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# Direct growth of aligned carbon nanotube field emitter arrays onto plastic substrates

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The direct growth of vertically aligned carbon nanotubes onto flexible plastic substrates using plasma-enhanced chemical vapor deposition is reported. We show that individual lines and dots of free-standing 20–50 nm diameter nanotubes can be grown onto chromium covered commercially available polyimide foil. The scalable deposition method allows large area coverage without degrading or bending the sensitive substrate material. Field emission measurements show a low turn-on field (3.2 V/$\mu$m) and a low threshold field (4.2 V/$\mu$m). The result establishes a method of flexible field emitter fabrication, which is well suited for display production and integration of nanotubes into plastic electronics. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1630167]

Since the first observation of carbon nanotubes (CNTs),[1] literature has reported considerable progress in synthesis giving rise to a wide range of possible applications for their unique structure and properties. An inherent small tip radius, a high aspect ratio, combined with chemical inertness and mechanical strength make CNTs ideal field emission electron sources.[2,3] Even more defect-rich carbon nanofibers (CNFs) exhibit remarkable field-emission characteristics and good current stability.[4,5] Their high surface area makes CNTs also attractive for applications such as electrochemistry, electrodes for fuel cells, and supercapacitors.[6–9]

Numerous methods have been used to grow CNTs, including arc-discharge, laser ablation, and chemical vapor deposition.[10,11] However, only a few methods allow controlled growth directly on a substrate, which is important for many applications, especially as the individual manipulation of CNTs is difficult and expensive due to their size. Selective, aligned growth of CNTs on silicon and glass substrates has been demonstrated by plasma enhanced chemical vapor deposition (PECVD).[12–14] However, despite the high level of control, PECVD growth typically involves processing temperatures over 500 °C, which significantly limits the choice of possible substrate materials and integration processes.

The controllable growth of nanotubes on plastic substrates would open up many applications such as in fuel cells or field emission devices. Flexible CNT field emitter devices on low cost polymer substrates could so far only be realized recently by an indirect, solution based method.[15] Despite giving a flexible device structure, this approach does not allow a nanoscale definition desired for integrated semiconductor device structures.

Recently it was demonstrated that plasma enhancement enables carbon nanotube growth on silicon at substrate temperatures as low as 120 °C.[16] This letter reports the direct growth of vertically aligned carbon nanofibers and their nanoscale patterning on flexible plastic substrates. We show

that a dc glow discharge chemical vapor deposition system using acetylene as carbon precursor and ammonia as an etchant can be used to selectively grow CNTs onto sensitive polymer-based substrates without causing degradation or stress-related curvature. Apart from homogeneously covering large substrate areas, the Ni catalyst was patterned by electron (e)-beam lithography to create single lines or isolated free-standing aligned nanofibers. We further demonstrate that the as-grown CNFs exhibit a relatively low threshold field (4.2 V/$\mu$m) for electron emission, establishing a reliable method to fabricate flexible field emitters.

As flexible substrate material, we used 177-$\mu$m-thick, commercially available Kapton® polyimide foil (DuPont). Polyimides (PIs) are common in microelectronics as interlayer dielectrics or passivation layers and can be structured by plasma etching or laser ablation.[17,18] PIs are also available as negative type photoresist allowing various methods of pattern transfer. PI foils have been used as substrate material for flexible thin-film transistors,[19] demonstrating the compatibility with thin-film processing.

The aligned CNFs were grown using a dc PECVD system in a stainless steel diffusion pumped vacuum chamber with a base pressure below $10^{-6}$ mbar. A 70-nm-thick conductive Cr underlayer and a 6-nm-thick Ni catalyst were deposited by magnetron sputtering onto the polymer foil. Cr shows good adhesion on PI due to the formation of interface bonds.[20] The Ni catalyst was patterned either by disposable shadow masks for 10 $\mu$m feature sizes or by e-beam lithography using poly-(methylmethacrylate) as photoresist for 100 nm feature sizes.

The PECVD growth procedure is reported in detail elsewhere.[16] Briefly, the CNFs were grown at 200 °C, initiating a dc glow discharge plasma of $C_2H_2$ and $NH_3$ (ratio 30:200 sccm) by applying a fixed voltage of 650 V between the heater stage and the gas shower head (anode, 2 cm above stage). The temperature was measured with a thermocouple mounted on a polyimide substrate of equivalent original sample thickness. The stable discharge was maintained for 1 h at a total pressure of 1.5 mbar.

The dimensions and structure of the as-grown CNFs

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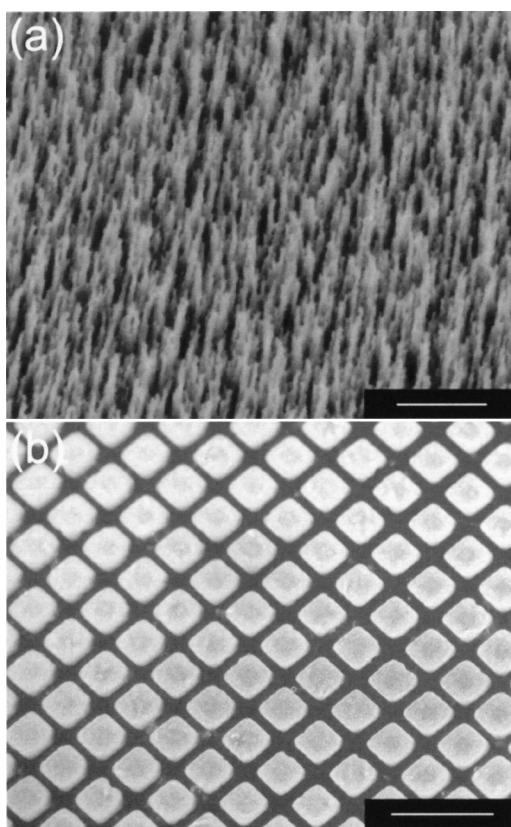
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FIG. 1. SEM photographs of CNF films grown at 200 °C, −650 V bias, $C_2H_2$:$NH_3$ flow ratio 30:200 sccm for 1 h from (a) unpatterned Ni and (b) Ni patterned by shadow masks onto Cr covered polyimide foil [scale bars: (a) 500 nm, (b) 10 $\mu$m].

were analyzed by scanning electron microscopy (SEM) (Jeol 6340 FEGSEM), Raman spectroscopy (Renishaw MicroRaman 1000) and high-resolution transmission electron microscopy (HREM) (Jeol JEM 4000EX, 400 kV). For HREM analysis the CNFs were removed from the substrate and dispersed onto Cu transmission electron microscopy (TEM) grids or lacey carbon grids. The field emission measurements were carried out in a parallel plate configuration at a pressure of $2 \times 10^{-7}$ mbar. Indium tin oxide coated glass was used as the anode, which was separated 500 $\mu$m from the sample by polytetrafluoroethene spacers.

Figure 1 shows SEM images of vertically aligned CNF films grown from unpatterned Ni [Fig. 1(a)] and Ni patterned by shadow masks [Fig. 1(b)] on Cr covered polyimide foil. Limited by the heater setup, we realized a homogeneous CNF coverage of several square centimeters of plastic foil. For plasma processing at low temperatures, the Cr covered polyimide foil did not show any bending and maintained its flexibility. Growth at substrate temperatures above 250 °C led to brittleness of the polymer and substrate curvature. The curvature is partly due to stress in the PI/Cr bilayer, as a single-sided sputtered Cr layer thicker than 150 nm bends the polymer foil even before processing. This effect can be avoided by double-sided Cr deposition.

Figures 2(a)–2(c) show SEM images of aligned CNFs grown from e-beam patterned Ni on Cr covered polyimide foil. The use of solvents during the e-beam lithography pattern transfer did not affect the substrate material. Single 100 nm wide lines and 100 nm diameter dots of Ni could be
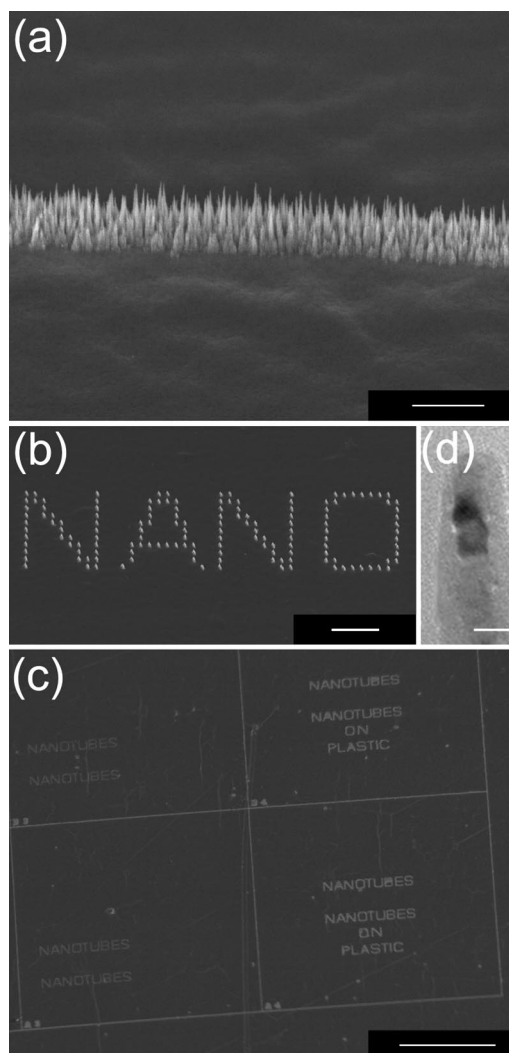


FIG. 2. (a)–(c) SEM photographs of vertically aligned CNFs grown from e-beam patterned single 100 nm wide lines and 100 nm diameter dots of Ni onto Cr covered plastic foil. (d) TEM image of as-grown CNF [scale bars: (a) 1, (b) 5, (c) 100 $\mu$m, (d) 15 nm].

patterned to create corresponding patterns of aligned fibers [Figs. 2(a) and 2(b)]. The high dilution of the carbon source gas by $NH_3$ minimized the detrimental deposition of amorphous carbon Raman spectroscopy showed the characteristic carbon D and G peaks on the patterned area, whereas no carbon signal was seen on the substrate in between, demonstrating the selectiveness of the deposition. The PECVD growth rate was 0.2 nm/s, which is similar to the growth rate on silicon substrates with an oxide diffusion barrier.[16] Previously, annealing at temperatures of the order of 600 °C was used to nanostructure the Ni catalyst layer into nucleation islands.[13,14] Here the substrate temperature reaches only 200 °C and any nanostructuring is mainly due to the plasma.

HREM analysis shows that the as-grown CNFs are 20–50 nm in diameter and have defective carbon walls [Fig. 2(d)]. An elongated Ni particle was found at the tip of the CNFs, suggesting a tip growth mechanism. At low temperatures, growth is dominated by surface diffusion of carbon on the Ni catalyst,[16] which, upon nucleation and the formation of the nanofiber, is detached from the substrate and carried upwards by the growing structure.

Figure 3 shows the field emission characteristics of a

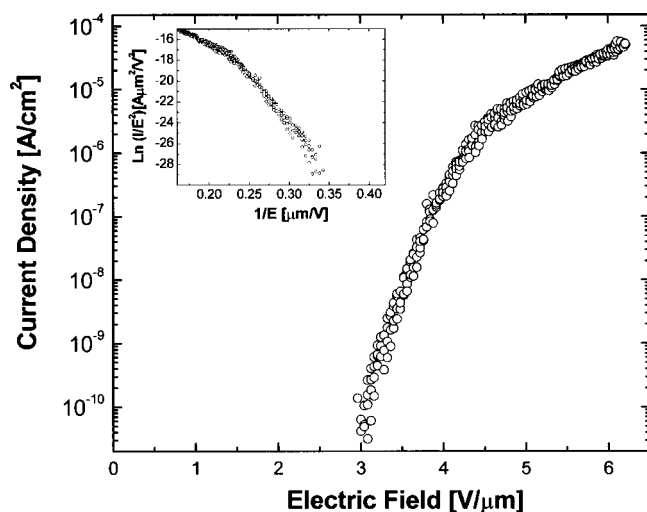Appl. Phys. Lett., Vol. 83, No. 22, 1 December 2003

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FIG. 3. Emission current density as a function of the applied electric field for the CNF emitters on Cr covered polyimide foil measured in parallel plate configuration. The anode area was 0.25 cm$^2$. The inset shows the corresponding FN plot.

square patterned CNF film on Cr covered polyimide foil measured with a 0.25 cm$^2$ anode area. The data were obtained by sweeping the voltage several times from 0 to 3200 V, measuring in the upsweep as well as in the downsweep. No hysteresis-like behavior was seen. The current density was calculated referring to the anode area. The $J-E$ curve in Fig. 3 shows a turn-on field, i.e., the field for which $J$ is $10^{-9}$ A/cm$^2$, of 3.2 V/$\mu$m. The threshold field, i.e., the field for which $J$ is $10^{-6}$ A/cm$^2$, is 4.2 V/$\mu$m. This emission behavior compares well to that observed for CNTs grown by PECVD on standard substrates.[21,22] As a reference, a Cr/PI film was tested at the same conditions. Compared to Fig. 3, the current measured for the reference sample is in the noise level at applied fields below 5 V/$\mu$m. Hence, it is possible to exclude substrate contributions to the observed emitted current.

The corresponding Fowler–Nordheim (FN) plot is shown in the inset of Fig. 3. The linear behavior of the curve confirms that the observed current is generated by field emitted electrons. An effective field enhancement factor $\beta$ calculated from the nonsaturated FN region is about 850, assuming a work function of 5 eV.[23] A purely geometric $\beta$ factor $(h/r)$ calculated from the height $(h)$ and the radius $(r)$ of the nanofibers is an order of magnitude lower ($\sim$20). This discrepancy, found for most CNT field emitters, is not yet fully understood. In a dense mat of nanotubes the emission occurs mainly from a few sharper or longer structures. Adjacent nanotubes screen the field enhancement of their neighbors. This limits the total emitted current. Compared to a solution based fabrication of flexible field emitter arrays using self-assembly,[15] PECVD allows accurate control of nanotube alignment, coverage, and density. Therefore, the field emission currents can be increased by creating a pattern of suitably spaced CNFs, in order to minimize electric field shielding effects.[22] Further, the nanoscale size definition and selectiveness of the deposition allows the integration of individual emitters or emitter arrays into active controlling circuitry.

In conclusion, we demonstrated the controlled, selective growth of vertically aligned carbon nanofibers on flexible plastic substrates. The PECVD method allows industrial upscaling for large area deposition. The as-grown CNFs show a low threshold field of 4.2 V/$\mu$m comparable to nanotubes grown at high temperatures. The result establishes a reliable and scalable method of flexible field emitter fabrication, which is well suited for display production and integration of CNFs into plastic electronics.

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