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Growth of vertically aligned arrays of carbon nanotubes for high field emission

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ABSTRACT

Vertically aligned multi-walled carbon nanotubes have been grown on Ni-coated silicon substrates, by using either direct current diode or triode plasma-enhanced chemical vapor deposition at low temperature (around 620 °C). Acetylene gas has been used as the carbon source while ammonia and hydrogen have been used for etching. However densely packed (~ 10^9 cm^{-2}) CNTs were obtained when the pressure was ~ 100 Pa. The alignment of nanotubes is a necessary, but not a sufficient condition in order to get an efficient electron emission: the growth of nanotubes should be controlled along regular arrays, in order to minimize the electrostatic interactions between them. So a three dimensional numerical simulation has been developed to calculate the local electric field in the vicinity of the tips for a finite square array of nanotubes and thus to calculate the maximum of the electron emission current density as a function of the spacing between nanotubes. Finally the triode plasma-enhanced process combined with pre-patterned catalyst films (using different lithography techniques) has been chosen in order to grow regular arrays of aligned CNTs with different pitches in the micrometer range. The comparison between the experimental and the simulation data permits to define the most efficient CNT-based electron field emitters.

Keywords: Direct current plasma-enhanced CVD; Carbon nanotubes; Electron field emission

1. Introduction

Thermionic cathodes used in high power microwave tubes for telecommunications are sensitive to poisoning materials and require a high-temperature operation and long turn-on times. In contrast, field emission occurs at room temperature from an unheated "cold cathode" under the influence of a very large electric field (a few 10^7 V/cm). Field emission sources also offer several attractive characteristics such as instantaneous response to field variation, resistance to temperature fluctuation and radiation, high degree of focusability in electron optics and ballistic transport. Thus, due to their high aspect ratio whisker-like shape and their chemical inertness, carbon nanotubes (CNTs) are considered as very promising electron sources in a high frequency (~ 20 GHz)/high power (10 W) microwave amplifier. Several teams tried to construct vacuum microdiodes or microtriodes using cold cathodes based on carbon nanotubes [1,2]. For the field emission (FE) application considered here, where very high current densities (≥ 500 mA/cm^2) are required, the controlled production of emission sources, based on vertically aligned carbon nanotubes are needed. However this is not a sufficient condition, because previous works [3,4] showed that closely packed arrays of CNTs are not ideal for FE applications: close packing of tubes screens the local electric field, thus reducing the field enhancement of the tubes.

In the present study, we confirm, basing our argument on past experiments using various catalyst assisted chemical vapor deposition (CVD) techniques [5–7], that only direct current plasma-enhanced CVD, allows to control the growth of well-aligned multi-walled carbon nanotubes (MWCNTs). We propose a physical explanation of the CNT alignment. Then we develop a three dimensional (3D) numerical simulation to assess the local electric field in the vicinity of the tips and the emission current density for a finite square array of CNTs [8,9]. Lastly we

focus on the growth of different arrays of well-aligned free-standing MWCNTs on pre-patterned Ni dots using either optical or electron-beam (e-beam) lithography, in order to define the array configuration leading to the highest electron field emission.

2. Experimental details

A schematic description of the experimental set-up combining hot-wire CVD (HWCVD) and direct current plasma-enhanced CVD (dc PECVD) has been reported earlier [6]. The tungsten filament (0.38 mm in diameter) is fed by a dc source around 13 A (250 W), allowing the filament temperature, measured with a single wavelength (red) pyrometer, to stabilize at ~ 1800 °C. The cathode (Mo substrate-holder) can be negatively dc-biased compared to the anode (Mo grid) up to − 450 V (with current densities of ions impinging on the cathode between 2 and 4 mA/cm^2). The distance between the tungsten wire and the cathode is fixed to ~ 15 mm whereas the distance between the anode and the cathode is fixed to 8 mm. In the gas mixture injected into the reactor, acetylene (C_2H_2) is the deposition gas whereas ammonia (NH_3) and molecular hydrogen (H_2) are the etching gases. During the growth, the total gas flow rate is fixed at 100 sccm under ~ 200 Pa pressure. The growth time is 15 min.

We used also a triode PECVD reactor, where a mesh electrode (grid) is installed between the cathode (power electrode) and the anode (ground electrode) [7]. The mesh grid is placed 10 mm above the cathode. The cathode is negatively biased at − 600 V while the mesh can be biased between + 300 V and − 300 V. C_2H_2 and NH_3 are used with the flow rates of 50 and 50 sccm, respectively. The total gas pressure during the growth is kept at 266 Pa and the growth time is 20 min.

As mentioned earlier, the growth of CNTs by CVD techniques needs to be assisted by a catalyst (nickel nanoparticles in our case). So the substrates consist of highly n-doped silicon covered with a thin TiN (10 nm thick) diffusion barrier layer, preventing the formation of $NiSi_x$. These substrates are then covered with a ~ 7 nm Ni thick layer. Prior to growth and during the deposition process, HWCVD generates radicals (essentially atomic hydrogen) whereas dc PECVD generates radicals, excited metastables and ions. So prior to growth, either a flow of H_2 during 5 min in the case of HWCVD or an NH_3 plasma exposure during 2 min in the case of dc PECVD is used to break up the Ni thin film into nanoparticles which seed the CNT growth. For the catalyst patterning, we use optical lithography for micron-sized dots and e-beam lithography for submicron-sized dots. In the latter case, a high molecular weight resist is spin coated onto the substrate and baked. High resolution e-beam is then used with an exposure dose of 400 μC/cm^2 to define an array of circular holes in the resist [8].

The surface morphology of the grown MWCNTs was investigated with an FEG high resolution scanning electron microscope and the carbon bonding was assessed by Raman spectroscopy using the 632.8 nm laser excitation [8].

3. Results and discussion

In the first part, we studied the HWCVD growth mode, setting the filament temperature at 1800 °C, the substrate temperature at 620 °C, the gas ratio C_2H_2/H_2 at 10%/90% and the deposition time at 15 min. Dense tangled and curled up nanotubes, with a length of several microns, were observed [6,8]. The growth rate was estimated at 100 nm/s. When NH_3 was added in the gas mixture at the expense of H_2, a small amount of amorphous carbon was observed [6]. This suggested that the decreased concentration of H radicals and the increased concentration of NH_2 radicals, generated by the HWCVD process, deteriorated the CNT structure.

Then we used the dc PECVD growth mode with the substrate temperature set at 620 °C, the same gas ratio C_2H_2/H_2 as mentioned previously and the cathode negatively biased up to − 375 V compared to the anode [6]. Short (several hundreds of nm long) aligned nanotubes were observed. So the growth rate was estimated at some 10 nm/s.

Finally with the triode PECVD reactor, it was shown that the length and density of the grown CNTs is controlled by the mesh electrode bias which in turn controls the plasma density and the ion bombardment of the substrate [7].

The explanation of the alignment of CNTs is probably due to the energy and flux of the positive ions bombarding the cathode surface: in a dc glow discharge, most of the voltage drop occurs in the cathode fall region, whose dimension is a function of the material used for the cathode (Mo) and the nature of the discharge gas (mainly H_2 or NH_3). Taking into account the pressure used in the reactors (200 or 266 Pa), the cathode dark space thickness is estimated at 3 mm in the case of the diode or at 6 mm in the case of the triode, which leads to an electric field of ~ 0.1 V/μm or 0.18 V/μm in the cathode sheath respectively. As the ions detected are $C_2H_2^+$, NH_3^+ [10] and H_3^+ [11], and due to the low collisional mean free path (0.1 mm), these ions hit the cathode surface with an energy of ~ 10 eV, more than enough to

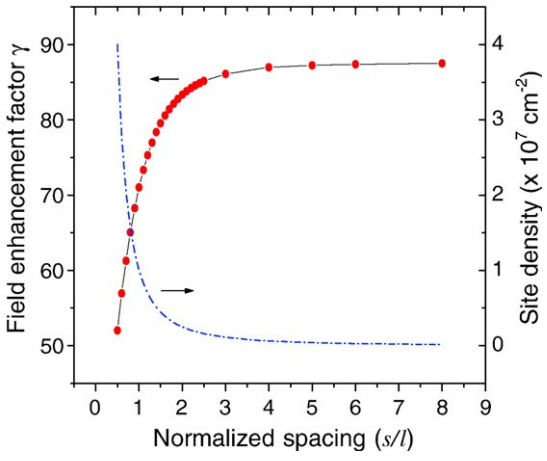

Fig. 1. Field enhancement factor γ (red points) and nanotube density (dashed–dotted line) as a function of nanotube spacing s (normalized to nanotube length l) for the array N1–20 (carbon nanotubes are 1 μm long with a diameter of 20 nm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

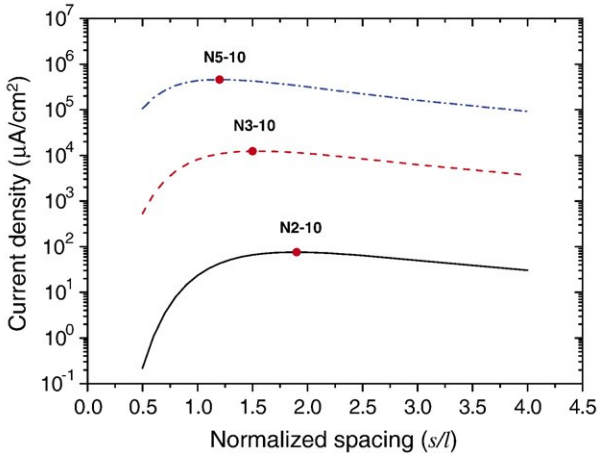

Fig. 2. Emission current densities calculated for the arrays N2-10 (solid line), N3-10 (dashed line) and N5-10 (dashed-dotted line) as a function of the normalized spacing s/l. Applied electric field is 15 V/μm.

impede the growth of carbon nanostructures parallel to the surface.

To conclude this first part, using the dc PECVD processes, it has been possible to synthesize densely packed ($\sim 10^9$ cm^{-2}) aligned CNTs [6,7] using Ni as catalyst and TiN as diffusion barrier.

In the second part of this work, a 3D computation based on the boundary element method has been used to assess the field enhancement factor γ (defined as the local electric field normalized to the applied electric field) for a finite square array of carbon nanotubes [8,9]. We define as N1-20 the array of nanotubes for which each nanotube belonging to the array has a length l of 1 μm and a diameter d of 20 nm, so that 2 l/d = 100. The dependency of γ as a function of the spacing s between nanotubes (normalized to the nanotube length l) is shown in Fig. 1 (red points). γ saturates when s/l is ≥ 5. As s decreases, γ decreases due to the increasing screening effect between neighboring nanotubes [8]. The number of emitting sources per unit area increases inversely proportional to s^2 (dashed-dotted line in Fig. 1). So the total emitted current density for the array N1-20, as deduced from the Fowler-Nordheim equation, goes through a maximum as a function of s/l for a given value of the external electric field [8]. When the nanotube length increases from 2 to 5 μm with a diameter fixed at 10 nm, the emission current density increases abruptly with the ratio l/d [6] (see Fig. 2). Simultaneously it may be noted that the maximum current density shifts to lower values of the normalized spacing s/l, from 2 to 1.25.

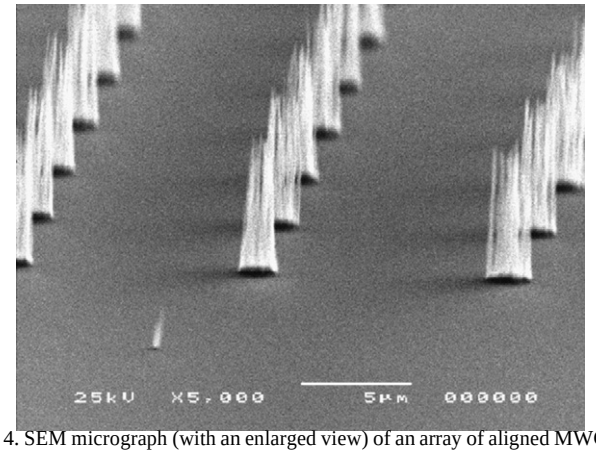

Fig. 4. SEM micrograph (with an enlarged view) of an array of aligned MWCNTs on Ni dots (1.6 μm in diameter) realized by optical lithography. The dot pitch is 10 μm.

In the last part of this work, taking into account the above-mentioned numerical results, we produced patterned arrays of aligned MWCNTs using the triode plasma technique and Ni as the catalyst. The square arrays of catalyst dots are defined by the lattice translation vector (pitch) which is the minimum distance between two bundles of CNTs or two individual CNTs. The two patterning techniques are the optical UV lithography (with a resolution of ~1 μm) and the e-beam lithography (with a resolution down to 50 nm).

We selected values of pitch: 3.3 μm, 5 μm and 10 μm in the case of optical lithography (1.6 μm Ni dot) and 2 μm, 3 μm,...up

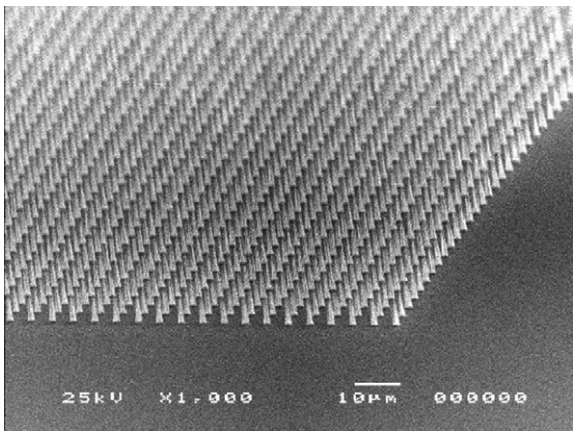

Fig. 3. SEM low-magnification micrograph (general view) of an array of aligned MWCNTS on Ni dots (1.6 μm in diameter) realized by optical lithography. The dot pitch is 5 μm.

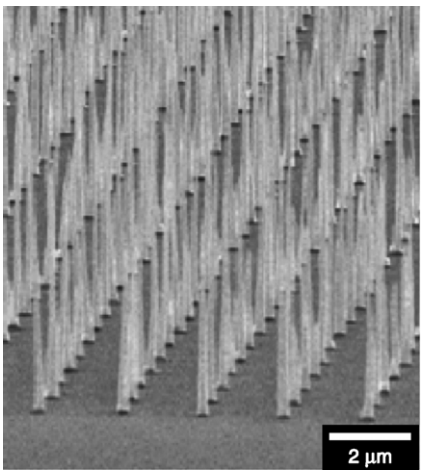

Fig. 5. SEM micrograph of an array of aligned MWCNTs on Ni dots (260 nm in diameter) realized by e-beam lithography. The dot pitch is 2 μm.

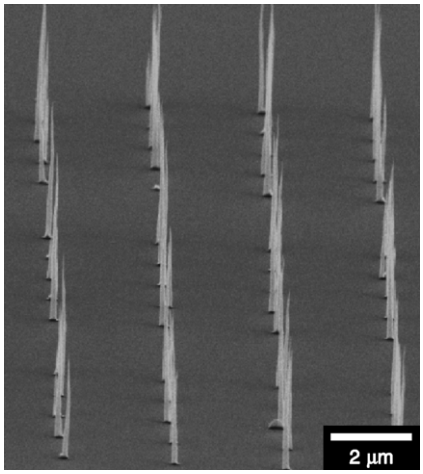

Fig. 6. SEM micrograph of an array of aligned MWCNTs on Ni dots (180 nm in diameter) realized by e-beam lithography. The dot pitch is 2.8 µm.

to 8 µm in the case of e-beam lithography (~ 200 nm Ni dot). In the same run (15 min deposition time), we realized the growth of CNT arrays on the different pre-patterned catalyst dots. Figs. 3 and 4 are SEM micrographs showing the growth of CNT arrays on 1.6 µm Ni dots with the pitches of 5 µm and 10 µm respectively. For both arrays, about a dozen CNTs are observed on each dot with an average length of 8.9 µm and a widely distributed diameter (centered around 230 nm). Figs. 5 and 6 are SEM micrographs showing the growth of CNT arrays on 260 nm and 180 nm Ni dots associated with the pitches of 2 µm and 2.8 µm respectively. In these cases, we observe a single tapered CNT per dot with an average length of 4.2 µm and 3.8 µm respectively. In Fig. 6 the diameter of the carbon nanotube is 140 nm at the basis and 45 nm at the tip. All these results confirm that the size of the Ni dot determines the diameter and number of CNTs per dot. Provided the diameter of the Ni catalyst dots is b200 nm, each dot produces one MWCNT [12].

Emission current densities were measured for some of these CNT arrays. Though the current density magnitudes are higher for the e-beam arrays than for the optical arrays, the maximum emission current never exceeded 0.4 A/cm^2, value measured in a previous work with a pitch fixed at 10 µm [13]. One possible explanation is that, owing to the high value (50%) of the mass flow ratio of C_2H_2 in the C_2H_2:NH_3 plasma used during the deposition, removal of excess carbon species is not sufficient, leading to amorphous carbon deposit which limits the electron emission from the nanotubes. One way to solve this problem would be to decrease the ratio, because not only does NH_3 generate atomic hydrogen species, it also suppresses the decomposition of C_2H_2, thus encouraging the production of a-C free CNTs.

4. Conclusion

First this work confirmed that it is possible to control the growth of aligned multi-walled carbon nanotubes by using a dc plasma-enhanced CVD in the presence of C_2H_2 and NH_3. We explained how the positive ions in the cathode sheath of the plasma can force the CNTs to grow perpendicular to the substrate. In the second part, a 3D calculation of the local electric field for a finite square array of CNTs allowed to assess the evolution of the emission current density issued from such an array as a function of the length, the diameter and the spacing between nanotubes, and thus to define the geometrical parameters leading to a maximum in the current density. In the last part of this work, we realized several arrays of aligned CNTs using different patterning techniques and we found that a possible way to achieve the highest field emission is to use e-beam lithography in order to control the growth of arrays of long (N5 µm) CNTs on Ni dots (b200 nm in size) and change the array pitch in the 10 µm range.

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