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Electrical and optical properties of carbon nanotube/polypyrrole addressable intra-connects

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ABSTRACT

Carbon nanotube (CNT) intra-connects (bridges spanning across in-plane electrodes) were electroplated with polypyrrole (PPy), an electrically conductive polymer (ECP). Sharp metal electrodes initiated the CNT growth at pre-selected locations. The CNT bridge was then used as an electrode for conductive polymer electro-deposition. The samples were characterized by Raman spectroscopy and current–voltage measurements. We found that current–gate voltage (I_{ds}–V_{gs}) characteristics changed dramatically for the electroplated structures when the polymer exceeded a threshold thickness, in the order of 80 nm. In addition, the CNT/PPy structures exhibited large sensitivity to UV radiation: the current substantially reduced upon irradiation with moderate UV intensity values.

1. Introduction

Carbon nanotubes (CNT) and electrically conductive polymer (ECP) have attracted much interest in recent years. Since its first discovery [1], CNT have been studied extensively as biosensors, field effect transistors and single electron devices [2–4]. CNT have shown remarkable electrical, optical, chemical and mechanical properties [5–8]. However, growth of CNT at pre-designated positions remains a challenge. Metal contacts for CNT-based devices are mostly post-fabricated after dispersing the CNT on a substrate. Random growth of CNT between electrodes has been demonstrated, too [9,10]. We have demonstrated [11] a reliable growth of CNT intra-connect between pre-fabricated electrodes: the electrode tips were made sharp enough to initiate growth of a CNT channel between them at a yield of 30%. Here we use this technique to fabricate CNT intra-connects, which are further electroplated with conductive polymer.

Polypyrrole (PPy) is a widely used electrically conductive polymer (ECP) for electronic, optical and biological purposes. Its properties are controllable by adjusting the doping level and type of dopant [12–16]. Polymeric-based and all-polymer transistor have been realized as well ([17–18] and references therein). However, most of the CNT/PPy structures thus far, have been realized in a bulk or thin film forms, portraying a complex charge hopping between the dispersed CNT and the backbones of PPy. It has been shown recently [19] that the detection of molecules is dramatically improved when employing single channel field effect transistors (FET). One, therefore, may aim at functionalized low dimensional polymeric channels as sensitive biosensors. Growth of low dimension polypyrrole channels is very challenging. Photoresist materials, used in the process of nano-device fabrication, add undesired surface states to the structure and its removal poses a substantial difficulty [20]. A different method would be to fabricate CNT channel(s) first; then, use the resultant bridge as an electrode for further electro-deposition of the ECP. Yet, the question to be asked is: what would be a desirable polymeric thickness on top of that CNT 'electrode'? To this end we opt to fabricate a platform for extremely thin wire transducers made of CNT/PPy complexes. As we shall see below, despite the apparent imperfection of the CNT intra-connect (multi-channels made of either SWCNT or MWCNT), the overall device response has been found to be independent of the number of separated CNT channels involved. As will also be apparent below, the devices exhibited a sharp characteristics transition as the polymer sheath became larger than 80 nm.

2. Experiments

The intra-connects have been fabricated between a layout of metal electrode tips (Fig. 1) using chemical vapor deposition (CVD). A detailed description of the process and the electrodes is provided elsewhere [20]. Typical distance between the two electrode tips was 1 μm though the electrode layout had patterns of co-aligned and laterally shifted tips (Fig. 1 inset) as well. The morphology, electrical conductivity, photo-conductivity, optical properties of CNT intra-connects were then studied by the use of scanning elec-

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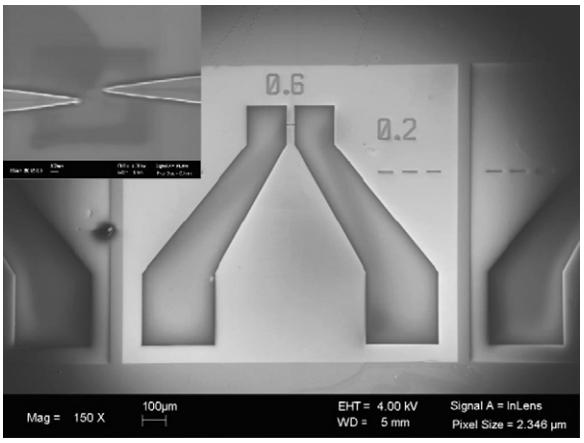

Fig. 1. SEM image of the metal electrodes. The distance between the two tips was 1 μm. Electrode configuration included lateral tip displacement as well (inset). The CNT intra-connect was fabricated by the use of CVD and later was electroplated with PPy. The polymer was coating the electrodes as well as the bridge but was confined only to the conductive area (Fig. 2(a)).

tron microscopy (SEM), atomic force microscope (AFM), Raman spectroscopy, current–voltage (I_{ds}–V_{ds}) and current–gate voltage (I_{ds}–V_{gs}) characteristic measurement.

Polypyrrole (PPy) was synthesized by electrochemical oxidation of pyrrole. A 273 EG&G Princeton Applied Research Potentiostat/Galvanostat was used for the electro-polymerization process. The electro-polymerization process was carried out in a three-electrode-cell configuration. The cell contained aqueous solution of 0.5 M pyrrole and 0.5 M potassium chloride (KCl) (Sigma–Aldrich) without further purification. The CNT intra-connects were used as working electrodes. A platinum wire and Ag/AgCl electrode were used as a counter and a reference electrode, respectively. A constant potential bias of 0.8 V was applied to enable the deposition of PPy. The film thickness was determined by the deposition time, typically on the order of 30 s. The black film covered the metal electrodes and the CNT bridge alike yet, was limited to only conductive surfaces. The sample was later cleaned with deionized water and let dry out under nitrogen gas.

Randomly dispersed film experiments employed single-wall carbon nanotubes (SWCNT). The tubes were purchased from CarboLex Co. with 60–70% purity, purified and dispersed by use of a sonicator in ethanol for a few hours. As-purchased tubes display a distribution of diameters. However after purification and functionalization, the majority of tubes were of (11,9) type having a diameter of 1.37 nm, as determined by their low frequency Raman spectra. The tubes were functionalized with either poly(vinyl pyrrolidone) (PVP) of molecular weight (MW) 40,000 and poly(ethylene imine) (PEI) of MW 630,000, in order to obtain wrapped tubes either in small bundles or, as individuals, *p*- or *n*-type, respectively. The ratio of the polymer and SWCNT was fixed at 2:1 for both cases resulting in uniform films. Wrapping was helpful in minimizing the tube agglomeration. SEM images of CNT intra-connects before and after the electro-deposition are shown in Fig. 2(a) and (b), respectively. High-resolution field emission scanning electron microscopy (FE-SEM, LEO 1530VP) has been used.

3. Results and discussion

3.1. Raman spectroscopy

Raman spectroscopy was used to evaluate the intra-connects. The electrodes were imaged in the far field and the beam of Ar ion laser at 514.5 nm was focused accurately in-between the tips. The tip construction made it very easy to identify the CNT intra-connect under test. A double spectrometer (0.25 cm) and a cooled CCD array were used to detect the scattered signals. The background signal was subtracted and the experimental data was fitted with several Guassian distributions. Results for the high-frequency spectra are shown in Fig. 2(c). By fitting, one can identify three major peaks, as expected for both CNT and PPy [21]. These are: CNT-only: 1350, 1585, 1619; PPy only: 1330, 1370, 1584 and the complex CNT/PPy: 1357, 1585 cm^{-1}, respectively. The relative peak position of the com-

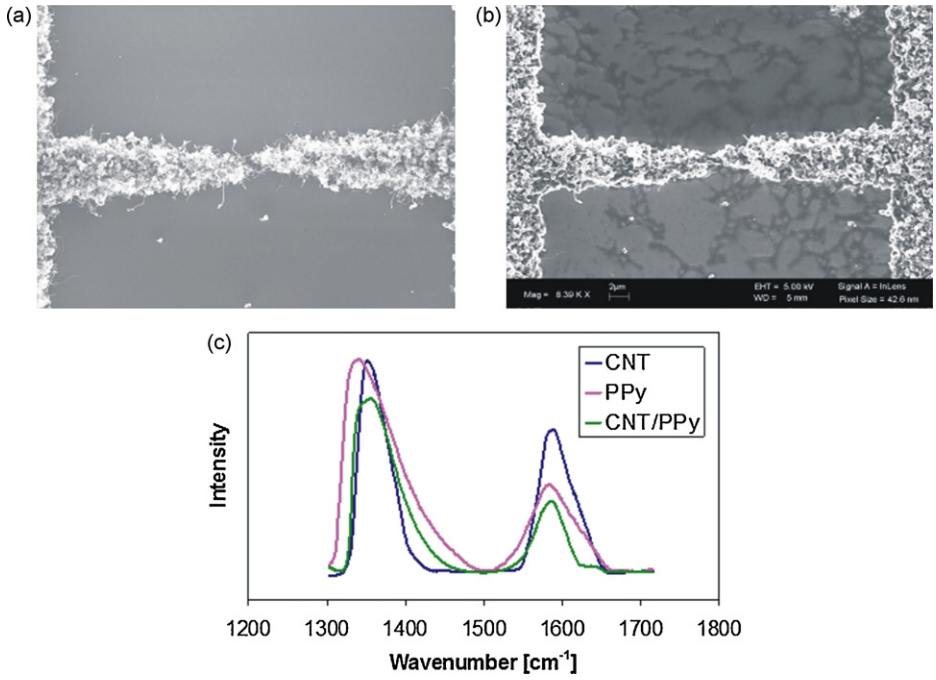

Fig. 2. SEM images of multiple (three) CNT intra-connects before (a) and after (b) electro-polymerization with PPy. (c) High-frequency Raman scattering from only CNT intra-connect, PPy electroplated on conductive glass and CNT/electroplated-PPy intra-connects. The peaks for each component was, only CNT: 1350, 1585, 1619 cm^{-1}, only PPy: 1330, 1370, 1584 cm^{-1} by use of fitting. The electroplated bridges exhibited peaks at 1357, 1585 cm^{-1}, respectively.