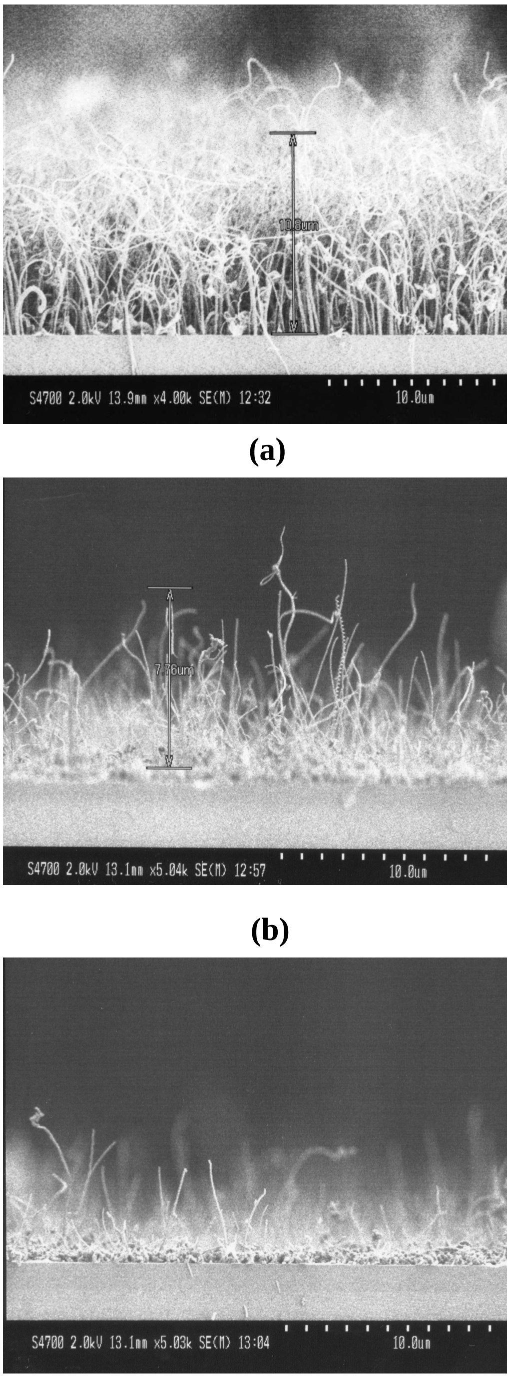


(a)

(b)

(c)

Figure 1



(a)

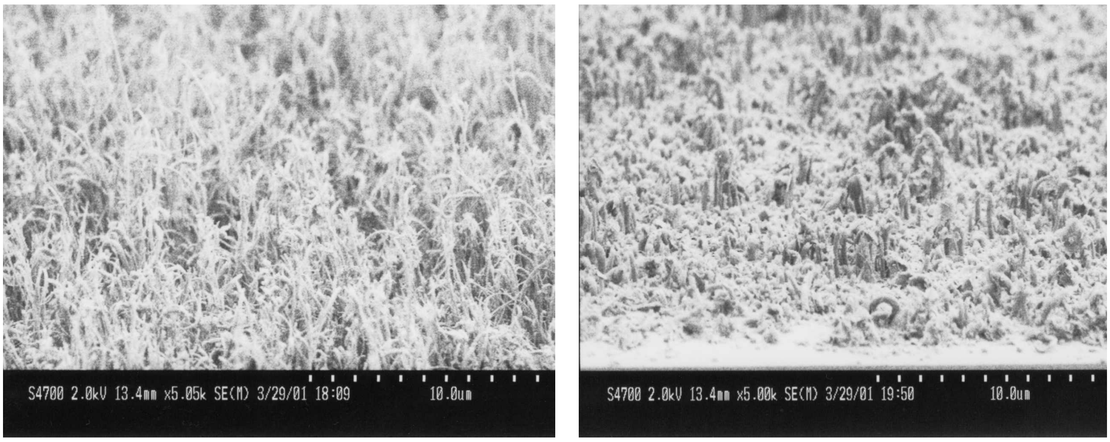
(b)

(c)

Figure 2

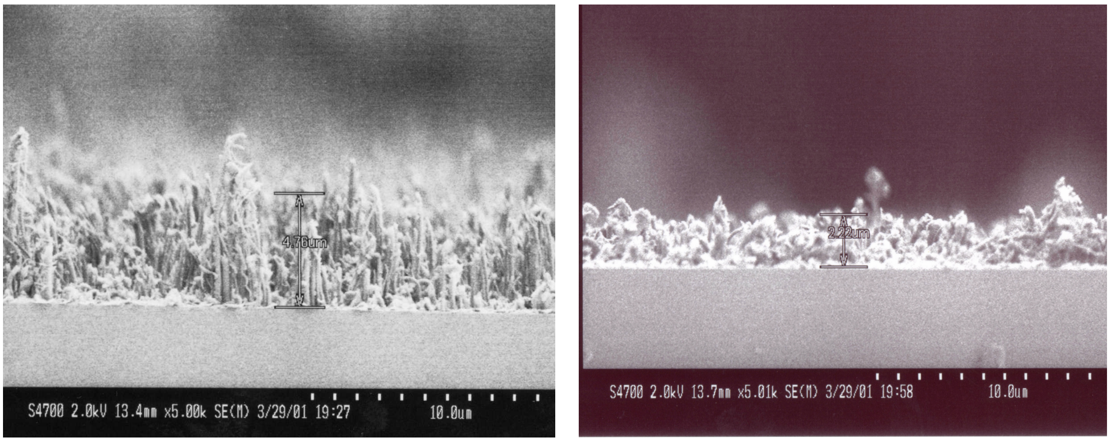
Figure 1.SEM micrographs of CNTs treated by ELTs for different excimer laser energy densities of (a) untreated, (b) 100 mJ/cm^2, and (c) 200 mJ/cm^2. The laser beam overlap was maintained at 50%.

Figure 2. Cross-sectional SEM micrographs of CNTs treated by ELTs for different excimer laser energy densities of (a) untreated, (b) 100 mJ/cm^2, and (c) 200 mJ/cm^2. The laser beam overlap was maintained at 50%.



(a) **(b)**

Figure 3. SEM micrographs of CNTs treated by ELTs for different excimer laser energy densities of (a) 100 mJ/cm^2 and (b) 200 mJ/cm^2. The laser beam overlap was maintained at 99%.



(a) **(b)**

Figure 4. Cross-sectional SEM micrographs of CNTs treated by ELTs for different excimer laser energy densities of (a) 100 mJ/cm^2 and (b) 200 mJ/cm^2. The laser overlap was maintained at 99%.

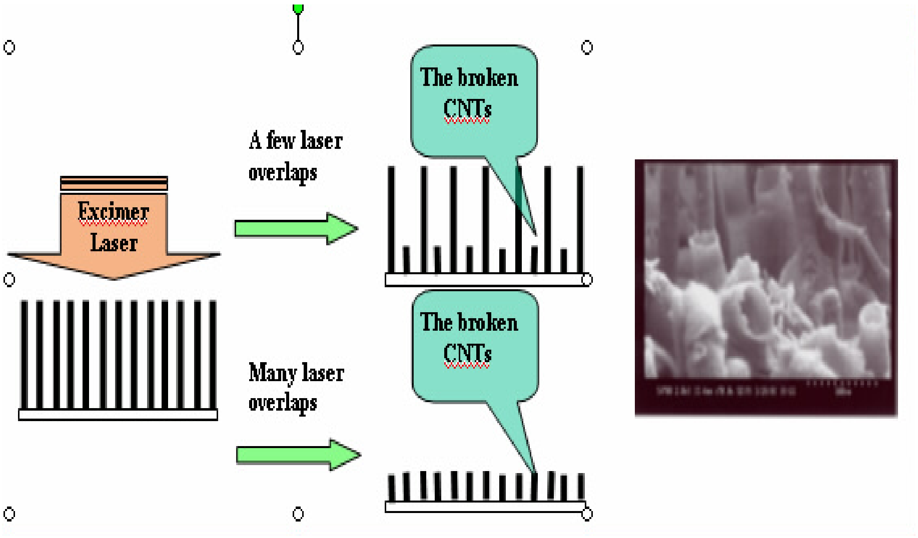


Figure 5. . The mechanism of ELT-CNT and SEM micrograph of the CNTs broken by ELT

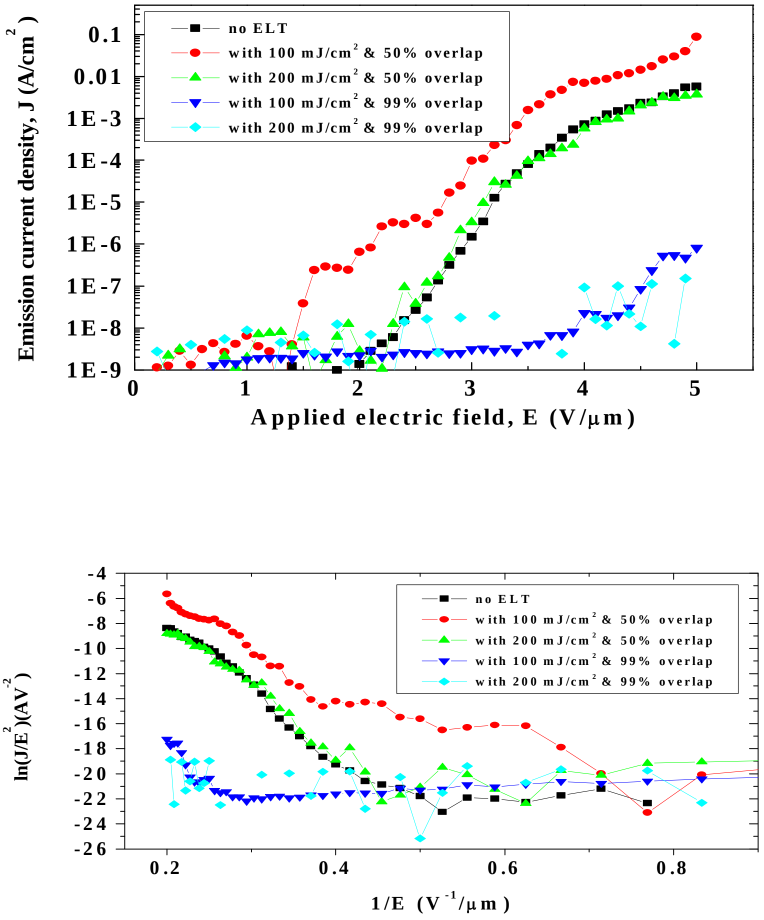


Figure 6.(a) Characteristic emission current density (J) versus applied electric field (E) for the CNTs with different ELT conditions. (b) The corresponding F-N plots.