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Freestanding vertically aligned arrays of individual carbon nanotubes on metallic substrates for field emission cathodes

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Direct growth of individual and vertically aligned carbon nanotubes (CNTs) onto a metallic tip apex using a two-chamber radio-frequency plasma-enhanced chemical vapor deposition is reported. Individual Ni nanocatalysts, obtained by a sol–gel combustion technique, were dots for the nucleation of individual CNTs that were freestanding, clean, and vertically aligned by the presence of a controlled applied field. The arrays of CNTs obtained, having a low-density spatial distribution to avoid mutual electrostatic field screening, gave uniform stable overall field emission patterns after a conditioning process. Effective total current densities up to 1 A/cm² can be extracted. © 2004 American Institute of Physics. [DOI: 10.1063/1.1773366]

Favorable electron emission properties from carbon compounds have been reported.¹⁻⁹ Even more interesting, from a field emission (FE) viewpoint, is the carbon nanotube (CNT) due to its high aspect ratio and surface stability.^{10,11} They can be directly grown on a flat electrode/surface, thus removing the need of a three-dimensional lithographic fabrication of sharp tips for FE. Vertically aligned CNTs tend to possess better FE properties than nonaligned CNTs,¹² and this was attributed to the potentially large number of exposed tip ends of the aligned CNTs in arrays, which are sites that present high electric field enhancement,¹³ i.e., FE areas. In the literature today, aligned CNTs have been deposited from various plasma-enhanced chemical vapor deposition (PECVD) techniques.^{14–18} More recently, it has been shown that the nucleation of single isolated vertical CNTs was obtained when the size of the catalyst is under 100 nm, with practically 100% yield using a glow discharge PECVD.^{17,19,20} The vertical direction of the CNTs was related to the presence of the electric field intrinsic in this process. The most important observation and result, for the use of CNTs as cold cathodes, were that these isolated CNTs in the array structures exhibited remarkable uniformity in terms of diameter and height.²⁰ They were determined, respectively, by the size of the catalyst dots and by the growth conditions (gas composition, flux and total pressure P, temperature of the substrate T and growth time).

However, in most of these studies electron lithography microfabrication processes prepared catalyst nanodots having diameters less than 100 nm. For possible extension of these vertically aligned individual CNT array cathodes to large production applications with high throughput fabrication process, we have to tackle the two following problems. (1) Is there a lower-cost, nonlithographic fabrication process available for direct growth of individual vertically aligned CNTs on metallic surfaces, and (2) are their FE properties compatible with the industrial environment, as in field emission displays, for example?

We report in this letter the direct growth of arrays of isolated and vertically aligned CNTs on a metallic surface using radio-frequency plasma-enhanced chemical vapor deposition (rf PECVD). We also show that, after a conditioning process, these arrays of isolated CNTs become stable and uniform emitters in vacuum of $10^{-6}-10^{-8}$ Torr.

Our CVD growth was performed in a homemade twochamber reactor [Fig. 1(a)]. The concept of a two-chamber reactor allowed splitting between the plasma production from the applied local field on the metallic growth support. By monitoring the values of the polarization potentials V_1 and V_2 applied to electrodes E_1 and S, we have direct control of not only the flux and the energy of the incident ions from the plasma, but also of the local electric field at the cathode substrate during CNT growth. The metallic supports we used here were Ta tips with apex radii of about 400 μ m.

Our catalyst nanodots were Ni nanoparticles synthesized by a sol–gel combustion process.²¹ We mixed an aqueous solution containing nickel acetate tetrahydrate and methyl hydrazine with 2-propanol solution at room temperature, with constant stirring for 1 day. This solution of metal acetate was then dried at ~50 °C in air atmosphere until complete evaporation of the solvent, and then it was heated at 400 °C for 1 h under nitrogen atmosphere. Finally, by mechanical filtration, the powder obtained was calibrated in order to have Ni nanoparticles with diameters in the range of 100 nm.²²

The main characteristics of growth and the results are the following.

(1) The Ni nanoparticles were mechanically dispersed onto the metallic support surface at the desired density. Figure 1(b) indicates that dispersion of individual nanosize Ni clusters can be obtained with this lithographic-free process. This deposit was cleaned in the growth chamber by sputtering with hydrogen ions for ~5 min at *T* between 700 and 800 °C, prior to the growth process. The parameters V_1 , V_2 , *T* and *P* defined the height of the CNTs for a given growth time. As an example, we have obtained CNTs with height between 2 and 10 μ m in 20 min for V_1 =50 V and 100 V $\leq V_2 \leq$ 300 V, under typical conditions of C₂H₂: NH₃ flow of 2:3 sccm and *P*=0.1 Torr. Figure 1(c) reveals that the nucleation area of the CNTs was delineated by the presence of the Ni

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FIG. 1. (a) Schematic drawing of the two-chamber rf PECVD reactor. A resistive coil heater obtained the temperature T of the sample, measured by a thermocouple and a micropyrometer. (b) Dispersion on the surface of the Ni nanoclusters (diameter ~ 100 nm) obtained by a sol-gel combustion process. In this example the distances between the nanoclusters were in the range of $1-2 \mu m$. (c) Overall and (d) detailed scanning electron microscopy photos of the direct growth of freestanding, isolated vertically aligned CNTs on the apex of a metallic support tip. Confinement of the CNTs on the apex of the Ta tip was the consequence of voluntary localized deposition of the Ni nanocatalysts only onto this area. (e) Characteristic histogram of the CNT height distribution over the metallic tip apex showing that more than 65% of the CNTs have heights between 3.5 and 4.5 μm .

clusters, and Figs. 1(d) and 2 show scanning electron microscopy images characteristic of the CNTs obtained.

- (2) The majority of CNTs were freestanding, isolated and vertically aligned on the metallic surface [Figs. 1(c) and 1(d)]. In most cases, with a catalysts size of \sim 100 nm, there was only nucleation of a single CNT per dot, in agreement with former analysis.²⁰ Note that, as observed in Ref. 20, the ion sputtering during growth resulted in the nucleation of "clean" CNTs.
- (3) At some catalyst sites, two or more CNTs can nucleate [Figs. 2(b) and 2(c)]. This situation happens when the size of the catalyst is greater than 100 nm,²⁰ or when an aggregation of several Ni nanoclusters happened. However, within such situations, only one of the CNTs had a dominant height and it will be then the field emitting CNT.
- (4) The statistical spacing between the different nanotubes across the arrayed distribution presented good spatial distribution, mainly greater than the height of the CNTs [Fig. 2(a)]. Note that the optimum FE conditions were reached when the emitters were spaced about twice their height apart to avoid electrostatic field screening.²³
- (5) The histogram of the heights of the CNTs within an array showed tight dispersion around a mean value. Figure 1(e) is a characteristic distribution for a given growth. Note that to achieve good emission uniformity the structural variation between emitters must be as small as possible.

In the last part of this letter, we report about the FE efficiency of these cathodes. In our FE experimental procedure, the metallic support tip covered with the CNT array was in front of a fluorescent screen/metallic anode and all the I-V measurements were done within this diode setup, where I and V were, respectively, the FE total current and voltage. Since the emission area was confined to the end of the support tip covered with the CNT arrays, it was estimated to be a zone of about 100 μ m diameter or less [Fig. 1(c)]. The FE behavior of the arrayed CNTs, after a conditioning process described later, shown Fowler-Nordheim behavior, i.e., linear variation of $\ln(I/V^2)$ vs (1/V). Figure 3 is a characteristic example of the I-V evolution of these cathodes. The FE stability was good even for a working pressure of 10⁻⁷ Torr (inset in Fig. 3). We obtained reproducible and stable total currents up to $\sim 20 \ \mu A$ from these cathodes, which means effective current densities from 0.3 to 1 A/cm². This behavior was perfectly coherent with the FE behavior of individual CNTs that has been analyzed in Ref. 10, showing that one CNT acted as a high aspect ratio metallic tubular tip with a work function in the range of 4 eV.

However, in the case of an array having the height distribution given in Fig. 1(e), the following conditioning process is mandatory to end up with a uniform stable overall FE current. The conditioning process we propose is a two-step procedure. In the first step, the heights of the CNTs of the emitting array were first standardized. Then, in the second step, the apexes of these field emitters were cleaned *in situ* by using field desorption and Nottingham effects.



FIG. 2. Scanning electron microscopy observations of freestanding CNTs on a metallic cathode support. (a) One CNT per Ni catalyst dot (majority of the CNTs obtained). (b) Two CNTs per Ni dot. (c) Multiple CNTs per Ni dot.



FIG. 3. I-V characteristics of the arrayed CNTs followed Fowler–Nordheim behavior. The inset shows the stability of the FE current for more than 6 h of continuous emission at 1 μ A in 10⁻⁷ Torr. Note that the likely cause of the fluctuation of the stability curve shown in the inset was retro-ion bombardment due to the bad vacuum conditions (10⁻⁷ Torr).

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FIG. 4. Numerical simulation showing the contribution of CNTs to the overall FE current during the conditioning process. The two insets are FE patterns before (curve 1) and after conditioning (curve 3) coming from a CNT array area about 100 μ m in diameter. The ring on the FE pattern in inset 3 was an artifact due to the reflection of light on the glass support of the fluorescent screen.

From the as-growth height distribution, only the few highest CNTs of the array will contribute to the FE current (curve 1 in Fig. 4), the FE patterns were then nonuniform and spotty (inset 1 in Fig. 4). To standardize the height of the CNTs we increased the voltage applied to induce selective field evaporation among the CNTs. The field evaporation¹⁰ will act preferentially on the highest CNTs, leading to shortening (or eventual destruction) of them. As a consequence, there is a concomitant increase in the uniformity of the FE patterns due to the increase in the number of contributing CNTs for FE. The optimum was reached when the majority of the CNTs of the array having the same height contribute to the formation of the FE pattern (inset and curve 3 in Fig. 4). A numerical simulation taking into account such evolution due to the conditioning process confirmed that a greater number of CNTs would then contribute to the FE pattern, as shown by the evolution from curve 1 to curve 3 in Fig. 4. As the height of the emitting CNTs decreased by field evaporation during the conditioning process, the FE voltages for the same overall current must increase in relation with the decrease of the field enhancement factor.¹³ In the example in Fig. 4, if V_0 is the FE voltage for curve 1, the FE voltages for curves 2 and 3 to obtain the same overall current are, respectively, 1.06 and $1.20V_0$. These values are comparable to our experimental data for a 2 μ A total current a voltage of 2200 V was needed before conditioning and 2650 then 2800 V after mild and severe conditioning processes.

In a following second step, the stability of the overall FE current was obtained by field desorbing the adsorbed species at the apexes of the CNTs with the help of the Nottingham effect similar to the cleaning procedure analysis described in detail in Ref. 10. Note that this last step can be done either at room temperature or under heat treatment.

In conclusion, we have presented a fabrication process of arrays of individual CNTs using a cost-effective, lithographic-free, chemical technology. Direct growth on metallic surfaces of freestanding, individual, vertically aligned CNTs allowed direct use of these arrays as cold cathodes, after a two-step conditioning process that assumed an optimum setting for a uniform and stable overall FE of the arrays. The results establish a scalable method of field emitter fabrication, which can address the present uniformity problem of FE from CNT mats and is well suited for field emission display production.

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