High-performance thin-film-transistors based on semiconducting-enriched single-walled carbon nanotubes processed by electrical-breakdown strategy

B. Aïssa a,b,*, M. Nedil c, M.A. Habib d, E.H. Abdul-Hafidh e, F. Rosei a

a Centre Énergie, Matériaux et Télécommunications, INRS, 1650, boulevard Lionel-Boulet, Varennes, Quebec J3X 152, Canada
b Qatar Environment and Energy Research Institute (QEERI), Qatar Foundation, P.O. Box 5825, Doha, Qatar
c Teleb Wireless Underground Communication Laboratory, UQAT, 675, 1ère Avenue, Val d'Or, Quebec J9P 1Y3, Canada
d Computer Sciences and Engineering Department, Yanbu University College, P.O. Box 30031, Saudi Arabia
e High Energy Physics Department, Yanbu University College, P.O. Box 30031, Saudi Arabia

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A B S T R A C T
Over the past two decades, among remarkable variety of nanomaterials, single-walled carbon nanotubes (SWCNTs) remain the most intriguing and uniquely well suited materials for applications in high-performance electronics. The most advanced technologies require the ability to form purely semiconducting SWCNTs. Here, we report on our strategy based on the well known progressive electrical breakdown process that offer this capability and serves as highly efficient means for selectively removing metallic carbon nanotubes from electronically heterogeneous random networks, deposited on silicon substrates in a thin film transistor (TFT) configuration. We demonstrate the successful achievement of semiconducting enriched-SWCNT networks in TFT scheme that reach On/Off switching ratios of ~100,000, on-conductance of 20 μA, and a subthreshold swing of less than 165 mV/decades. The obtained TFT devices were then protected with thin film poly(methyl methacrylate) (PMMA) to keep the percolation level of the SWCNTs network spatially and temporally stable, while protecting it from atmosphere exchanges. TFT devices were found to be air-stable and maintained their excellent characteristics in ambient atmosphere for more than 4 months. This approach could work as a platform for future nanotube-based nanoelectronics.

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1. Introduction

The development of high performance thin film transistor (TFTs) is a major challenge for materials community. There is a particular need to develop air-stable transistor channel for nanoelectronics to realize the benefits of advanced circuit design. Currently, advanced researches are developing TFTs using various organic and inorganic semiconducting materials for applications, such as flexible displays [1] and sensors [2], whereby the performance metric is not driven by Moore's law scaling as in conventional microelectronics but is rather determined by the low-cost per unit area and compatibility with large substrates. The most common TFTs use amorphous silicon (α-Si) or polysilicon as transistor channel [2]. Amorphous silicon TFTs satisfy the requirements of large area, low to-middle displaying speed, [3] good uniformity and stability, where the poly-silicon TFTs own mainly the advantage of high electronic mobility. However, these two types of TFTs have their critical limitation so that neither of them can be widely applied in more advanced displays. Amorphous silicon is sensitive to light but its carrier mobility is less than 2 cm2/V s, [4] which does not satisfy, for e.g., the requirement of the high-speed electronic devices [5]. Though polysilicon TFT’s mobility is large enough, it lacks flexibility and transparency, which is fatal for flexible devices. Metal oxide TFT is one of the innovations to meet the requirements of mobility and transparency simultaneously [6]. However, present metal oxide TFT is unstable because it is sensitive to light, temperature and water vapor. Also, it is unstable and can subject negative gate bias (V_G) stress effect under illumination which can result on a negative threshold voltage (V_T) shift (i.e., light induced negative V_T shift) [7]. In contrast, single-walled carbon nanotubes (SWCNTs) are well-known for their high mobility at room temperature, high On/Off
switching ratio, and small operation voltage [8–12]. They have been used for sensors [13–16] and digital circuits such as ring oscillators, simple logic gates (inverters, NOR, NAND) [17–21], decoders [17], SRAM [19] and delay flipflops [21]. Furthermore, carbon nanotubes (CNTs) are flexible materials, and their solution is compatible with printed electronics [5,6].

These attractive properties satisfy the requirements of thin film transistors, making CNTs materials among the most promising candidates as a high-performance TFT channel material. However, metallic (m) and semiconducting (s) nanotubes may be joined covalently [22,23] during synthesis and no methods exist for reliably preparing only (m) or (s) nanotubes, or nanotube junctions by a selective synthesis process. In addition to this lack of pre-synthesis' control, the nanotubes' tendency to bundle together, is also one of the main challenges to their large application for electronics. As a post-synthesis’ (m) and (s) nanotubes selection, an electrical breakdown of SWCNTs, i.e., "electrical-burning" process, has been proposed as a selective mechanism for preferentially eliminating metallic nanotubes among semiconducting ones as a bottom-up approach to build SWCNT circuits [24–31].

In the present work, we report on the application of a progressive electrical-breakdown to process an enriched-semiconducting population SWCNTs that are acting as transistor active TFT channel. The aim is obviously not to demonstrate again the efficiency of such a process – which is known to be dependent on the nanotube's morphological and structural properties together with the distribution of metallic to semiconducting nanotubes within the same network – but focus is mainly put on the qualitative and quantitative study of the obtained performances. Indeed, electronic performance, rarely observed all together, such as an On/Off transistor switching ratio up to $10^6$, an on-conductance of 20 μA, a subthreshold swing of less than 165 mV/decade were obtained. Subsequently, the obtained TFT devices were then protected with thin film poly(methyl methacrylate) (PMMA) to keep the percolation level of the SWCNTs network spatially and temporally stable, while protecting it from atmospheric environment influences (e.g., adsorption of hydrocarbons molecules, humidity etc.). TFT devices were found to be air-stable and maintained their excellent characteristics in ambient atmosphere for more than 4 months. This approach could work as a platform for future nanotube-based nanoelectronics.

2. Experimental

SWCNTs were synthesized by using the developed plasma torch technology (details can be found in Ref. [32]). This process produces SWCNTs where the growth takes place in the gas-phase. The as-grown sootlike SWCNTs were subsequently purified by an acidic treatment through refluxing in a 3M-HNO$_3$ (Sigma Aldrich) solution [33].

The plasma-grown CNTs were characterized by scanning electron microscopy (SEM) using a JEOL JSM-6300 F microscope and bright field transmission electron microscopy (TEM) using a JEOL JEM-2100 F FEG-TEM (200 kV) microscope. Raman measurements were performed with the 514.5 nm (2.41 eV) laser radiation of an Ar$^+$ laser focused onto the sample with a spot diameter of 1 μm (fieldRaman spectroscopy, Renishaw Imaging Microscope Wire$^TM$), and to prevent the modification of the sample (photodecomposition), Raman scattering was excited with a power normally not exceeding 1 mW. Raman spectra were taken with a backscattering geometry, at room temperature in 100–2000 cm$^{-1}$ region. Transport properties were measured at room temperature in air with a semiconductor parameter analyzer HP4155C, Agilent Technologies.

Fig. 1. (a) Typical SEM micrograph of the as-grown SWCNT materials. Solid arrows indicate the residual metal catalyst. Dashed arrows indicate concomitant plasma grown C-nanostructures. (b) Representative TEM images of SWCNT rope showing individual nanotube having a 1.2 nm-diam. The inset shows the histogram of the SWCNT diameter distribution.

3. Results and discussions

Fig. 1a shows a SEM micrograph of the as-grown SWCNT materials, which mainly consist of densely entangled SWCNTs bundles having diameters ranging from few nm up to ~15 nm. The bundles are often twisted and looped. Moreover, other graphitized carbon nanostructures and amorphous carbon are inevitably produced by the torch plasma process. Some of these C-nanostructures are visible in the SEM micrograph (dashed arrows shown in Fig. 1a), together with residual Fe metal catalyst particles (indicated by solid arrows in the figure). High resolution TEM micrographs of these bundles are displayed in Fig. 1b, revealing that they are consisting of SWCNT with individual diameter is in the nanometer range (SWCNT-diam. of ~1.2 nm were the most observed in the present case as shown by the statistical histogram in the inset of Fig. 1b). These SWCNTs-bundles were often found to length few μm leading thereby to SWCNT having an aspect ratio over three orders of magnitudes.
Structural information on the diameter of nanotubes in a given sample can be directly obtained by analyzing Raman spectra, particularly in the low frequency region where the radial breathing mode (RBM) occurs. A typical Raman spectrum (Fig. 2) of the as-grown SWCNTs shows a clear RBM centered at 186 cm\(^{-1}\). This RBM is seen to be intense and very narrow, a typical characteristic of the high quality SWCNTs material. The frequency positions of the RBM vibrational mode can be used to determine the nanotubes' diameters by means of the relationship reported by Bandow et al. [34]:

\[
d_i(\text{nm}) = \frac{223.75}{d} \text{ (cm}^{-1}\text{)}
\]

where \(d_i\) and \(w\) are the diameter of nanotubes and the frequency of the RBM vibrational mode, respectively. Our SWCNTs are found to have a narrow diameter distribution centered around 1.20 nm, in total accordance with the real space observations by TEM. The RBM band consists rather of four main components (by the RBM peak deconvolution) at 177, 186, and 197 and 208 cm\(^{-1}\) (the 186 cm\(^{-1}\) peak being the most prominent one, as shown in the inset of Fig. 2 and represents almost 60% of the peak area). These peaks can be assigned to nanotube diameters of 1.26, 1.20, 1.13 and 1.07 nm, respectively [34]. On the other hand, according to the well known diameter–chirality dependence formula [35] and by considering all the possible \((n,m)\) chiralities [namely, (5,13), (13,5), (4,13), (13,4), (4,12), (12,4), (14,1), (114), (3,12), (12,3)] for the four nanotube diameters identified above, we find that almost 80% of these nanotubes are expected to be semiconducting, especially if the occurrence of the nanotubes is weighted, for example, by the percentage of their associated RBM peaks areas. It is worth noting here that even if the quantification of the electronic population of the nanotubes is habitually achieved by optical absorbance process, resonance Raman scattering analysis could also permit to have an accurate idea about the nanotube's species (for more details, see Ref. [36]). In the present case, systematic Raman scattering mapping was conducted on ten different batches of SWCNTs mats. The obtained % is found much higher than the statistically expected 66/33% of s-CNT/m-CNT (which is obtained when all nanotubes diameters and associated chiralities are produced by the same growth process). In fact, the ratio of s-CNTs to m-CNTs has been shown to be growth process dependent. For examples, Jorio and coworkers [36] reported a semiconductor-to-metal ratio of 11:1 (i.e., ~92% of s-CNT), while Yiming et al. [37] showed that ~90% of their nanotubes are semiconducting. However, it's worth mentioning here that even if all diameters determined by Raman scattering do agree perfectly with those observed by TEM, these results have to be taken with high care, since, ideally, the whole Raman wavelengths should be involved (from theoretically viewpoint, the entire UV-IR light spectrum) to point-out all the existing diameters and all their corresponding chiralities.

In addition, the transverse modes (G and D bands, centered at 1600 and 1350 cm\(^{-1}\), respectively) are also consistent with the typical signature of SWCNTs, where the D peak is due to the presence of other carbon structures which are inevitably produced by the torch plasma process as observed earlier. However, the rather very low D-to-G peak intensity ratio of 0.01 indicates the overall high structural quality of the as-produced SWCNTs. On the other hand, a lineshape analysis of the tangential G-band feature for semiconducting SWCNT bundle, showing that only two components are present, where both the higher (1580 cm\(^{-1}\)) and the lower (1530 cm\(^{-1}\)) frequency components having a Lorentzian lineshape (since the excitation of low frequency optical plasmons in the metallic nanotube is responsible for the peak known as the Breit–Wigner–Fano (BWF) line shape in the G-band Raman spectra) [38]. However, here again, and as discussed above, this information has to be taken with care, since up to now, it has been well accepted that optical spectra (absorption, resonance Raman scattering etc.) are dominated by absorption/emission of light polarized parallel to the tube axis, involving transitions between electronic states at van Hove singularities (VHSs) in the joint density of states that are only in resonance with the excitation light wavelength (514.5 nm in the present case) [39], and then other possible diameters having different chiralities and hence different electronic character could be also present in the SWCNTs materials.

All the TFT devices were fabricated on SiO\(_2\)/Si substrate (Si resistivity below 0.01 Ω cm and thermally grown SiO\(_2\) oxide of 100 nm-thickness). The purified SWCNTs were first ultrasonicated in dimethylformamide (1 mg/ml) solution for 5 h to dissolve the SWCNT bundles. The solution was then centrifuged at 13,000 rpm for 20 min to select well-dispersed, narrow bundles of the SWCNTs. The centrifuged solution was then drop (10 μL) casted on the SiO\(_2\) surface (held at 50°C for solvent evaporation). Ti/Au (20/180 nm) drain, source and back-gated electrodes were then deposited by PLD (pulsed laser deposition, using ArF excimer laser, 193 nm) in a TFT scheme (Fig. 3). Finally, a thin film of PMMA (Miller-Stephenson Chemical Co., Inc.) was directly deposited (by drop casting) onto the nanotubes network, to spatially maintain the SWCNTs' percolation distribution and to protect the TFT active channel from long term oxidation. This latter detail was found to be the key element for the air-stability and long-term reproducibility of electrical behavior. The channel length and width were initially designed to be 10 and 50 μm, respectively.

To selectively remove the metallic-SWCNTs that could be present either within the same bundle of SWCNT and/or interconnected with semiconducting ones (see schematic of Fig. 3c), we introduced a progressive electrical breakdown process. Hereafter, we discuss quantitatively and qualitatively the device characteristics achieved during the electrical-breakdown procedure. The On/Off transistor switching ratios show significant improvements but were found to be inevitably accompanied by significant degradation of the ON-current. This issue is described in detail hereinafter.
Fig. 3. (a and b) Schematic of the random SWCNT network back-gated TFT assembly. (c) Schematic of the possible distribution of m-CNT/s-CNT in the SWCNTs mats.

Fig. 4a and b shows the linear and semi logarithmic plots of a sequence of transfer characteristics (conductance $G$ as a function of gate voltage $V_G$) as a function electrical-breakdown steps. The gate voltage $V_G$ was first fixed at 50 V to inhibit the p-type s-SWCNTs, and then the source-drain voltage ($V_{SD}$) was incremented by a step of 250 mV from 0 to 100 V. This gives a total of 400 iterations to reach the final $V_{SD}$ value. This process is repeated several times. Comparatively to the original channel characteristics (i.e., before the breakdown process), the On-conductance is reduced by typically 230 μS, which is accompanied simultaneously by an increase of the On/Off switching ratios of almost 5 orders of magnitudes (see Fig. 4c), consequence of a selective removing of m-SWCNTs. The burning of metallic nanotubes has a direct effect on the On-state conductance as well, which was found to be reduced beyond the 90% (from 250 to 20 μS). This result would not be expected if only the metallic SWCNTs were removed, leaving all semiconducting SWCNTs intact. Instead, we conclude that some s-SWCNTs are also removed by the process. The unintended removal of semiconducting nanotubes can be due to several causes such as variation in contact resistances for each SWCNT, screening of the gate field by charge defects and adjacent SWCNTs, and the chirality-dependent breakdown temperature [40]. Moreover, in a random network, the presence of a highly resistive metallic SWCNT can result in
Fig. 5. Experimental variation of the TFT threshold voltages with respect to the On/Off switching ratios. The inset indicates the evolution of the subthreshold swing $S$ as a function of the TFT threshold voltages.

Fig. 6. Steps of the burning process of the metallic nanotubes contents in the TFT network. (a) Quantification of the On-conductance decrease and (b) the corresponding loss of the metallic SWCNTs content as a function of the breakdown operation time. (c) Evolution of the TFT On/Off transistor switching ratios as a function of the intensity of the breakdown electrical field.

The first observed On-conductance loss of 60 $\mu$S and the 35 $\mu$S one recorded for the Off-conductance-state seems to happen when a large amount of metallic nanotubes (which is present in the TFT network) burn simultaneously. Besides the decrease of the current (conductance) saturation value, the sequence of the step-by-step decrease in Fig. 6a and b shows nonlinearity as m-SWCNTs are removed. The partial electrical-breakdown of a SWCNT at constant voltage proceeds in a series of discrete steps that likely correspond to the loss (/burning) of fixed amount of metallic nanotube within the bundle and/or the metallic bundle within the network. This step-by-step decrease also indicates that at high bias all the SWCNT bundles contributed to the transport and the same amount of m-SWCNT is burning at each step. The final decrease of 15 $\mu$S (On-state) and 1.5 $\mu$S in the Off state could mean that the process has reached its limit where no more m-SWCNT could be burned. Finally, at fixed burning time corresponding to 1 s, an electrical
field varying from 2 to 200 kV/cm was applied at the source/drain channel. The corresponding On/Off switching-ratios were found to systematically increase with respect to the electrical field-intensity and hence to the amount of the m-SWCNT that were effectively burnt in the TFT channel (Fig. 6c).

Finally, the SWCNTs arrays were then incorporated into the polymer matrix. A thin film of PMMA was directly deposited (by drop coating) onto the nanotubes arrays. The SWCNTs/PMMA matrix was then cured for 1 h at 90 °C under atmospheric conditions. Our microscopic observations (SEM and optical, not shown here) show that not just the vacant voids regions, but the entire surface of the laterally SWCNTs network has been coated with a thin coating of PMMA, without any apparent disruption, suggesting that high intercalation of the PMMA polymer into the SWCNTs network was successfully achieved. Electronic performances of TFT devices for which the channel network are coated with PMMA were systematically recorded and compared to those measured under air.

Fig. 7 shows the transfer characteristics of TFT with and without PMMA coating, taken at day 1 and after 1 and 4 months. All the measured TFT characteristics were found to achieve long-term stability operation under ambient conditions (i.e., within a maximum fluctuation of less than 4% after more than 4 months duration time while the unprotected TFT shows large fluctuations. It is worth noting at the end, that the choice of a random network instead of aligned arrays was dictated, among other reasons, by the low degree of complexity of the TFT elaboration. We have shown that SWCNTs are particularly suitable for electronic applications with demanding requirements. The main challenges in developing a technology based on transistor devices that each incorporates an individual SWCNT are to overcome: (i) the electrical heterogeneity of as-synthesized SWCNTs, in which the properties depend on the structure and diameter of the nanotube, (ii) the high impedances and low current outputs associated with single SWCNT, and (iii) difficulty in directed assembly of each SWCNT, as required for deterministic integration into circuits. An alternative to face these challenges involves the use of effective thin films consisting of large numbers of SWCNTs in the form of random networks or aligned arrays. In contrast to the more widely explored single tube strategies, in the present work, each device incorporates thousands or tens of thousands of SWCNTs. Obviously, films based on random networks are distinguished by the ease of fabrication, and could in fact be used to form transistors and simple circuits (e.g., logic gates). Such an approach might represent a viable route to a technology due to statistics that minimize the device-level effects of electronic heterogeneity in the SWCNTs, the large active areas and high current outputs provided by the large numbers of SWCNTs in each device, and relaxed requirements of precise spatial position or orientation of any individual tube in the film.

Those based on aligned arrays however offer the same advantages cited above with the exception that they are in fact more complex to elaborate and need often additional post synthesis process. However their electronic performances are more reproducible.

4. Conclusions

In summary, we have shown the engineering of electronic population in random networks of SWCNTs for high performance TFT, by means of progressive electrical-breakdown process that selectively burn the metallic CNT content in the transistor channel and leading thereby to the fabrication of high mobility TFTs devices. The transistors exhibit excellent performances. We then demonstrated that by protecting the active SWCNTs channel from atmosphere exchanges with thin film PMMA, the corresponding TFT devices are air-stable and maintained their excellent characteristics in ambient atmosphere for more than 4 months. This is a promising approach to realizing high-performances nanoelectronic devices based CNT.

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References


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1375. 356–359.

043121-(1–4).

084313-(1–9).

In the present work, all the possible chiral indices were calculated using Matlab® solution software.

3717–1875.

1.56–1.61.

971–974.

11774–11775.

356–359.

1783–1875.

295202.