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Enhancement of the field emission properties of low-temperature-growth multi-wall carbon nanotubes by KrF excimer laser irradiation post-treatment

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Abstract

Multi-wall carbon nanotube (CNT) films were fabricated by microwave plasma chemical vapor deposition at low temperatures (~500 °C). The films when properly post-treated by laser irradiation exhibited a factor of 2–3 enhancement in the emission current, while the turn-on field (E_{on}) was reduced from 4.89–5.22 to 2.88–3.15 V/µm. The introduction of excessive oxygen during laser irradiation, however, degrades the performance of field emission properties drastically. Raman spectroscopy measurements revealed the intimate correlation between the parameter I_D/I_G (intensity ratio between the two representative Raman peaks seen in carbon nanotubes) and the field emission performance. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses showed that the irradiation-induced modification of the tube morphology and crystallinity might be responsible for the observations.

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Keywords: Carbon nanotube; Field emission; Laser irradiation; Post-treatment

1. Introduction

Carbon nanotubes (CNTs) [1] are one-dimensional (1-D) nano-materials with excellent technological application potential, including field emission [2], microelectronic devices [3] and micro-gun [4], due to their high field emission current density, low turn-on field and stable currents. Colbert and Smalley [5] observed the enhancement of field emission of CNTs by using laser irradiation and they interpreted this effect as being due to the presence of localized plasma induced by instant vaporization of CNTs and ionization of the species. In this study, the microwave plasma chemical vapor deposition (MP-CVD) system was used to synthesize carbon nanotubes. We then used a KrF excimer laser to practice the post-treatment on the obtained CNTs. The effects of the post-treatment parameters such as laser power density, count number of the delivered laser pulses, and

* Corresponding author. Tel.: +886 3 5712121 56187. *E-mail address:* leechia2002@yahoo.com.tw (C.-H. Li). precursor atmosphere on the field emission characteristics of the CNTs are discussed.

2. Experiments

For fabricating CNTs, we first prepared a fully cleaned p-(100) Si substrate, and then layers of 40 nm Ti and 20 nm Ni were deposited sequentially on the Si substrate using E-gun vapor deposition at a base pressure of 10^{-6} Torr. The coated substrate was then immediately loaded into the MP-CVD chamber for hydrogen plasma pre-treatment. The pre-treatment was conducted by applying microwave with the power of 800 W to the chamber with a 90 sccm flowing hydrogen gas (corresponding to a background pressure of 24 Torr) while keeping the substrate temperature at 500 °C for 15 min. Finally, a continuous process was practiced for growing the multi-wall carbon nanotubes (MWNTs) by raising the microwave power to 1200 W and switching the reaction gas to mixed H₂/CH₄ with a ratio of 9:1. The substrate temperature remained at 500 °C and no bias was intentionally applied to the substrate.

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Fig. 1. SEM images of MWNT films: (a) as-grown films; (b) after irradiated with laser power density of 9 mJ/cm², and (c) 14 mJ/cm².



Fig. 2. The Raman spectra for MWNT films treated with different parameters. (a) The influence of laser power density; curves (1)–(3) show the spectra for the asgrown film, laser irradiated in air at 8.87 mJ/cm², and 14.23 mJ/cm², respectively. (b) The I_D/I_G variation with the irradiated laser power density. (c) Effects of delivered laser pulse counts (*n*); curves (1)–(5) represent the result for as-grown, n=2, n=5, n=10, and n=20 cases. (d) The corresponding I_D/I_G for the conditions depicted in (c). (e) Effects of oxygen pressure (PO₂) during irradiation; curves (1)–(4) are for the as-grown, $PO_2=5 \times 10^{-5}$, 5×10^{-1} , and 760 Torr, respectively. (f) The I_D/I_G for the corresponding conditions in (e). Note: each curve has been displaced vertically for clarity.

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