Synthesis and dry deposition of SWCNT networks for flexible, transparent conductors and field effect transistors

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1. Introduction

Single-walled carbon nanotube (SWCNT) networks are a promising material for future flexible electronics due to their unique optical and electrical properties. When developing e.g. foldable displays, highly transparent as well as flexible thin films are needed, having both metallic as well as semiconducting electrical properties. Currently used materials for transparent films are transparent metal oxides, such as indium-tin oxide (ITO), which have high refractive index and haze, spectrally non-uniform optical transmission, limited flexibility, restricted chemical robustness and depleted raw material supply. Semiconducting polymers have been actively developed for decades to manufacture flexible, transparent thin film transistors. However, they are unstable in air and exhibit relatively slow charge carrier mobilities, and require vacuum deposition for reasonable mobility films. SWCNT thin films relatively transparent, yet either semiconducting or metallic, depending on their thickness as well as on the properties on the tubes. In this paper, we present an aerosol CVD-based process to dry-deposit large area SWCNT-networks with tuneable conductivity and optical transmittance. These SWCNT-networks can be chemically doped to reach sheet resistance as low as 110 $\Omega/\square$ at 90 % optical transmittance. No time and resource consuming and potentially detrimental liquid purification and dispersion steps are needed. Wide application potential is shown by fabricating SWCNT-network thin-film transistors (TFTs).

2. Experimental

SWCNTs were synthesized by thermal decomposition of ferrocene vapour in a carbon monoxide (CO) atmosphere as described elsewhere (1). The SWCNTs form small bundles in the gas phase, which were collected by a membrane filter at the outlet of the reactor to form a SWCNT-network. The sheet resistance, $R_s$, and transmittance, $T$, were controlled by network deposition time. The network was transferred from a low adhesive force filter to various substrates by a simple room temperature press transfer process. Usable substrates range from flexible polymers, e.g. polyethylene terephthalate (PET), to glass, quartz, silicon and various metals. A substrate and a SWCNT-network on a filter were pressed together with a pressure of 10\textsuperscript{7} Pa. No dispersion or purification steps were needed prior to the transfer, thus making the process of film preparation very rapid. The transfer process required less than 15 s to complete. Importantly, utilizing masks beneath the filter, SWCNT-network patterning can be achieved. In addition to filtering, SWCNT bundles were collected via electric field onto Si wafers for TFT-FET manufacturing. SWCNTs were characterised by optical methods (Raman and absorption) as well as on SEM and TEM. SEM was used to determine bundle length for samples collected onto on the insulating SiO2 substrates. TEM was used to determine bundle diameter for samples collected onto the holey carbon coated TEM grids. Optical absorption was used to estimate SWCNT mean diameter.

3. Results and discussions

The electrical conductivity of a SWCNT-network is limited by highly resistive junctions between SWCNT-bundles (2,3). Therefore, increasing the length of the SWCNT-bundles is expected to decrease the network resistivity. To study the effect of the SWCNT-bundle dimensions on the electrical conductivity of the networks, we prepared samples with different bundle lengths of 1.3 ± 0.8, 3.3 ± 1.4 and 9.4 ± 1.4 $\mu$m by controlling the tube growth conditions i.e. residence time and gas temperature in the floating catalyst reactor. Bundle diameter distributions were found to be overlapping with mean diameters of 7, 8 and 13 nm, respectively. The optical spectra of the as deposited SWCNTs revealed high quality tubes. The resistance was found to be strongly dependent on the average bundle length in the SWCNT-network. $R_s$ of the sample containing the shortest bundles (1.3 µm) was 22 k$\Omega$/µm at $T=90\%$. The samples with longer bundles (3.3 and 9.4 µm) yielded SWCNT-networks with $R_s$ of 2700 and 820 $\Omega/\square$, respectively.

To decrease the $R_s$ of our SWCNT-networks, we developed a fast post-deposition treatment. The SWCNT-network was first densified by drop casting of ethanol and subsequent drying in lab atmosphere. During evaporation, the surface tension of the ethanol compressed the network in the out-of-plane direction. This increased the network connectivity as the network morphology approached the 2-dimensional limit, was observed from the SEM images. The densification was followed by 60 s dipping into concentrated HNO$_3$ and de-ionized water rinsing for 15 s to chemically dope the semiconducting SWCNTs and to decrease the interbundle...
junction resistance (2, 3). The improved SWCNT conductivity due to ethanol densification and HNO$_3$ treatments are depicted in Fig.1. Importantly, SWCNT-network $R$, dropped to as low as 110 Ω/□ at $T=90\%$. For comparison, data for commercially available ITO-films on flexible substrates are also shown in Fig.1. The chemical treatment by HNO$_3$ has been demonstrated in previous studies, but with significantly longer treatment durations of 15 min, 60 min and 3 h. In our case, SWCNT films were doped within 1 min, which was confirmed by optical absorption and Raman measurements. The suppression of optical transitions suggest a shift of the Fermi level. We observed a significant decrease in Raman intensity and an up-shift of G band in the acid treated samples, indicating p-type doping of the SWCNTs. This p-type doping may decrease the resistance of the SWCNT-network by enhancing conduction of semiconducting tubes. However, according to Nirmalraj et al. (3) the main role of the acid treatment should be attributed to a decrease in the junction resistance between the bundles.

SWCNT-networks with a density below the metallic percolation threshold can be used as a channel of a TFT. SWCNT-networks with 3.3 µm average bundle length were press-transferred onto a boron-doped Si-substrate with 100 nm SiO$_2$ gate dielectric. Source and drain electrodes were lithographically patterned on top of the SWCNT-network, which was removed outside of the channel area by O$_2$ plasma etching. The I$_{Vg}$ curve of a typical transistor with a low density SWCNT-network exhibiting and on/off ratio of 10$^5$ and mobility of $\sim$2 cm$^2$/Vs is shown in the Fig.2. Higher density networks (2-3 min deposition) exhibited mobility over 20 cm$^2$/Vs, but had reduced on/off ratios. A similar dry-transfer technique was applied to the fabrication of TFTs on flexible and transparent polymer material. When collecting percolating SWCNT networks via electric field directly from the reactor gas onto both silicon and polymer substrates, TFTs with similar properties were manufactured.

4. Conclusions

We have developed a novel, ambient temperature and ambient pressure method for manufacturing SWCNT thin films based transparent, flexible electrodes and thin film field effect transistors. This method is based on floating catalyst, high temperature CVD synthesis of high quality SWCNTs from CO using Fe nanoparticle catalyst followed by SWCNT ambient temperature, direct, dry deposition onto the substrate. SWCNT-PET conducting films show transparency-sheet resistance properties similar to ITO-PET films. SWCNT network TFTs on both silicon as well as polymeric substrates exhibit mobilities above 1 cm$^2$/Vs and on/off ratio of 10$^5$.

Acknowledgments

The authors thank Dr. A. S. Anisimov and Dr. K. Grigoras for their assistance with experiments, Dr. I. S. Anoshkin, Dr. S. D. Shandakov and Prof. Y. Ohno for fruitful discussions. This work was supported by Academy of Finland (projects No. 128445 and 128495), TEKES, NEDO and Aalto University through the Multidisciplinary Institute of Digitalization and Energy (MIDE) program.

References


Figure 1. The sheet resistance of nitric acid doped SWCNT films for given transmittance decreases when increasing the bundle length from 1.3 micron to 9.4 microns. The red horizontal line shows the characteristics of the ITO film deposited onto PET.

Figure 2. I-V$_g$ characteristics of a typical SWCNT-network transistor, which was fabricated on the SiO$_2$ covered Si surface.