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Transfer printing approach to all-carbon nanoelectronics

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ABSTRACT

Transfer printing methods are used to pattern and assemble monolithic carbon nanotube (CNT) thin-film transistors on large-area transparent, flexible substrates. Airbrushed CNT thin-films with sheet resistance 1 kΩ sq^{-1} at 80% transparency were used as electrodes, and high quality chemical vapor deposition (CVD)-grown CNT networks were used as the semiconductor component. Transfer printing was used to pre-pattern and assemble thin film transistors on polyethylene terephthalate (PET) substrates which incorporated Al_2O_3/poly-methylmethacrylate (PMMA) dielectric bi-layer. CNT-based ambipolar devices exhibit field-effect mobility in range 1–33 cm^2/V s and on/off ratio ~10^3, comparable to the control devices fabricated using Au as the electrode material.

1. Introduction

Carbon nanotube (CNT) thin-films have been successfully incorporated as both high-quality semiconductor [1–6] layers and electrodes [6–10] in large area flexible, transparent electronics. Semiconducting CNT thin-films are transparent, flexible, environmentally stable, and possess higher field-effect mobility than organic semiconductors (e.g. pentacene and P3HT) [5,11]. However, use of metal electrodes (e.g. Au, Ti, and Pd) make CNT thin-film transistors (TFTs) only partially transparent and sub-optimally flexible. Conventional transparent, conducting films (e.g. indium tin oxide (ITO)) have been used as electrode materials in organic TFTs [12] and CNT TFTs [13], but expensive growth techniques and inherent brittleness make these materials incompatible with flexible electronics. Alternatively, solution-processed CNT thin-films have been optimized to achieve sheet resistance and transparency that are comparable to ITO, as well as being more flexible than ITO [7,8,14,15]. Thus, CNT thin-films have been independently utilized as high quality active components and as electrodes. However, there have been limited efforts [6] to combine these two functionalities of CNT thin-films together to achieve carbon-based, all-transparent flexible electronics.

In this paper, we report on a novel transfer printing approach to assemble all-CNT devices using CVD-grown CNT thin-films as the active semiconducting layer and solution-processed CNT thin-films as the electrodes. A transfer printing method [16–19] was used to pattern the semiconducting CNT thin-film without exposure to any processing chemicals while an airbrushing method was used to produce the CNT thin-film electrodes. The airbrushing method allowed for rapid production of large area thin-films on a variety of substrates at room-temperature [20]. The sheet resistance of the CNT electrodes was ~1 kΩ sq^{-1} at 80% transparency and they exhibited superior flexibility as compared to conventional transparent conducting films such as doped In_2O_3. Gate leakage in printed CNT TFT devices was avoided by engineering an organic/inorganic hybrid dielectric. An Al_2O_3/poly-methylmethacrylate (PMMA) dielectric bi-layer was used to achieve a minimal gate-leakage near the resolution of the measurement set up (>100 pA). CNT-based devices on a polyethylene terephthalate (PET) substrate exhibited field-effect mobilities in the range 1–33 cm^2/V s and on/off ratios up to 10^4. In contrast to *p*-type control devices, these CNT-based devices showed ambipolar behavior that could be useful in complementary circuits.

2. Fabrication

2.1. Semiconducting carbon nanotube thin films

Semiconducting CNT thin-films were grown on thermally oxidized, Si transfer substrates by CVD using iron nanoparticles as a catalyst [19]. A transfer printing approach was used to pattern the semiconducting CNT thin-films, as described in Ref. [19]. Briefly, the growth substrate containing a CNT thin-film was pressed against a PET stamp at 400 psi, 140 °C for 3 min. CNTs in direct contact with the raised parts of the PET stamp were transfer printed while CNTs not in contact with the stamp (under recessed areas of the PET stamp) remained unaffected on the growth substrate. The resulting patterned CNT thin-film consisted of isolated

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areas 200 μm × 300 μm in size with edge roughness on the order of ±5 μm. A SEM micrograph of the edge of a patterned CNT thin-film is shown in Fig. 1(a).

To facilitate the transfer printing of the patterned CNT thin-films, the surface energy of uncovered areas of the SiO_2/Si transfer substrates was reduced using a self-assembled monolayer (SAM) treatment method, as described in Ref. [19]. Briefly, areas of the SiO_2/Si substrate uncovered by the patterning of the CNT thin-film were treated with a (tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane SAM. This SAM, acting as a release layer, decreases the adhesion between the transfer and device substrates [16]. The release layer, however, should only cover bare regions of the transfer substrate and not the patterned areas of the CNT thin-film. This was achieved by coating a polydimethylsiloxane (PDMS) stamps with the release layer molecules and using micro-contact printing. The release layer-coated PDMS stamp was aligned and placed over the patterned CNT thin-film such that only raised areas of the PDMS stamp were in contact with the bare substrate. The PDMS stamp was gently removed after 15 min.

2.2. Carbon nanotube thin film electrodes

For the fabrication of electrodes, CNT powder (P3, Carbon Solutions, Inc.) was used as-purchased. These CNTs are functionalized with 4–6 atomic% carboxylic acid at 80–90% carbonaceous purity and were dispersed at a concentration of 1 mg/mL in a solution of 1% by wt. sodium dodecyl sulfate (SDS) in de-ionized (DI) water [9]. The CNT solution was first bath sonicated for 90 min and then centrifuged at 12,000 rpm for 40 min to remove impurities. The resulting well-dispersed, purified CNT solution was airbrushed (Aztek A470 airbrush kit, 40 psi) onto a desired substrate, in this case a Au coated Si wafer (at 165 °C) and then soaked in DI water for 30 min to remove the surfactant. It was observed that airbrushing a dilute CNT solution using multiple short pulses (approximately 0.5 s each) produced a more uniform thin-film compared to that produced by a continuous spray. Transparency versus sheet resistance measurements of these CNT thin-films were previously reported in Ref. [9]. The electrodes reported here are approximately 30 nm-thick with a sheet resistance of 1 kΩ sq^{-1} at 80% transparency (at wavelength of 550 nm).

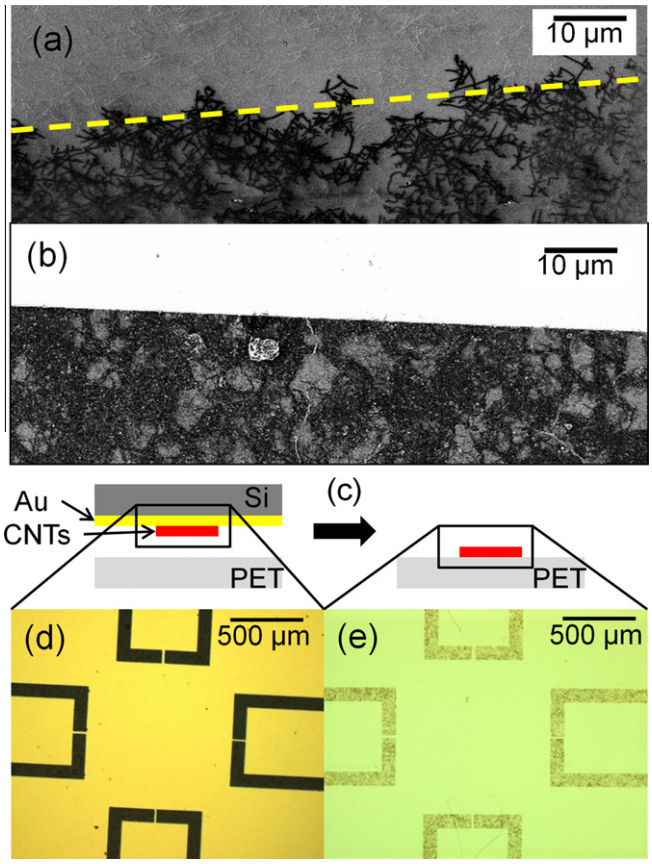

Fig. 1. (a) SEM micrograph of the edge of a CNT thin-film patterned by transfer printing method on thermally oxidized Si substrate. The dotted line is guide the eye along the edge. (b) SEM micrograph of the edge of an air-brushed CNT thin-film patterned by photolithography on Au carrier film. (c) Schematic of the transfer printing step used to transfer a patterned CNT thin-film from a 50 nm Au carrier film onto a PET device substrate. (d) Optical image of an airbrushed and patterned CNT thin-film on Au film before transfer printing. (e) Optical image of the CNT thin-film on PET substrate after transfer printing and etching of the Au film.

The transfer printing method from Section 2.1 could not be employed to pattern these airbrushed CNT thin-films because they transferred only partially onto a PET substrate, possibly due to a stronger CNT/Si adhesion strength compared to cohesion strength of 30 nm thick multilayered CNT thin-films. Thus, airbrushed CNT thin-films were patterned into electrodes using photolithography and O_2 plasma reactive ion etching (RIE) [19]. A SEM image of the edge of a patterned CNT thin-film is shown in Fig. 1(b). No significant change in sheet resistance was observed after patterning. Since, airbrushed CNTs transfer partially onto device substrates a carrier film was used to ensure complete transfer of CNT thin-film electrodes as follows. The CNTs were airbrushed and patterned onto a 50 nm-thick Au carrier film deposited by thermal evaporation onto a Si transfer substrate (Figs. 1(c) and 2(a)). As compared to the CNT thin-film, the Au carrier film has a weaker adhesion to the Si substrate, but yet a strong enough cohesion to allow complete and intact transfer of the CNT thin-film/Au bi-layer to a PET device substrate [16]. Other approaches such as airbrushing CNTs on a release layer-treated Si were investigated, but the resulting thin-films were too fragile to survive soaking in DI water. Using Au carrier films, we have also achieved proof-of-concept transfer printing of airbrushed CNTs to other polymer dielectric materials such as poly(4-methylstyrene), poly(alpha-methylstyrene), polystyrene, poly-4-hydroxystyrene, polyvinyl alcohol, polycarbonate, polyimide and polyvinyl nitrile. Fig. 1(d) and (e) shows optical images of patterned CNT thin-film electrodes on Au carrier film before transfer printing and CNT electrodes on a PET substrate after transfer printing and etching the Au film, respectively. Optical images show no visible degradation of edge resolution of CNT electrodes during transfer printing.

2.3. Assembling all-carbon nanotube devices

For all-CNT bottom gate TFTs, different device components were assembled in the following order: airbrushed and patterned CNT thin-film gate electrodes, gate dielectric layer, airbrushed and patterned CNT thin-film source–drain electrodes, and finally, CVD-grown and patterned CNT thin-films as the active layer. The CNT gate electrodes/Au bi-layer (discussed above in Section 2.2) was transfer printed from the Si transfer substrate to a PET device substrate at 400 psi, 120 °C for 3 min (Fig. 2(b)). The Au film was then removed from the PET substrate by soaking in a solution of Au etchant (GE-1848, Transene Company, Inc.) for 1 min. Neither optical images nor electrical resistance measurements showed any discernible effect of the wet chemistry Au etch on the CNT gate electrode or the PET substrate.

The gate dielectric layer was prepared by depositing a 50 nm thick Al_2O_3 layer onto the gate electrodes by e-beam evaporation followed by spin-coating an 800 nm-thick PMMA layer (Fig. 2(c)). Without the Al_2O_3 layer, gate leakage was observed even with a 2 μm thick stand-alone PMMA layer. The Al_2O_3 is used as a diffusion barrier for CNTs that appear to diffuse through the bulk of