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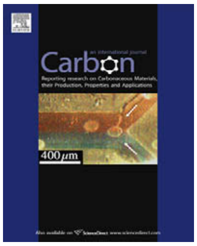

Fabrication of in-plane aligned carbon nanotube–polymer composite thin films

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ABSTRACT

In-plane aligned carbon nanotube–polymer composite thin films with submicrometer thickness on unmodified SiO_2 surfaces are fabricated using the spincoating alignment technique, which is simple, integratable to the manufacture process of organic devices, and applicable to various matrix polymers (e.g. polycarbonate and polythiophene). Controlled manipulation of the nanotube alignment in a polymer matrix is an effective method to tune the electrical conductivity of a 5 wt.% single-walled carbon nanotube–polycarbonate composite film spanning nearly four orders of magnitude.

1. Introduction

Controlled manipulation of one-dimensional nanostructures such as nanowires and carbon nanotubes (CNTs) is critical to their many potential applications [1,2]. The ability to align CNTs in a polymer matrix offers great potential for the development of active nanocomposites with anisotropic physical properties [3–7]. CNTs can be aligned in a matrix polymer film by blown bubble film process [1,2], mechanical stretching [3,6–10], layer-by-layer assembly and combing [5,11], electric field [12], and magnetic field [4], respectively. Among these alignment techniques, the mechanical stretching has become a popular method owing to its relative simplicity [3,6–10]. The mechanical stretching technique, however, has one major limitation: It works better with thicker CNT–polymer composite films because thicker films allow higher drawing ratio (the ratio of final film length to initial film length) and therefore better CNT alignment. The typical thickness of aligned CNT–polymer composite films ranges from 10 μm to 2 mm [3,6–10].

Active, isotropic CNT–polymer composite films have been used in organic light-emitting diodes [13], organic photovoltaic devices [14–17], optoelectronic memory devices [18], IR sensors [19], chemical sensors [20,21], and thermoelectric devices [22]. Submicrometer thin films of aligned CNT–polymer composites are desirable for many device-based applications, but they are difficult to make due to the lack of a simple alignment technique that is integratable to the device fabrication process and applicable to a wide range of matrix polymers. LeMieux and coworkers have found that spincoating of pure single-walled CNT (SWCNT) solutions onto chemically modified SiO_2 surfaces give rise to aligned SWCNTs [23]. They have shown that chemically modified surfaces with terminal amino group ($–NH_2$) or phenyl group ($–C_6H_5$) are necessary for nanotube adsorption and alignment. If a SWCNT solution is spincoated onto the unmodified SiO_2 surface, no nanotube absorption occurs [23]. It is not clear whether the spincoating alignment method is also applicable to a CNT–polymer solution because the addition of a matrix polymer introduces several uncertainties: (1) The CNT is coated with a layer of the matrix polymer [24], which blocks the direct interaction between the nanotube and the substrate; (2) The existence of the matrix polymer significantly increases the solution viscosity during the spincoating and drying process. In this article, we demonstrate the fabrication of in-plane aligned CNT–polymer composite thin films with submicrometer thickness on unmodified SiO_2 surfaces using the spincoating alignment technique, which is simple, integratable to the manufacture process of organic devices, and applicable to

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both insulating matrix polymers (e.g. polycarbonate) and electroactive matrix polymers (e.g. polythiophene).

2. Experimental Section

We recently discovered that rigid conjugated macromolecules, poly(*p*-phenyleneethynylene)s (PPE), can be used to noncovalently functionalize and solubilize CNTs, and disperse CNTs uniformly in polymer matrices [25–30]. Purified HiPco® SWCNTs ($\mathrm{SWCNTs}_{\mathrm{HiPco}}$) from Carbon Nanotechnologies, Inc. were used as received in this study without further purification. Polycarbonate (PC, Fig. 1) was purchased from Sigma–Aldrich Co. Regioregular poly(3-dodecylthiophene-2,5-diyl) (P3DT, Fig. 1) was purchased from Rieke Metals, Inc. Purified $\mathrm{SWCNTs}_{\mathrm{HiPco}}$ were solubilized in chloroform with standard PPE along with vigorous shaking and/or short bath sonication [25–30]. The mass ratio of PPE:SWCNT was kept at 0.4. The resulting $\mathrm{SWCNT}_{\mathrm{HiPco}}$ solution was then mixed with a PC or P3DT solution in chloroform to produce a homogeneous CNT-matrix polymer composite solution. The SWCNT loading values for both $\mathrm{SWCNT}_{\mathrm{HiPco}}$–PC and $\mathrm{SWCNT}_{\mathrm{HiPco}}$–P3DT were kept at 5 wt.%, which are based on purified SWCNTs only, and exclude the PPE. The resulting CNT-matrix polymer composite solution was further diluted to different concentrations with chloroform for alignment experiments.

In-plane aligned $\mathrm{SWCNT}_{\mathrm{HiPco}}$–polymer composite thin films (Figs. 2–4) were fabricated on silicon wafers by the following spincoating alignment procedure. Heavily doped *n*-type silicon wafers of (100) orientation and heavily doped *n*-type silicon wafers with 300 nm thick thermally grown $\mathrm{SiO_2}$ layer were purchased from Silicon Quest International, Inc. All substrates were cleaned in acetone by bath sonication for 20 min, followed by bath sonication in isopropyl alcohol for 30 min. A dilute $\mathrm{SWCNT}_{\mathrm{HiPco}}$–polymer composite solution was deposited onto the center of a spinning substrate at various speeds. The sample was then dried in a vacuum oven. The typical film thickness is in the range of 10–25 nm based on Scanning Electron Microscopy (SEM). SEM was performed using a Hitachi S-4800 field emission scanning electron microscope (accelerating voltage: 3 or 5 kV). No sample coating was used in the SEM experiment in order to avoid possible artifacts induced by the metal coating. The diameter of the SWCNTs shown in Figs. 2–4 was significantly inflated because the SEM image contrast stems from local potential differences between the conductive nanotube and insulating polymer matrix [31,32]. For the anisotropic conductivity measurement, a 4 mg/ml solution of $\mathrm{SWCNT}_{\mathrm{HiPco}}$–PC in chloroform was deposited onto a spinning silicon wafer with 300 nm $\mathrm{SiO_2}$ layer following previous procedure. 40 nm thick gold electrodes were then deposited through a shadow mask using Edward vacuum coating unit, with channel length of 27 μm and channel width 1.05 mm. The schematic device structures are shown in Fig. 4. The two-point probe electrical conductivity measurement was performed using a Keithley 2400 source meter through the computer controlled LabVIEW program.

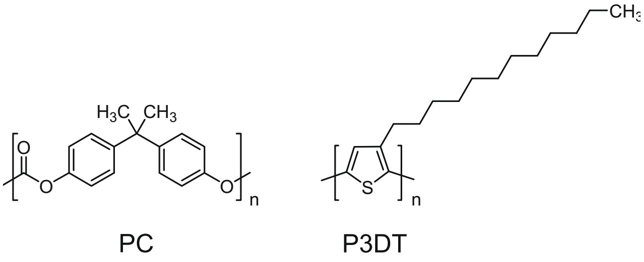

Fig. 1 – Chemical structures of two matrix polymers used in this study.

3. Results and discussion

A typical unmodified silicon wafer is covered with a thin layer of $\mathrm{SiO_2}$ about 2 nm thick [33]. Spincoating of homogeneous $\mathrm{SWCNT}_{\mathrm{HiPco}}$–PC and $\mathrm{SWCNT}_{\mathrm{HiPco}}$–P3DT solutions onto spinning *n*-type silicon wafers of (100) orientation gives rise to high quality SWCNT–polymer composite thin films (Figs. 2 and 3), which not only indicate a sufficiently strong interaction between SWCNT–polymer composites and bare silicon wafers, but also suggest that during the spincoating and drying process, the increased solution viscosity and the polymer coating of nanotubes successfully prevent the nonuniform aggregation of SWCNTs in a polymer matrix. The resulting nanocomposite thin films could be roughly divided into two zones: (1) Zone A: A smaller zone in the center where SWCNTs are only partially aligned along the radial direction and majority of nanotubes demonstrate a significant degree of waviness (Fig. 2); (2) Zone B: A bigger zone outside the center where

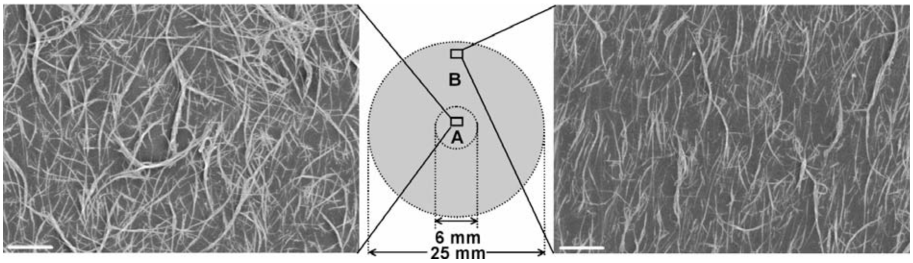

Fig. 2 – (Middle) Schematic drawing of aligned 5 wt.% $\mathrm{SWCNT}_{\mathrm{HiPco}}$–PC nanocomposite thin film on *n*-type silicon wafer of (100) orientation prepared from 4 mg/ml solution of $\mathrm{SWCNT}_{\mathrm{HiPco}}$–PC at the spincoating rate of 7000 RPM, which can be roughly divided into zone A and zone B based on the degree of nanotube alignment. (Left) SEM image of zone A, showing partially aligned SWCNTs in PC. (Right) SEM image of zone B, showing aligned SWCNTs in PC. Scale bar: 1 μm.