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In situ-grown carbon nanotube array with excellent field emission characteristics

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In situ catalytic thermal decomposition method was used for producing aligned multiwalled carbon nanotubes (MWNTs) in bulk quantities on stable and electrically conducting substrates. Very low turn-on electric fields of 0.75 V/μm and low threshold fields of $\sim$1.6 V/μm (for current density of 10 mA/cm^2) were obtained from the MWNT arrays grown on TiN substrate. Furthermore, large emission current densities of 1–3 A/cm^2 were obtained at reasonably low fields of less than $\sim$8 V/μm. These enhanced emission properties are tentatively attributed to the oriented and high-density nature of the emitting carbon nanotube structure and the high-conductivity, stable nature of the TiN substrate onto which the nanotubes are attached. © *2000 American Institute of Physics.* [S0003-6951(00)05325-0]

The recent discovery of electron emission from carbon nanotubes[1–9] has generated excitement since carbon nanotubes can serve as ideal, tiny electron emitters for developing efficient and inexpensive field emission devices such as vacuum microwave power amplifiers and flat panel displays. Several characteristics of carbon nanotubes suggest that they are suitable and promising for cold cathode applications since (i) they possess an inherently high aspect ratio (length/diameter ratio of >1000) with the resultant, large field amplification factor, (ii) they possess high chemical and mechanical stability, and (iii) they are capable of producing large current densities at modest, practical electrical field levels. Nanotube-based emission devices are also capable of exhibiting bright light emission for over 10 000 h.[5]

For field emission applications, the carbon nanotubes must be grown on electrically conductive substrates in order to be able to serve as a cathode and continuously supply electrons to the field emitter. The nucleation and growth of carbon nanotubes is conveniently achieved by a thin film deposition of a catalyst layer such as Ni, Co, and Fe on insulating substrates such as silica, alumina, or semiconducting substrates such as silicon. Typically, the initially continuous catalyst films are broken up into isolated islands whose average size is comparable to the nanotube diameter for nucleation of carbon nanotube growth. Thus, on insulating substrates, the electrical conduction (the continuous supply of electrons to the emitting tips) is mostly absent, either through the substrate thickness or along the substrate surface.

In spite of the encouraging progress in the carbon nanotube research, there is still a need for developing a synthesis method that is inexpensive and readily scalable to produce high-quality nanotubes for device applications. In particular, simple synthesis methods for preparing well-oriented nanotubes on highly conductive substrates suitable for field emission applications are lacking. For example, de Heer *et al.*[10] demonstrated field emission from thin films of aligned multiwalled carbon nanotubes (MWNTs) that were produced by drawing nanotube suspension through a ceramic filter (0.2 μm pore size). Li *et al.*[11] synthesized oriented MWNTs from the decomposition of acetylene at 700 °C over iron-nanoparticle-embedded mesoporous silica which is electrically insulating. High-purity aligned MWNTs were also produced between laser-etched tracks on cobalt films on insulating silica substrates from a catalytic decomposition of triazine at 1000 °C.[12] Large arrays of aligned MWNTs were grown normal to nickel-coated glass substrates by a plasma-enhanced hot filament chemical vapor deposition of acetylene and ammonia gases.[13] More recently, from prepatterned Fe-catalyst islands on porous silicon, Fan and co-workers[14] reported the growth of ''MWNT towers'' that showed good emission properties.

A common drawback with these methods[11–14] is that they require special processing of substrates or separate, predeposition of a catalyst layer on substrates in order to produce aligned MWNTs. We have recently reported a simple, inexpensive *in situ* method for preparing aligned MWNTs on electrically insulating substrates such as silica.[15] Our synthesis method is based on the catalytic decomposition of ferrocene–xylene mixture. In this letter, we report an *in situ* growth of aligned nanotubes on stable and highly conductive substrates of TiN, and discuss their excellent field emission properties.

In the two-stage reactor (described previously in Ref. 15) the xylene–ferrocene mixture (Fe $\sim$0.75 at. %) is continuously injected into the preheater (maintained at $\sim$200 °C) using a syringe pump. As the xylene–ferrocene vapors emerge at the outlet of the preheater a stream of Ar gas (with 10% hydrogen) sweeps the vapors into the furnace (maintained at $\sim$700 °C) where it is decomposed to produce high purity, aligned MWNT arrays on the inner walls of the furnace and the substrates placed inside the furnace. In a typical

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run, the silica tube reactor (inner diameter $\phi \sim 34$ mm) with a foot long preheater and two foot long furnace, are operated for two hours to produce ~0.4 g of high purity MWNTs for a xylene–ferrocene feed rate (R) of 1 ml/h. Under identical operating conditions, the combined wall and substrate nanotube material averaged ~1.85 g in a similar reactor with $\phi \sim 95$ mm and R~4.4 ml/h without noticeable degradation in the quality of the MWNTs. High resolution scanning electron microscopy (SEM) images and energy dispersive x-ray analysis of MWNT arrays produced by the method described in Ref. 15 suggest that the growth of the MWNT arrays begin after an initial deposition of an Fe layer on the silica substrates. Moreover, high resolution transmission electron microscopy (TEM) studies indicated good structural integrity of individual MWNTs with the most dominant outer diameter of ~25 nm. Further evidence for structural integrity was obtained from polarized micro-Raman spectroscopy.[16]

The field emission measurements were carried out at room temperature in a vacuum chamber with a 10^{-8} Torr base pressure. The experimental procedures for current density measurements were described in detail elsewhere.[17,18] Briefly, a voltage up to 2 kV was applied to a hemispherical molybdenum anode probe (radius of curvature $R \approx 250$ μm) which is 10–300 μm above the emitter surface. We used a translation stage in the vacuum chamber to control the distance between the anode and the cathode. A hemispherical probe approach is a better measurement technique than a parallel plate geometry because it avoids uncertainties caused by field enhancements at the edge of a planar anode or emitter, and it also allows easy measurements at many points on the sample. The emission current–voltage ($I-V$) characteristics were measured as a function of the anode–cathode distance (Z). At each distance, the anode voltage was raised from zero until the current density reached ~0.6 A/cm^2 and then decreased back to zero. The effective emission area (A) used for determining the current density was estimated as described in Ref. 8, and corresponds to an area within which $J \geqslant J_{\max}/2$, where $J_{\max}$ is the emission current density directly beneath the anode where the electric field is the highest. For $Z \ll 2R$, $A = 2\pi RZ(2^{1/n}-1)$, where $n = (V/I)(dI/dV)$. Typically, $n \sim 18$ for $J < 50$ mA/cm^2, decreasing gradually as the current density increases. The anode was then moved one step (3.3 μm) closer to the emitter surface, and the cycle was repeated.

While our thermal decomposition method[15] routinely produces well aligned MWNTs on silica, interestingly we found that the nanotube growth (aligned or unaligned) rarely occurred on polished metallic substrates, such as Mo, Ni, or stainless steel. This absence of nanotube growth may be related to the high mobility and lack of localization of carbon on the metal surface, or the difficulty of catalyst island formation due to the diffusional reaction and interfacial bonding between the Fe layer and the metal substrate at the furnace temperatures. We therefore embarked on a search for alternative *conducting* substrate materials that would allow nucleation and growth of aligned nanotubes.

The substrates utilized in the present investigation were of bulk ceramic type with the thickness of 1–3 mm. Various substrates studied here included conducting oxides (such as Mn–Zn ferrites, perovskite type La–Sr–Mn–O manganite and Y–Ba–Cu–O superconductor material), conducting carbides (such as WC, TiC), and conducting nitrides (such as TiN, ZrN, TaN). The oxide substrates were seen to be partially reduced and decomposed under our operating conditions, and no noticeable nanotube nucleation occurred. The carbide substrates produced much smaller number of nanotubes per unit substrate area than the nitride substrates. The best results for aligned nanotube growth were obtained for the TiN substrates (Fig. 1). TiN is a relatively stable material with excellent electrical conductivity (resistivity ~25 mΩ cm) and high melting point (~3200 °C), both of which are desirable for the stability of field emission cathode structure, especially for high current-density, high-power applications such as microwave amplifiers.

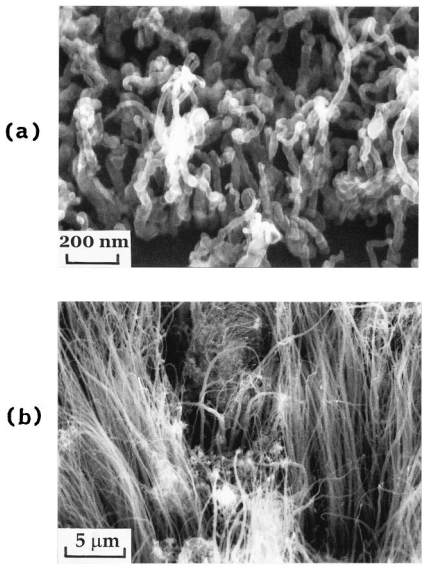

FIG. 1. SEM image of aligned MWNTs grown on (a) TiN substrates, (b) TaN substrates.

Shown in Fig. 1(a) is the SEM image (taken at an oblique angle, tilted by 30°) of the MWNT array grown on a TiN substrate from a thermal decomposition of xylene–ferrocene mixture at 700 °C for 15 min. A longer run time produces a similar microstructure except that the lengths of the MWNTs are increased. It is seen that a relatively uniform-sized MWNTs with ~40 nm average diameter are grown in an aligned fashion perpendicular to the substrate surface. The presence of Fe catalyst particle at the tips of the nanotubes suggest that the predominant growth occurs via the tip growth method.[19] The density of nanotube tips is relatively high, and is estimated to be about 30 per $(\mu\text{m})^2$ area, equivalent to $\sim 3\times 10^5$ per typical display pixel area of $(100\,\mu\text{m})^2$, or $\sim 3\times 10^9/\text{cm}^2$. The mechanism of nanotube alignment in the present work is not clearly understood. It may be due to the crowding mechanism[15] or due to the nucleation and out-growth of nanotubes from the pores[11] present in the TiN substrates. Further study is needed to understand the underlying mechanism(s) of the observed aligned growth. Figure 1(b) shows the MWNTs grown on the TaN substrate using the identical synthesis conditions noted above. The presence of well-aligned structure is evident, however, with a coarser structure with an average diameter of ~100 nm as compared to the ~40 nm diameter in the case of the TiN substrates.

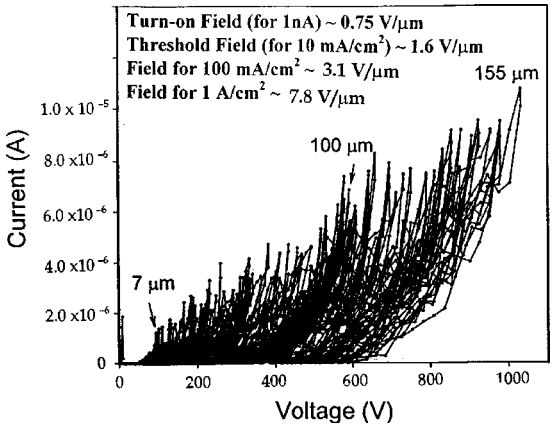

FIG. 2. Electron emission I-V curves for the MWNT array grown on TiN substrates.

The aligned MWNTs grown on the TiN substrate exhibit excellent field emission properties. Shown in Fig. 2 is the measured emission current as a function of applied voltage for a sample that was prepared at 700 °C in a 2 h run. Relatively smooth and consistent current–voltage ($I-V$) curves were obtained. Replotting of the data as $\log(I/V^2)$ vs $1/V$ indicates the Fowler–Nordheim type field emission behavior.[20] The turn-on field, as defined for an emission current of 1 nA, was less than 0.75 V/μm, which is one of the lowest turn-on field values that we have observed for several different types of SWNTs and MWNTs evaluated using the same experimental method. The threshold field (defined here as the field required to produce technologically useful current density of 10 mA/cm^2) was also low, being ~1.6 V/μm. The aligned nanotubes on TiN also exhibit very high field emission currents at relatively low applied fields; the field required to generate an order of magnitude higher emission current density of 100 mA/cm^2 was ~3.1 V/μm, and that for producing 1 A/cm^2 was ~7.8 V/μm. These high emission current densities and low threshold fields for the present MWNTs are comparable to or better than those for the SWNTs reported recently,[8] indicating that the MWNTs can be as efficient as the SWNTs in field emission.

Shown in Fig. 3 is the emission current density vs time at constant applied field of 6.3 V/μm (the applied voltage was 1000 V and the cathode–anode distance was 160 μm) for the MWNTs on TiN. The data was obtained under severe operating conditions, i.e., at high current density levels in order to provide a measure of stability/lifetime behavior for the field emission. As can be seen from the figure, the high emission current density of 1–3 A/cm^2 is maintained at the applied field for ~2 h, and in fact improved with time, which is interesting and deserves further investigation. The current density is then gradually reduced with time and stabilized after ~24 h at a level of ~110 mA/cm^2, which is still relatively high compared to 10 mA/cm^2. The eventual decrease of the emission current density seen in Fig. 3 after a few hours of continuous, high-current field emission may be caused by a number of different reasons, one possibility being the damage (by excessive resistive heating in the high current environment) in the nanotube structure near the emitting tips or the damage/change of the contact region near the bond interface of the nanotubes and the TiN substrate. Further studies are needed to fully understand the lifetime behavior of the carbon nanotube field emitters.

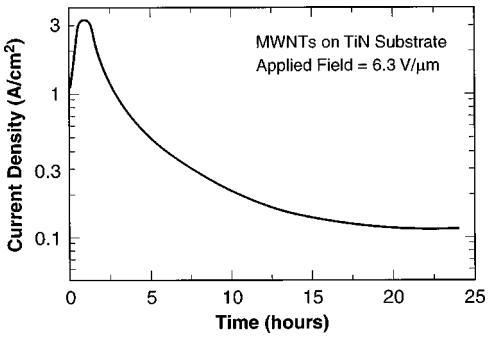

FIG. 3. Emission current density vs time at a constant applied field.

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