UV-assisted direct-writing fabrication and electrical properties of microfibre SWCNT/polyurethane nanocomposite based field effect transistors.

B. Aïssa[1] and M. A. El Khakani[1*]
R. D. Farahani[2], L. L. Lebel[2], and D. Therriault[2]

[1] National Institute of Scientific Research - Energy, Materials, and Telecommunications, 1650 Blvd. Lionel-Boulet, Varennes, Canada, J3X 1S2

[2] Center for Applied Research on Polymers (CREPEC) Mechanical Engineering Department, École Polytechnique de Montréal, P.O. Box 6079, Montreal, Canada, H3C 3A7.

*Electronic mail: elkhakani@emt.inrs.ca

We report on the fabrication and transport properties of single walled carbon nanotubes (SWCNT)/polyurethane (PU) nanocomposite microfibre based field effect transistor (FET). The UV-assisted direct-writing technology was used, and microfibers consisting of cylindrical micro-rods having different diameters and various SWCNT loads were fabricated directly onto SiO_2/Si substrates in a FET scheme. The room temperature *dc* electrical conductivities of these microfibers were shown to increase with respect to the SWCNT concentrations into the nanocomposite, and were about a ten orders of magnitude higher than that of the pure polyurethane, when SWCNT loads range from 0.1 to 2.5 wt. % only. Our results show that for SWCNT-loads $\leq$ 1.5 wt. %, all the microfibers behave as FET with a p-type transport. Their associated "on-current" and "on/off" switching ratios were found to be also dependant on the SWCNT concentrations. Effect of the microfiber diameters on the FET performances was also discussed

Flexible electronic devices are considered appliances of great potential. Due to their high-aspect ratio, small diameter, light weight, high mechanical strength, excellent electrical and thermal conductivities, and notable flexibility [1-3], carbon nanotubes (CNTs) are recognized as being the ultimate carbon fibres for high performances multifunctional composites, and are hence regarded as promising candidates for use in flexible electronic devices such as sensors, transistors, energy storage devices, etc.[4–6].

Since the development of a thin-film transistor (TFT) based CNTs as a channel[7], many researches on the fabrication of flexible CNT-FET devices have been performed. Nevertheless, several significant scientific and technologic challenges still to be overcome, particularly, the difficulty to obtain long nanotubes, in order to fabricate cost effective nanocomposite-based microdevices. In order to obtain CNT-micro/nanowires of sufficient length, one way would be to incorporate nanotubes inside the polymer matrix and form the fibres. However, one of the problems associated with such process is the dispersion of CNTs mats into the host polymer matrix due to the chemical incompatibility and the van der Waals forces between the two materials phases. Several attempts have been made to uniformly disperse CNTs into polymer composites such as functionalization, in situ polymerization, and dispersion of CNTs and polymers in organic solvents through sonification, etc.[8-10]

In this letter, we propose the fabrication of field effect transistor (FET) based on nanocomposite microfibers of polyurethane (PU) and single walled carbon nanotubes (SWCNT), directly on substrate, by using our developed UV-assisted direct-writing technology. Nanocomposite microfibers, consisting of cylindrical micro-rods having different diameters with various SWCNT loads were used as transistor active channel in the FET schemes. The room temperature *dc* electrical conductivity of these microfibres was shown to increase with respect to the SWCNT concentrations into the nanocomposite. Moreover, for the low SWCNT loads ≤ 1.5 wt. %, all the

measured microfibers showed a FET behaviours, where charges were transported by holes (i.e., p-type FET). Moreover, their associated "on-current" and "on/off" switching ratios were found to be also dependant on the SWCNT concentrations and on the microfiber diameters.

The SWCNT materials were produced by using our excimer UV-laser ablation method [11], and purified through refluxing in a nitric acid [12]. The grown CNTs were characterized by scanning electron microscopy (SEM) using a Jeol JSM-6300 F microscope. Bright field transmission electron microscopy (TEM) images were obtained using a Jeol JEM-2100 F FEG-TEM (200 kV) microscope. The Raman measurements were performed with the 514.5 nm (2.41 eV) using Renishaw Imaging Microscope Wire ™. Electrical transport properties were characterized at room temperature in air using Hewlett-Packard 4140B semiconductor parameter analyzer.

The nanocomposite material was a mixture of SWCNT and a polyurethane (PU) matrix (NEA123MB, Norland Products). Before mixing with the polymer, the weighted amount of SWCNT was first dispersed in a solution of 0.1 mM of zinc protoporphyrin IX (ZnPP, Sigma-Aldrich) following the method developed in [12-13]. Finally, the nanocomposite microfibers were fabricated by the ultraviolet-assisted direct-write (UV-DW) method [12-13] (see scheme Fig. 2 (a)).

Fig. 1(a) shows the typical SEM micrograph of the as-grown (AG) SWCNT materials, which consist of well defined and clear bundles of 10-15 nm-diam. Representative TEM micrographs of these bundles, seen in Fig. 1(b), reveal that those ropes are consisting of SWCNT, having a mean diameter of ~1.2 nm. A typical Raman spectrum (Fig. 1(c)) of the AG-SWNCT shows clear radial breathing mode (RBM) centered at 183 cm^{-1} and attributed to the strong presence of SWNCT having a mean diameter of 1.22 nm[14] (in total agreement with TEM observations). In addition, transversal modes (G and D-bands, centered at ~1600 and 1350 cm^{-1}, respectively) are also consistent with the typical signature of SWCNT, where the D peak is due to the presence of non-nanotubes carbon structures which are inevitably produced by the laser ablation process [11].

However, the rather high G-to-D peak intensity ratio indicates the overall high-structural quality of the laser produced SWCNT. Prior to their incorporation inside the polyurethane matrix, the laser-ablated material was purified [12-13]. Based on our previous observations, the whole incorporation process involving carboxylic groups graphing on SWCNT during purification, a solubilization using the ZnPP non-covalent functionalization, and the high shear mixing using the three-roll mixer were efficient to obtain a fairly uniform dispersion at the micro/nanoscopic scale[12-13]. Figure 2(a) shows an illustration of the UV-DW fabrication technology used to fabricate the nanocomposite filament (microfiber), directly between two metallic Ti/Mo electrodes (pre-deposited by pulsed laser deposition (PLD)) onto SiO_2/Si substrate. Doing so, their electrical properties can be directly investigated, in the FET scheme, where metal-electrodes are used as source and drain electrodes, and the p-doped bottom silicon substrate (resistivity of 0.01 ohms cm) as a back gate (as schematically illustrated in Fig. 3(a)).

Figure 2 (b) shows the relationship between the experimentally measured electrical conductivity of the fabricated nanocomposite microfibers with respect to their nanotubes contents. With an increase of SWCNT level, the conductivity gradually increases and is about a ten orders of magnitude higher than that of the pure PU, when SWCNT loads reach ~ 2.5 wt. %. The stepwise change in the conductivity of the composites is a result of the gradual formation of an interconnected network of SWCNT inside the microfiber, according to the well known percolation behaviour [15]. The best fit of our data to the known power law $\sigma \sim (p-p_c)^B$, (p is the weight fraction of CNT, p_c is the percolation threshold, and B is the critical exponent)[16] gives B = 2.1, (close the theoretical universal scaling value B=2)[17], and percolation threshold of $p_c \sim 0.08$ wt. %, which is found to be quite low, and can be attributed to the large one dimensional aspect ratio and relatively well dispersion of SWCNT into the composite material.

Prototypical FET based nanocomposite microfiber exhibit very promising characteristics rarely observed simultaneously. Figures 3 (b) shows the output characteristics I_{SD}-V_{SD} for various gate voltages V_G, obtained on single microfiber of 200 μm in diam. and SWCNT load of 0.5 wt. % . The recorded behaviour is similar to conventional p-type FET, and was confirmed by the corresponding transfer characteristics (I_{SD} as a function of the V_G, at V_{SD} = 10 V) shown in figure 3 (c). Indeed, the conductance (or I_{SD} current) of the device is seen to reach its highest values in the negative V_G range, corresponding to the "on-state" of the FET, and its lowest value, corresponding to the "off-state", for the positive V_G values, showing thereby an on/off switching ratio of 10^3 and an "on-current" as high as 70 μA. Similar results were observed on ten devices, which were recorded using the same device structure and obviously the same load of nanotubes.

For the same nanocomposite microfiber dimension (i.e., 200 μm-diam.), and for CNTs loads spanning the whole 0 –2.5 wt. % range, the obtained "on/off" ratios deduced from the transfer characteristics were reported in figure 3(a). First, no FET response was observed for the pure polymer containing only the ZnPP molecules, while a clear switching transistor was observed for the entire microfiber-based channel FET having a SWCNT-loads ≤ 1.5 wt. %. The "on/off" ratio is seen to reach its highest values for the lowest nanotubes charges. Indeed, for CNT loads of 0.1 and 0.2 wt. %, the correspondent switching ratio exceeds the exceptional value of 5 orders of magnitudes, while it is of 3, 2 and 1 orders of magnitudes for SWCNT loads of 0.5, 0.7 and 1.5 wt. %, respectively. Following this tendency, no FET behavior was observed for CNT contents starting from 2 wt. % and above. This is believed to be highly due to the formation of a percolated metallic CNT pathway within the composite, inhibiting thereby the FET response.

These excellent performances, especially with the lowest nanotubes loads, can be attributed to (*i*) the possible alignment of SWCNT into the polymer along the microfiber axis, during the extrusion of the nanocomposite, and (*ii*) the presence of exclusively narrower diameters in the

SWCNT (1.2 nm-diam.) corresponding to a relatively large band gap of ~ 0.7 eV [18], where indeed, it is well known that large tube diameters having a narrow band gap are difficult to turn off by the electrical gate field [19].

Finally, at the CNT load of 0.2 wt. % which corresponds to the highest "on/off" ratio (~10^5), various FET devices having a single nanocomposite microfiber channel of diameter ranging from 100 to 500 μm, were fabricated and measured according to the method described here above.

The measured "on-current: I_{ON}" –which correspond to I_{SD} taken at the fully-open FET channel-, have clearly shown that the smaller is the microfiber diameter, the lower is the FET's "on-current" (Fig. 4(b)). More importantly, regardless of the conductance value itself, -which depends on the number of effective active channels into the nanocomposite, nanotube chirality, etc.- I_{ON} was shown to vary proportionally to the quadratic value of the microfiber diameter (*d*), and hence to its lateral surface, matching perfectly the current flux thought a surface phenomenon. On the other hand, similar trend was observed when plotting the "off-current: I_{OFF}" of those FETs devices (which correspond to the fully-closed FET channel). This perfect similarity was shown to result to an "on/off" switching ratios almost constant (~10^5) with respect to microfiber diameter (Fig. 4(c)). In sum, shortening the channel diameter seems to not bring any further improvement in the transistor switching ratio, which is believed to result mainly from the ratio of the semiconducting to the metallic nanotubes that are effectively gated into the microfiber FET channel, rather than the dimensions involved. However, this observed trend has to be taken with a care, especially when recalling that the contact resistance at the microfiber/electrode interface plays a central role in the on- and off-current under measurement.

In conclusion, we have demonstrate a direct approach involving the UV-assisted direct-writing technology to prepare functional FET devices, where the transistor channel is composed of a nanocomposite microfibers of PU and SWCNT mats. In addition to the CMOS compatibility

without the need of additional masks to form the FET-channel between electrodes, and without any additional alignment processes, we have reported very promising characteristics of these devices, such an "on/off" ratio around 10^5, and I_{ON} as high as 70 μA. We anticipate that the UV-DW microfabrication method demonstrated here opens new prospects for the manufacturing of complex nanocomposite flexible devices for many technologic applications, especially for the future development of flexible FET and TFT based on polymer/SWCNT nanocomposite material.

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Figures captions:

Figure 1: (a) Typical SEM image of the excimer UV-laser grown SWCNTs; (b) representative TEM image of SWCNT rope. The inset shows a close-up view of the SWCNTs bundle; (c) typical Raman spectrum excited at 514 nm of our SWCNTs, where the RBM, D and G bands are identified.

Figure 2: (a) Schematic of the nanocomposite microfibers fabricated by the ultraviolet-assisted direct-write (UV-DW) process directly on pre-patterned substrate. (b) Relationship between the experimentally measured electrical *dc* conductivity and the weight percentage of SWCNT in the PU/SWCNT nanocomposite microfiber.

Figure 3: The experimental microfiber FET device is schematically depicted in (a) where the lower panel shows an angle SEM view of nanocomposite filament fabricated directly on SiO_2/Si substrate. (b) example of the Typical I_{SD}-V_{SD} output characteristics, at various V_G values, for the microfiber-based FET devices having SWCNT load of 0.5 wt. % and diameter of ~200 μm, with (c) their corresponding transfer characteristics ($I_{SD} = f(V_G)$ at V_{SD} = 10 V).

Figure 4: (a) Associated on/off transistor switching ratios of the microfiber-based FET devices as a function of the SWCNT-loads in the nanocomposite. (b) The experimentally measured "on-" and "off- current" of the microfiber-based FET devices, taken at a gate voltage of -50 and + 50 V, respectively, as a function of the microfiber diameter (*d*). (c) Plot of the corresponding on/off ratios as a function of microfiber diameter (*d*).