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Surface effects on network formation of conjugated polymer wrapped semiconducting single walled carbon nanotubes and thin film transistor performance

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ABSTRACT

SWCNT network morphology and TFT performance of polyfluorene wrapped sc-SWCNT on different substrates is reported. The polymer/tube weight ratio and concentration impacts network formation and device performance. Hydrophilic SiO_2 surfaces show stronger adsorption compared to poly-L-lysine treated SiO_2, which leads to more uniform and higher density networks. TFTs with mobility up to 38 cm^2/Vs with <10% variability and on/off ratios on the order of 10^5 were obtained using an iterative dip-coating process.

1. Introduction

Semiconducting SWCNTs hold great promise as a solution processable semiconductor in thin film transistors (TFT) because they can be easily deposited using various methods such as dip or spray coating, ink-jet or gravure printing, and membrane filter collecting from aerosol chemical vapor deposition [1–7]. However, to enable the integration of TFTs into arrays and logic circuits, SWCNT network formation must be better understood in order to control the uniformity and density of the network and minimize device variability [8]. The presence of excipients to stabilize SWCNT dispersions, such as ionic surfactants in water or conjugated polymers in organic solvents, will impact the adhesion and film-forming mechanism, as will the substrate surface energy and charge, affecting the network quality and device performance.

A substantive body of work has been accomplished thus far in which aqueous dispersions of enriched sc-SWCNTs, typically obtained via chromatography [9,10] or density gradient ultracentrifugation [11], are used to fabricate TFTs and their adhesion to SiO_2 or PET has been drastically improved by using an adhesion promoter having free amine groups such as (3-aminopropyl)trimethoxysilane (APTMS) or poly-L-lysine (PLL) [12–15]. The binding mechanism largely involves an interaction between the amine groups in the adhesion layer and the acid groups of the surfactants used to disperse the tubes, but also direct interactions between the charged adhesion layer and the hydrophobic regions of the SWCNTs should not be discounted [16,17].

SWCNTs can also be enriched by conjugated polymer extraction (CPE) in an aromatic organic solvent system [18–22]. In contrast to aqueous dispersions, CPE derived dispersions of sc-SWCNT have higher tube concentration, less excess dispersant and no significant ionic component, allowing one to work with a broader range of conditions to optimize thin-film formation. Very little has been reported regarding thin-film formation of these types of polymer wrapped tube dispersions on different substrates, given that adhesion layers are rarely used. Liu et al. has recently reported that hydrophilic and partially negatively charged surfaces are favorable to adhere SWCNTs wrapped with poly[(9,9-dioctylfluorene-2,7-diyl)-co-(1,4-benzo-2,1,3-thiadiazole)], whereby hydrogen bonding between silanol groups on the SiO_2 surface and the benzothiadiazole moiety provided strong adhesion and the use of positively charged adhesion layers provided no added benefit [23]. Cao et al. recently reported the use of PLL coated SiO_2 and PET in the fabrication of screen printed TFTs using poly(di-alkylfluorene) wrapped SWCNTs, yet they did not elaborate on the benefits of using the adhesion layer [24]. Device performance variability will be compounded by variation in print resolution and registration, hence it is important to gain further understanding on the interplay between surface energy, network morphology (uniformity, density) and device performance variability (mobility, on/off ratio,

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on-current) in order to optimize deposition conditions and mitigate printing limitations.

In this paper, we systematically compare the network formation of poly(9,9-di-n-dodecylfluorene) (PFDD) SWCNT dispersions on SiO$_2$ substrates with and without PLL as a function of SWCNT concentration and polymer to SWCNT ratio. We also fabricated TFTs using a simple dip-coating process varying the number of coating cycles in order to optimize device performance and minimize the variability. To our knowledge, the effect of concentration and polymer:SWCNT ratio on network formation and TFT performance has not been reported.

2. Materials and methods

2.1. Purification of sc-SWCNTs

Raw plasma SWCNT material (RN-000) was obtained from Raymor Nanotech. The enrichment process is described elsewhere and provides a comparable material to IsoSol-S100 (NanoIntegris) [21]. SWCNTs are filtered and rinsed with toluene and re-dispersed with PFDD solution to adjust the concentration and weight ratio of the PFDD/SWCNT dispersion.

2.2. TFT device fabrication and characterization

Top contact TFT devices were fabricated on a silicon wafer with a 100 nm thick thermal oxide layer. The chip was first cleaned using Piranha solution (1:2 (v/v) of 98% H$_2$SO$_4$ and 35% H$_2$O$_2$) for 30 min at 90 °C. After thoroughly rinsing with distilled water and isopropanol, the chip was blow-dried with nitrogen. For PLL coated wafers, several drops of 0.1% wt/vol poly-L-lysine solution were spread on the chip for 5 min before rinsing and drying. PFDD/SWCNT dispersions in toluene were bath sonicated for 5 min immediately before usage. The tube solution was spread on PLL treated or bare SiO$_2$ substrates for 10 min under toluene vapor, not allowing the solvent to evaporate. Then the chip was rinsed with 5 ml of toluene and blow-dried with nitrogen before being annealed at 200 °C for 1 h under ambient conditions. Top contacts (5 nm Ti followed by 100 nm Pd) were deposited through a shadow mask using an e-beam evaporator. The channel width is 100 μm and channel length is 25 μm. *I–V* curves were collected on a probe station in ambient condition and the mobility was calculated from the I_{SD}–V_G transfer curve in the linear regime based on a parallel plate model [21]. Due to the low channel width/length ratio (4:1) the measured current was down-corrected by a factor of 1.61 in order to remove contributions arising from tubes outside the defined channel area. Our correction factor is based on a previously determined channel ratio scaling factor (Figs. S1 and S2).

3. Results and discussion

We first tested the adsorption of PFDD enriched/wrapped SWCNT dispersions in toluene with different polymer/tube weight ratios on PLL treated SiO$_2$ while maintaining the tube concentration constant at 9 mg/L [21]. The PLL treated SiO$_2$ substrates were soaked in different tube dispersions for 10 min before rinsing with toluene. As shown in the scanning electron microscopy (SEM) images in Fig. 1a–c, at a 1/1 weight ratio, a moderate tube density is obtained with uncoated areas being quite evident, whereas at a 4/1 weight ratio we obtained a uniform tube network. At a ratio of 20/1, a sparse network is obtained relative to the 4/1 weight ratio and interestingly, the tubes show a certain degree of alignment along the solvent rinsing direction, consistent with a weaker tube–substrate interaction due to the presence of a vast excess polymer. Next, we evaluated different concentrations while

maintaining a constant 4/1 PFDD/tube ratio. As shown in Fig. 1b, d, and e , when the SWCNT concentration increased from 1.0, 3.0 to 9.0 mg/L, the tube network density increased correspondingly from 3.4 ± 1.0, 17 ± 2.9 to 39 ± 1.5 tubes/μm^2 as assessed by SEM. However, increasing the nanotube concentration further to 27 mg/L lead to non-uniform networks (Fig. 1f) and the network density also decreased to 24 ± 5.5 tubes/ μm^2. We have qualitatively observed that as the tube concentration increases at a fixed polymer/tube ratio, a larger proportion of polymer interacts with the tubes leading to a decrease in fluorescence originating from the PFDD. This is likely due to more inter-molecular interactions between tubes and polymers in solution which would lead to more effective energy transfer from PFDD to the SWCNTs.

Comparatively, a SiO$_2$ surface cleaned with piranha solution is much more hydrophilic having a water contact angle near 0° vs 55° for a PLL treated SiO$_2$. The former is also slightly negatively charged. We evaluated the network uniformity and density using the same PFDD/tube solutions (*vide infra*) on freshly cleaned SiO$_2$, and the SEM images are shown on Fig. 2. Interestingly, the PFDD wrapped SWCNTs show stronger adhesion onto bare SiO$_2$ surfaces. At 9 mg/L concentration and a 4/1 PFDD/SWCNT weight ratio, uniform and dense networks are observed. Higher polymer ratio (20/1) leads to poor adhesion. At the 4/1 weight ratio, in contrast to the PLL coated SiO$_2$, the tube density consistently increased from 3.8 ± 0.5, 31 ± 2.8, 68 ± 3.0 to 87 ± 4.5 tubes/μm^2 as the solution concentration changed from 1.0, 3.0, 9.0 to 27.0 mg/L respectively (Fig. 2 b, d–f). Hence, PLL may provide a means of self-limiting the SWCNT density onto a substrate, while a more hydrophilic and slightly negatively charged surface enables denser networks to be formed if desired.

In order to further compare the quality of the networks between bare and PLL treated SiO$_2$, we fabricated TFT devices by evaporating source and drain electrodes through a shadow mask onto networks made using 4/1 PFDD/SWCNT solutions at various concentrations. The resulting devices have top Ti/Pd contacts and common bottom gate (doped silicon layer) whereby SiO$_2$ serves as the dielectric [21]. The channel length and width for these devices are 25 and 100 μm respectively, and the reported data are the average taken from 25 devices over a 5 × 5 mm^2 area (Table 1). We chose the device geometry and spacing in order to determine the reproducibility over a larger area that would be consistent with fully printed TFT arrays. Under controlled conditions, the results are reproducible from wafer to wafer. In general, TFT devices on PLL treated surfaces have larger hysteresis and more negative threshold voltage when the transistors were turned off (Fig. S3). For TFTs on both PLL/SiO$_2$ and SiO$_2$, we tested some devices at $V_G \sim 15$ V and didn't find obvious n-type behavior under the ambient conditions used. For 1.0 mg/L concentration samples, the networks are below the percolation threshold and thus no TFT performance is reported. As the solution concentration increases, we obtained higher mobility and on currents, correlating well with the network density obtained from SEM imaging. Devices on bare SiO$_2$ also show better performance compared to those on PLL at the same tube concentration due to the higher tube density. The 9 mg/L solution gave the highest network density (39 tubes/μm^2) and mobility (8.1 ± 2.1 cm^2/Vs) on PLL coated SiO$_2$. This mobility is very similar to that observed by Zhou and co-workers in which screen printed TFTs using polymer sorted tubes (IsoSol-S100) were coated onto a PLL treated SiO$_2$ and PET substrate [24]. Comparatively, the 9 mg/L solutions yielded 68 tubes/μm^2 and a mobility of 18 ± 1.6 cm^2/Vs on bare SiO$_2$. Furthermore, on bare SiO$_2$, the network density and mobility increased consistently with the solution concentration, reaching a mobility of 25 ± 3.8 cm^2/Vs as the tube network density increased to 87 per μm^2 at 27 mg/L concentration. High current on/off ratios on the order of 10^6 were obtained for all these devices,