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Novel carbon nanotube network deposition technique for electronic device fabrication

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We present a novel dry and room-temperature method for the deposition of random carbon nanotube networks (CNTNs) onto various substrates. This method is based on natural charging of carbon nanotube (CNT) bundles in the gas-phase and their efficient deposition directly downstream of the synthesis reactor by means of an electric field. The density of the deposited CNTNs was controllably adjusted by varying the deposition time and the electric field strength. Application of this deposition technique for the fabrication of single-walled CNTN-based field-effect transistors (FETs), where a random CNTN serves as a transport channel, is presented.

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1 Introduction A carbon nanotube network (CNTN) is an emerging class of material that attracts growing research interest from the scientific and application perspective. An interconnected random network of single-walled CNTs (SWCNTs) retains remarkable properties of individual CNTs while providing processing capabilities of mass fabrication techniques. By ensemble averaging over a large number of individual tubes, the effects of tube to tube variations in position and chirality are reduced, yielding a CNTN with uniform properties, attractive for the low-cost and high performance device fabrication [1–4]. Nowadays there are several techniques of CNTNs fabrication including localized synthesis processes on the substrate, that require high growth temperatures, or remote synthesis processes, involving either transferring the CNTNs to the surface or depositing CNTNs from liquid dispersions. The latter requires CNT purification, dispersion in solutions using solubilization agents and, after the deposition, removing the surfactants. We present an alternative and very simple deposition method wherein SWCNT synthesis and assembly into random networks is accomplished in a single-step process. This method allows direct deposition of CNTNs

from the gas-phase at room temperature onto various substrates, including those that cannot stand high temperatures and aggressive acid environment, thus being compatible with sensitive electronic applications. Moreover, since the deposition technique is dry, the obtained CNTN consists of pristine chemically unmodified SWCNTs, that are not damaged during the CNTN preparation step. Therefore the presented technique is capable of providing the CNT material with its original properties, such as remarkable electrical conductivity, flexibility, and thermal conductivity.

2 Carbon nanotube network synthesis and deposition

2.1 Synthesis A floating catalyst (aerosol) chemical vapor deposition technique was employed for the synthesis of SWCNTs. The experiments were carried out in a vertical laminar flow reactor operated at ambient pressure. The schematic of the reactor can be seen in Fig. 1(A). SWCNTs were produced in the gas-phase via thermal decomposition of ferrocene ($FeCp_2$), forming catalyst nanoparticles, in the presence of carbon monoxide (CO).

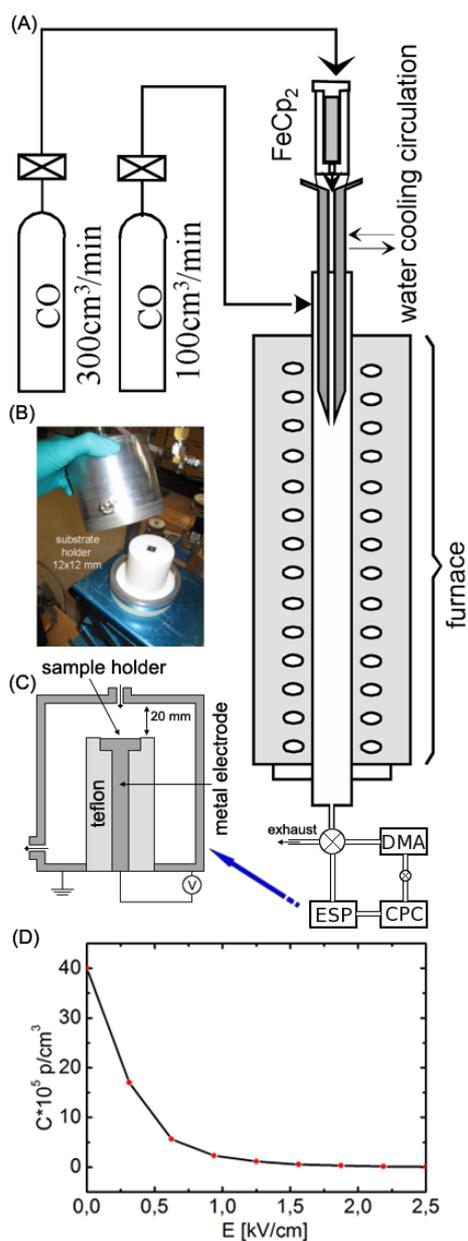phys. stat. sol. (b) 245, No. 10 (2008)

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Figure 1 (A) Schematics of the reactor for SWCNT synthesis. (B) Photograph of an electrostatic precipitator (ESP), and (C) its schematic. (D) The dependence of particle concentration in the ESP (measured by CPC) on the applied electric field.

The experimental set-up consisted of a precursor feed system, a furnace and CNT collection/analysis devices. In order to vaporise ferrocene a flow of CO carrier gas (300 cm³/min) was continuously passed through a cartridge containing the precursor powder mixed with silicon dioxide powder (Strem Chemicals, 99%, weight ratio $FeCp_2$: SiO_2 =1: 4) at ambient temperature with the flow direction downward. The precursor vapour was introduced

via water-cooled injection probe (held at constant temperature of 24 °C), into the high temperature zone of the reactor and mixed with an additional CO flow (100 cm³/min) to adjust the residence time and flow in the furnace. The peculiarity of the floating catalyst (aerosol) synthesis process is that the carbon precursor decomposition and CNT formation take place entirely in the gas-phase, on the surface of suspended in the gas catalyst particles. The on-line aerosol mobility number size distribution (NSD) measurements, using differential mobility analyser (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3022), were performed prior to the CNTN deposition in order to detect the SWCNT formation, and, by measuring the electrical mobility of aerosol particles in an electric field, distinguish small bundles of CNTs from catalyst particle aggregates [5]. By varying the growth conditions (i.e. growth temperature window) the average length of the nanotubes could be controlled (3 µm - 100 nm at the reactor temperatures of 800 °C-1150°C, respectively).

Figure 2 (B) displays a TEM micrograph of the as-grown SWCNT bundle, fabricated at 1000 °C in a floating catalyst reactor. From this figure it is evident that individual SWCNTs entangle with each other, forming CNT bundles to minimize their free energy, with few tubes in a bundle (up to 7 SWCNTs in a bundle), located parallel to each other. A SEM image of a CNTN deposited on a Si/SiO_2 surface is shown in Fig. 2(A).

Raman spectra of as-grown CNTs using 633 nm and 488 nm laser excitations confirmed that the nanotubes were single-walled, showing the sharp G-band and characteristical for a SWCNT radial breathing mode (RBM), as seen in Fig. 2 (C). Qualitatively different lineshapes of the G-band (1590 cm^{-1}) for the semiconducting and metallic tubes can be observed in Fig. 2(C): the red laser of 633 nm excites metallic tubes in that diameter range (the lower frequency spectrum presents a very broad Breit-Wigner-Fano lineshape) and the blue laser of 488 nm excites semiconducting tubes (both upper and lower frequency modes have a narrow Lorentzian lineshape) [6]. The intensity ratio of the D-band, associated with defects in carbon nanotubes, relative to the G-band is very low ($I_D/I_G = 1/30$). That indicates high quality of as-produced SWCNTs. The diameters of SWCNTs (d), that are in resonance with the laser used, can be calculated from the frequency of the RBM (ω_{RBM}) according to the relation $\omega_{RBM} = A/d + B$, where $A = 223.5$ cm^{-1} and $B = 12.5$ cm^{-1}, as deduced in [7]. For the laser of 633 nm the main RBM peaks appear in the range of 196-282 cm^{-1} and for the laser of 488 nm - in the range of 153-204 cm^{-1}, which correspond to the the SWCNT diameter ranges of 1.2-0.8 nm and 1.6-1.2 nm, respectively.

2.2 Deposition In our earlier studies it was shown that CNTs synthesized by the floating catalyst (aerosol) method form spontaneously-charged (92-99%) bundles carrying up to 5 elementary electrical charges [8,9]. On-line DMA measurements of ferrocene vapor de-
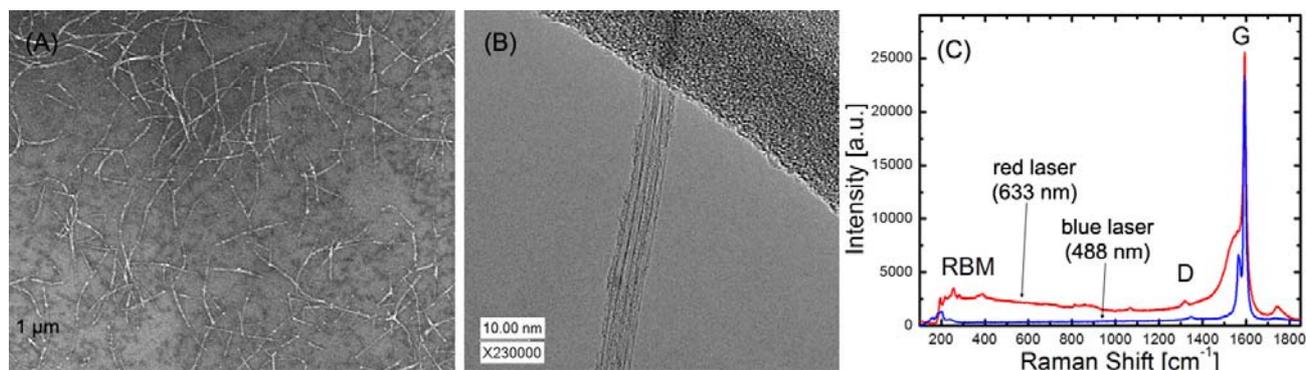
Figure 2 (A) SEM image of a CNTN on a Si/SiO$_2$ surface with an average density of ~ 4 CNT bundles/µm^2, synthesized at the reactor temperature of 1000 °C. (B) TEM image of a SWCNT bundle, fabricated at 1000 °C in a floating catalyst reactor. (C) Raman spectra of as-grown CNTs using 633 nm (red) and 488 nm (blue) laser excitations.

composition in CO atmosphere revealed the formation of positively- and negatively-charged SWCNT bundles, which was explained in the framework of aggregation processes leading to the energy release due to the minimization of the surface energy and emission of electrons and positive adsorbent molecules from the surface of CNTs [8]. This charging phenomenon of CNTs was used for the realization of an efficient CNTN deposition using an electrostatic precipitator (ESP) in order to collect CNTs directly from the gas phase downstream of the reactor at room temperature.

The ESP is a vertical cylindrical chamber typically used in the field of aerosol science to collect charged particles from the gas flow by means of a homogeneous electric field [10, 11]. The photograph and the schematic of the ESP are shown in Figs. 1(B) and (C), respectively. The substrate was placed on top of the horizontal electrode in the center of the ESP, mounted at a distance of 20 mm from the aerosol inlet and surrounded by an electrical shielding so to prevent an electrostatic field below the sample holder. The sample holder was made 12x12 mm. When introduced through a nozzle (with a diameter of ∼4 mm) into the ESP, the aerosol flow (here, small SWCNT bundles in the flow of the carrier gas) expands, reducing the velocity, and spreads out because the flow tends to go around the obstacle. Without an application of an electric field, CNTs in a carrier gas are driven only by the drag forces, due to the flow field, and Brownian motion. Therefore, very few nanotubes land onto the substrate surface and a CNTN deposition requires hours without an electric field. In order to guide CNT bundles towards the substrate, a constant electric field (with a typical strength of more than 2 kV/cm to provide conditions for the most efficient deposition, see Fig. 1(D)) was applied between the central electrode, where the substrate was placed, and the outer part of the chamber, where the aerosol flow enters the ESP.

Therefore random CNTN deposition at room temperature directly onto various substrates (e.g. Si, Si/SiO$_2$, polymer substrates, glass, quartz etc.) was achieved. The den-

sity of the CNTNs was adjusted in a wide range by varying the deposition time under certain operating conditions from several seconds, obtaining a low density CNTN close to the percolation threshold ($\sim 1 - 2$ CNT bundles/µm^2), to several minutes, resulting in a high density CNTN ($\sim 8 - 12$ CNT bundles/µm^2). Thus the electrical performance of the networks could be tuned in accordance with the percolation theory [3, 12, 13]. The CNTN density was estimated counting the number of CNT bundles in the ESP before and after an electric field application of a certain polarity by means of the CPC (TSI Model 3775), as shown in Fig. 1(D), taking into account that the concentration of negatively-charged CNTs is about six times higher than that of positively-charged CNTs at the synthesis temperature of 800 °C and two times higher at the temperature of 1000 °C, as was experimentally found in [8]. The estimated CNTN average density was verified by direct density measurements from SEM images. A SEM image of as-deposited CNTN, containing small SWCNT bundles with statistically calculated average length of 1.3 µm and density of ∼4 CNT bundles/µm^2 can be seen in Fig. 2(A).

3 Fabrication of field-effect transistors The technique presented here shows a simple and effective way to obtain nanotube networks as building blocks for various electronic applications. We have successfully applied it for the fabrication of SWCNT network-based field-effect transistors (FETs).

The CNTN was deposited onto a highly-boron doped Si substrate with a 100-nm thick thermally grown oxide, using the ESP downstream of the gas-phase synthesis reactor. Standard photolithography and lift-off were used in order to pattern CNTNs, forming the network along the transistor channel (see Fig. 3), and define source and drain electrodes (20 nm thick Ti/100 nm thick Au) on top of the network, aligned so to contact the CNTN channel. The device geometry was varied with the source-drain channel length L, ranging from 1 to 50 µm, and the channel width W, ranging from 10 to 200 µm. A SEM image of a typical
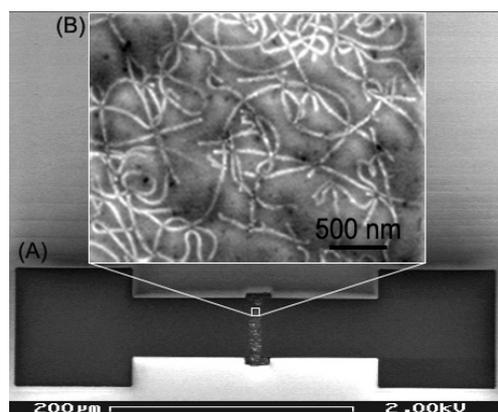
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Figure 3 (A) SEM image of a typical as-fabricated SWCNT network-based FET with Ti/Au electrodes and a CNTN as a transport channel ($L = 10$ μm and $W = 50$ μm). (B) SEM image of the CNTN between the electrodes.

Figure 4 I_{DS}-V_G characteristics for the three devices ($L = 50$ μm and $W = 50$ μm) with different CNTN densities varying from a dense network with >8 CNT bundles/μm^2 (curve (1)) to a more rarefied one with ∼1 CNT bundle/μm^2 (curve (3)). Curve (1) corresponds to the FET with an on-off ratio of ∼10, curve (2)-on-off ratio of 10^2 and curve (3)- on-off ratio of 10^4. Measurements were performed at room temperature, keeping $V_{DS} = 0.1$ V.

device with $L = 10$ μm and $W = 50$ μm is shown in Fig. 3.

Electrical measurements were carried out with an HP 4155A semiconductor parameter analyzer and microprobers in ambient conditions. The gate voltage was applied to the silicon substrate which acted as a back-gate for the transistor. High density random CNTNs, well above the percolation threshold (with the estimated average density of >8 CNT bundles/μm^2), exhibited semimetallic behavior with a weak gate response, yielding an on-off ratio of ∼10 (see Fig. 4, curve (1)). In these dense CNTNs metallic SWCNTs formed percolating paths across the source and drain electrodes thus the network exhibited high conductance under the application of all values of the gate voltage [1, 3, 14]. Whereas low density networks, near the percolation threshold (with the estimated average density of ∼1 CNT bundle/μm^2), showed p-type semiconducting behavior with an on-off ratio of ∼10^4 (Fig. 4, curve (3)). Therefore, by varying the density, the electrical performance of a CNTN could be changed from semiconducting to metallic, suitable for various electronic applications.

4 Conclusions We have developed an efficient dry and room-temperature method for the deposition of random CNTNs of various controllable densities onto substrates directly from the synthesis reactor. An electric field was used to guide the nanotubes, spontaneously charged during the floating catalyst (aerosol) synthesis, towards the substrate surface. This technique was applied for the fabrication of CNTN-based FETs on Si/SiO$_2$ substrates. The results demonstrated the feasibility of using the presented simple technique of CNTN deposition for the fabrication of low cost electronic devices.
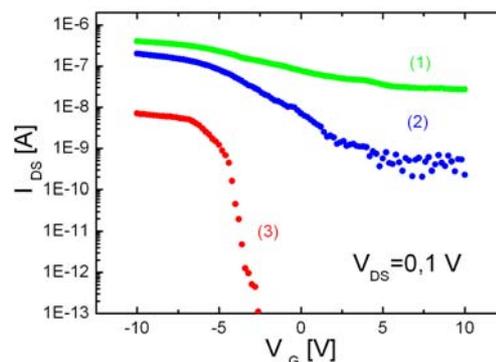
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