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Incorporating aligned carbon nanotube electrode arrays in organic thin-film transistors

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ABSTRACT
We introduce a very simple technique to obtain aligned carbon nanotube arrays tested in organic thin-film transistors based on poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) as the organic semiconductor. The technique to prepare aligned CNT electrode arrays was simple and resulted in organic thin-film transistors with a higher drain-source current and lower threshold voltage proving their effectiveness as injection electrodes. We believe that the aligned carbon nanotube electrode array can find important applications in organic microelectronic and biosensor devices.

Charge carrier injection at the organic semiconductor/metal electrode interface has an important impact on the performance of organic electronic devices that can limit the capacity to scale down devices. Carbon nanotubes (CNTs) are ideal candidates as electrode materials in organic electronics because of their high electrical conductivity, chemical stability and good mechanical properties.CNT electrode materials have been used in several devices such as transistors, light-emitting diodes and photodetectors. Better charge carrier injection with respect to gold electrodes has been achieved by incorporating carbon nanotube electrode arrays in transistors based on: pentacene, copper phthalocyanine, phenyl-C61-butyric acid methyl ester (PCBM), titanyl-phthalocyanine (TiOPc), poly-3(hexylthiophene) (P3HT) and P3HT/PCBM blends as the organic semiconductor, proving the efficacy of CNT to inject both electrons and holes charge carriers.

The improvement in charge carrier injection has been attributed to the favorable shape (one dimensional structure) and chemical compatibility of CNT/organic semiconductor interfaces, due to its validity over various organic semiconductors, belonging to different class of materials (polymers and small molecules) and deposited by different methods (via solution or vacuum-based deposition techniques). For example, such favorable shape can promote tunneling injection across a Schottky barrier contact, where the electrode workfunction mismatches the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) levels of the organic semiconductor. Recent studies conducted by Hamed Khoshnevis et al. show possible correlations with the CNT structure-relaxation and its improved mechanical viscoelastic properties. Indeed, current trends in micro- and nano-composites are focusing on the mechanical and functional reinforcement, not only in terms of mechanical properties but also electrical/thermal conduction, and optical properties.

In this work we investigate the effect of the CNT alignment morphology in organic thin-film transistors (OTFTs). A simple method was developed to incorporate aligned SWCNT electrode arrays into an OTFT structure. The CNT structure morphology from this method was compared with an alternative method reported in the literature, that results in non-aligned carbon nanotube electrode arrays. The OTFT structure was completed employing poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), as organic semiconductor and tested with conventional transistor output and transfer characteristics. The method employed to prepare aligned CNT electrode arrays was simple and resulted in OTFTs with lower threshold voltage and higher drain source current. The organic semiconductor MEH-PPV
was chosen for its well known electroluminescent properties\textsuperscript{21} that aims to the possibility to study its light-emitting properties as a future work.

**EXPERIMENTAL SECTION**

The OTFT structure (Fig. 1a) consisted in a bottom gated, bottom contacted configuration employing a highly doped silicon wafer (conductivity > 200 S/cm), with 250 nm of thermally grown SiO\textsubscript{2} (Addison Engineering, Inc.), as the gate electrode and dielectric, respectively.

A dense network of single wall carbon nanotubes (SWCNTs) was deposited following the filtration method,\textsuperscript{9,23} 7 ml of 2% sodium cholate (aq) dispersion of single walled CNTs (1 × 10\textsuperscript{8} mg ml\textsuperscript{-1}) was filtered through an amino-cellulose filter. The filter was subsequently set on top of Si/SiO\textsubscript{2} substrate and dissolved in a beaker containing acetone for ca 30 mins. The deposition of CNTs was completed by rinsing the substrates with acetone, isopropyl alcohol and water followed by gently drying with N\textsubscript{2} flow.

Photolithography lift-off technique was employed to deposit and pattern the Ti/Au (5 nm/40 nm) electrodes with concentric geometry to circumvent parasitic currents.\textsuperscript{10} The interelectrode distance ($L$, without considering the CNT extension into the channel) was 40 $\mu$m and the width was 2000 $\mu$m.

A vacuum annealing of the CNTs at 500 °C for 1 h at 4 × 10\textsuperscript{-6} mbar atmosphere was carried out to reduce the contact resistance between the metal electrodes and the CNTs.\textsuperscript{22}

Two methods were employed to remove the CNTs from the transistor channel. The first method consisted in aligned photolithography followed by a sequential sonication in deionized water and MF319 (Microchem) developer solution in two consecutive steps of two min each, resulting in aligned CNT electrode arrays, possibly due to the effect of the polar solvent and the ultrasonic waves on the CNT natural preferred arrangement, aligned vs non-aligned. The other method was achieved through photolithography and reactive ion etching with oxygen plasma resulting in non-aligned CNT electrode arrays. The structures where cleaned in sequential ultrasonic baths in remover PG, acetone and isopropanol for 5 min each, previous to the deposition of the organic semiconductor.

The transistor structures were completed by spin-coating (1000 rpm, 1 min) a solution of MEH-PPV (Sigma Aldrich, M.W. 55 000 Da) in toluene (5 mg ml\textsuperscript{-1}) resulting in a MEH-PPV layer with typical thickness of 40 nm.

The morphology of the structure was investigated (Figure 1 b, c) using Atomic Force Microscopy (AFM, Digital Instruments Dimension 3100) with a Si cantilever (radius < 10 nm), in tapping mode, in ambient conditions. Thin-film deposition and transistor characterization were carried out in a N\textsubscript{2} glove-box (H\textsubscript{2}O, O\textsubscript{2} < 1 ppm). The transistor electric characteristics were measured using a B1500A Agilent semiconductor parameter analyzer.

### RESULTS AND DISCUSSION

The CNTs extension into the channel was 1 $\mu$m and 4 $\mu$m for the aligned and non-aligned CNT electrode array structures (Figs. 1b and 1c). Although it remains unclear how the geometry of the electrodes affects the performance of the resulting transistor, a slight yet noticeable improvement with aligned CNT electrodes was visible in the transistor electric characteristics.

The electrical output and transfer characteristics of the MEH-PPV OTFTs, of aligned and non-aligned CNTs electrode arrays, showed a typical p-type unipolar behavior (Fig. 2a–2d). The shape of the output curves (Fig. 2a and 2c) in the linear region indicates an Ohmic behavior despite the work function mismatch between gold and CNTs with respect to MEH-PPV HOMO and LUMO levels (work function of Au and CNTs is located at -4.7,\textsuperscript{24} and -4.6 eV,\textsuperscript{25} respectively vs. vacuum level; and the HOMO and LUMO levels of MEH-PPV are located at -5.07 and -2.9 eV, respectively vs. vacuum level; and the HOMO and LUMO levels of MEH-PPV are located at -5.07 and -2.9 eV, respectively\textsuperscript{26}). The threshold voltage ($V_{\text{th}}$), deduced from the extrapolation at y=0 of the square root of the transistor current in the transfer curves at saturation, was 31 V for transistors with aligned CNT and 35 V for the non-aligned structures. The field effect mobility, deduced from the transfer curves at saturation\textsuperscript{27} was 3.1 × 10\textsuperscript{-6} and 4.7 × 10\textsuperscript{-6} cm\textsuperscript{2}/V·s, for the aligned and non-aligned CNTs transistors. The field effect mobility values here estimated are lower than the ones reported in the literature for MEH-PPV, from 10\textsuperscript{-5} to 10\textsuperscript{-4} cm\textsuperscript{2}/V·s,\textsuperscript{28,29} which can indicate the presence of charge carrier trapping due to electronic defects in the MEH-PPV film. A higher drain and source current and lower threshold voltage was found in aligned CNT with respect to the non-aligned array structure transistors demonstrating the applicability of the present method to deposit and pattern carbon nanotube electrode arrays to improve charge injection in organic thin-film transistors. We are currently investigating small molecule semiconducting channel materials deposited through vacuum sublimation and other techniques in order to further advance the device electric performance.

![FIG. 1. Structure of OTFTs with carbon nanotube electrode arrays; (a) lateral view schematic, (b) atomic force micrograph of non-aligned carbon nanotube electrode arrays, RMS roughness ($r_{\text{rms}}$)=1.26 nm; and (c) atomic force micrograph of aligned carbon nanotube electrode arrays, with $r_{\text{rms}}$=2.2 nm.](image-url)
CONCLUSIONS

CNTs are ideal electrode materials in organic electronics. A new and simple method to deposit aligned CNT electrode arrays from solution was introduced and used to investigate the effect of CNT morphology alignment in MEH-PPV based OTFTs. Transistors based on aligned CNT electrode array showed a moderate increase in the drain-source current and a lower threshold voltage with respect to transistors with non-aligned CNT electrode arrays. We believe in the general applicability of the present technique to deposit aligned carbon nanotubes to improve various organic electronic devices with a number of organic semiconductors including biosensors, energy storage and organic photovoltaics.

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