

Controlled Assembly of High Density SWNT Networks on a Flexible Parylene-C Substrate

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ABSTRACT

In this paper, we present a directed assembly technique for controlled micro-patterning of Single-Walled Carbon Nanotubes (SWNTs) on a flexible parylene-C substrate for electronic applications. The presented large scale fabrication of ordered carbon nanotube arrays and networks is achieved by performing site-selective fluidic assembly of SWNTs on a plasma treated parylene-C substrate. Parylene-C, which is lightweight, mechanically strong and stress-free material deposited at room temperature, is an emerging substrate material for flexible devices. The uniformly deposited nanotube lateral structures are formed directly on the parylene-C substrate without utilizing printing or transfer techniques. Both electrical and structural characterizations are performed on the SWNT-based devices on the flexible substrate. The developed nanotube patterning on polymeric substrates has immediate applications in wearable electronics and sensors, flexible field effect transistors (FETs) and lateral interconnects.

Keywords: Flexible Parylene-C substrates, Single-Walled Carbon Nanotubes, Nanoscale patterning, Dip coating.

1 INTRODUCTION

Single-Walled Carbon Nanotubes (SWNTs) with their attractive properties such as large surface-to-volume ratio, high packing density and long-range order may serve as the potential building blocks for the next generation of nanoscale devices. [1, 2] The integration of ordered arrays of carbon nanotubes on to rigid as well as flexible substrates offers many opportunities for realizing novel multifunctional devices. [3-5] The transfer of vertically or horizontally aligned carbon nanotube structures are often realized utilizing complicated steps of site-selective CVD nanotube growth or conformal contact printing. [6, 7] The major problem of CVD based approach is the requirement of high processing temperatures ($\sim 800^{\circ}\text{C}$) which is not CMOS compatible and also can't be applied to most polymeric devices. PDMS stamps are also utilized as an intermediate carrier to transfer-print SWNTs on to different substrates including plastic sheets. [8] Though challenging, it is highly desirable to fabricate integrated nanotube-polymer flexible electronic devices at room temperature in a simple and cost-effective way. Here, we present a novel technique for localized patterning of SWNT networks on a

flexible Parylene-C substrate by utilizing surface controlled microfluidic assembly technique (Fig.1).

Unlike most rigid substrates which can be chemically functionalized for large-scale assembly of carbon nanotubes, [9, 10] the soft polymer surfaces are hydrophobic and their properties cannot be easily altered chemically. The low surface energy makes the direct assembly of nanotubes on a hydrophobic surface a challenging task. To overcome these challenges, we developed a plasma treatment method to modify the surface properties of the polymer for effective direct assembly of carbon nanotubes onto its surface. The previous SWNT patterning approach used a PDMS substrate which was also flexible. [11] A major limitation of the previous approach, however, was the requirement of a shadow mask which limited the flexibility in pattern dimensions. In this study, we utilized photolithography for the large-scale assembly of SWNT arrays on parylene-C substrates.

This versatile technology has direct applications in the realization of nanoscale devices on flexible substrates potentially useful in numerous fields including flexible electronics, wearable nanosensors, CNT-field effect transistors and lateral CNT interconnects.

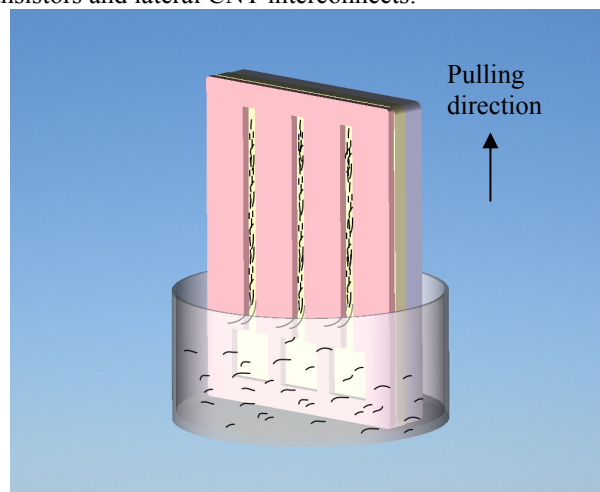


Fig.1 Schematic drawing of the surface controlled microfluidic assembly technique.

2 FABRICATION PROCESS

The fabrication process is shown in Fig.2 and starts with the deposition of a $10\mu\text{m}$ parylene-C layer on top of a

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15mm×15mm silicon substrate. Next, a brief O₂ plasma treatment is utilized to render the as-deposited hydrophobic parylene-C surface hydrophilic. Parylene-C, is known to have very low permeability to moisture and corrosive gases and has been historically utilized in encapsulation applications. Along with its ability to create a true pin-hole free insulation, the high resistivity, $6 \times 10^{16} \Omega\text{-cm}$, and high breakdown voltage (300Volts/ μm), all indicate that Parylene-C has excellent dielectric properties. The physical properties such as its high tensile strength (10,000psi) and mechanical strength (Young's modulus of 400Kpsi) [12] suggest that it is also a very promising candidate amongst materials for flexible substrates. The surface property of the plasma treated parylene-C substrates was studied by measuring contact angles in a dynamic mode (Phoenix 300 Plus, SEO). The contact angle before oxygen plasma treatment of parylene-C was $97.2^\circ \pm 4.2^\circ$ [13]. After the oxygen plasma treatment, the parylene-C surface became hydrophilic (contact angle was around $4.82^\circ \pm 0.57^\circ$). Fig. 3 shows the contact angle measurements from the parylene-C surface. The hydrophilic property of parylene-C surface is relatively stable after plasma modification (for at least 2 hours following the plasma treatment). This characteristic will be utilized for the SWNT fluidic assembly.

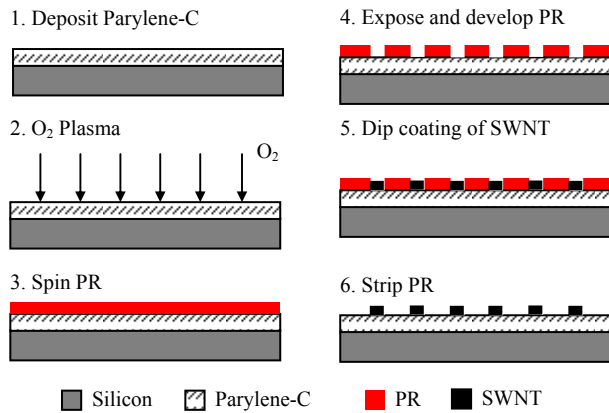


Fig.2 Fabrication process flow.

We then performed photolithography to create trenches ($30\mu\text{m} \times 1.1\text{mm}$) on the silicon die. The patterned substrate was first vertically submerged into an aqueous solution containing SWNTs using a dip coater (KSV Instruments). The substrate was then gradually pulled upward from the solution with a constant pulling speed of 0.1 mm/min. Due to the hydrophobic nature of the top photoresist surface, surface controlled microfluidic assembly technique can be utilized to selectively assemble SWNTs inside the hydrophilic trenches. After assembly of the SWNTs, the photoresist was next removed in acetone in a gentle manner, leaving the assembled SWNT arrays intact on desired parylene-C sites. The thin ($10\mu\text{m}$) layer of parylene-C film with SWNT patterns was next peeled off from the silicon substrate and is ready for characterization.

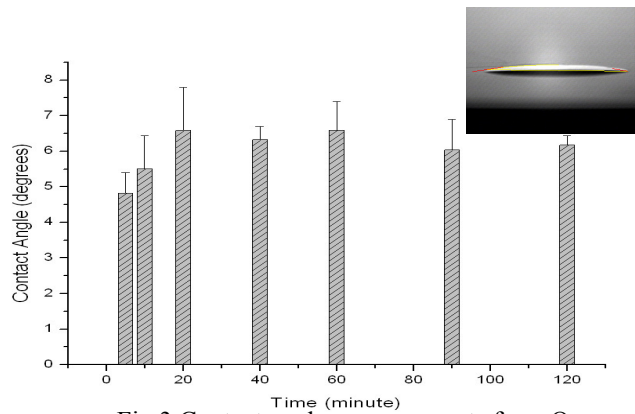


Fig.3 Contact angle measurements from O₂ plasma treated Parylene-C substrates.

3 RESULTS

3.1 Dip Coating Process

Commercially available SWNTs (Nantero Inc.) dispensed in an aqueous solution are used in our experiments. The SWNT solutions consist of about 0.23wt% SWNTs with lengths ranging from 1 to $5\mu\text{m}$. The SWNTs are terminated with carboxylic acid groups, which adsorb ions such as H⁺ and OH⁻ from the aqueous solution resulting in the presence of a net charge on the surface of the SWNTs. The patterned substrate was first vertically submerged into the solution containing SWNTs. The substrate was next gradually pulled out of the solution with a constant pulling speed of 0.1mm/min using a dip coater. Fig.4 shows the SEM micrographs of the assembled SWNT patterns, and the inset shows the details of the assembled SWNT networks inside the trenches. The assembled nanotube patterns retain their original shape after the removal of the photoresist layer. The assembled SWNT structures are dense and show complete coverage over the parylene-C surface. In addition, the boundaries of the nanotube micropatterns are well defined.

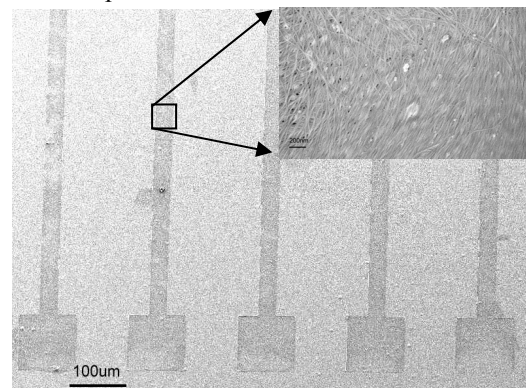


Fig.4 shows the SEM micrograph of the assembled SWNT patterns, and the inset shows the details of the assembled SWNT networks inside the trenches.

3.2 I-V Characterization

A potential application of the assembled SWNT microstructures is in macroelectronics, specifically in flexible devices. We next conduct electrical characterization of the assembled nanotube microstructures on Parylene-C substrates. The dimensions of the tested nanotube microlines are 30 μm in width and 1mm in length. The measured I-V results are shown in Fig. 5. The two-terminal resistance measurements from the nanotube strips ranged from 15K Ω to 21K Ω . To test the reliability of the assembled SWNTs on the defined trenches, a repeatability test was performed on the same sample which demonstrated a variation of less than 1% and is shown in Fig. 6.

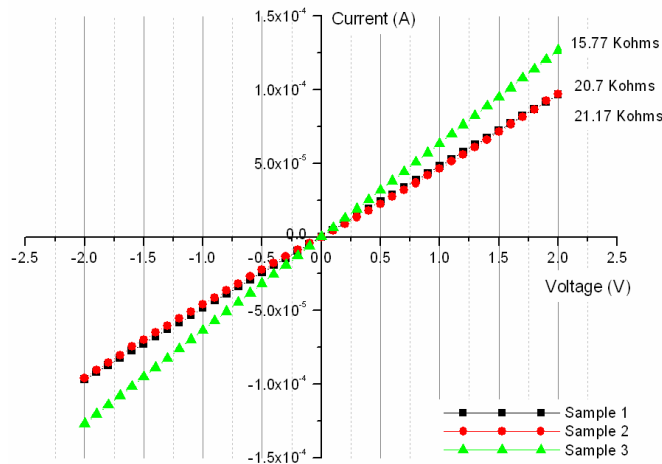


Fig.5 I-V measurements from assembled SWNT networks.

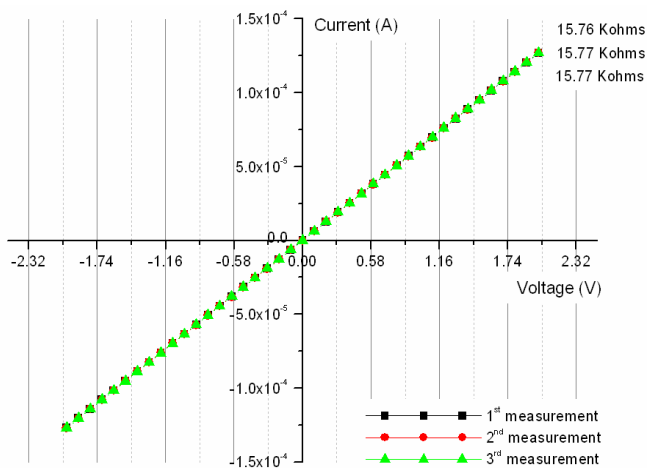


Fig.6 Repeatability test on the same sample where the variation is found to be less than 1%.

3.3 Raman Spectroscopy Measurements

To further characterize the structural properties of the assembled SWNTs, the Raman spectra analysis was performed. We obtained an estimation of the SWNT

diameter distribution using Raman spectroscopy with a 783 nm excitation. The diameter, chirality and phonon structure are reflected in the first and second order Raman frequencies. For example, the radial breathing mode (RBM) is usually located between 75 and 300 cm^{-1} . [14] The diameter of the assembled SWNT is calculated from equation $d \text{ (nm)} = 248/[\omega(\text{cm}^{-1})]$, [15] where d is the diameter of the assembled SWNTs, and ω is the RBM frequency. Fig. 7 shows the spectral range between 100 to 450 cm^{-1} , with radial breathing mode (RBM) of SWNT peaks at frequencies around 160, 210, and 270 cm^{-1} (taken from 4 different spot areas). RBM analysis revealed that the observed frequencies of the RBM peaks correspond to SWNT diameters in the range of 0.9 – 1.55 nm. The peak at 210 cm^{-1} indicated a dominant SWNT of approximately 1.18 nm.

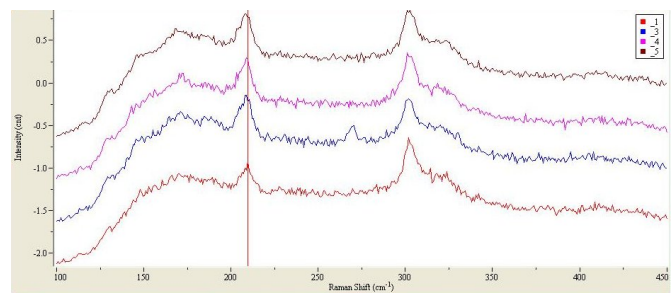


Fig.7 Raman spectra measured from 4 different points of the same SWNT networks.

The D band located around 1300 cm^{-1} is due to defects or disordered features in the nanotubes. The G mode is usually located between 1500 and 1600 cm^{-1} , which corresponds to the tangential C-C bond stretching in the graphite plane. As observed in Fig. 8, the observed peak is located at 1585 cm^{-1} , and a minor shoulder shifted to lower frequencies by around 25 cm^{-1} , indicating the presence of semiconducting SWNTs. [16] Our results show that the electrical behavior of high-density SWNT micro-patterns is linear or metallic, which is suitable for high-performance flexible interconnect applications.

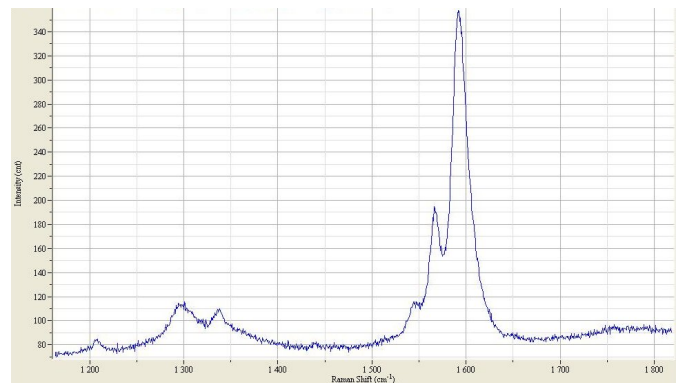


Fig.8 Raman spectra measurement showing G and D band of SWNT networks.

4 CONCLUSIONS

In summary, we report the patterned assembly of SWNT microscale networks with controllable dimensions on a flexible parylene-C substrate using surface controlled microfluidic assembly. The surface properties of the oxygen plasma treated parylene-C were characterized by contact angle measurements which indicated that following the O₂ plasma treatment, the parylene-C surface became hydrophilic with a contact angle of about $4.82^{\circ} \pm 0.57^{\circ}$ and stayed hydrophilic for at least 2 hours. The two-terminal resistance of the SWNT microlines ranged from 15K Ω to 21K Ω . Repeatability tests were performed on the sample which had a variation in resistance of less than 1%. Raman spectroscopy analysis revealed that the observed frequencies of the RBM peaks correspond to SWNTs with diameters ranging 0.9 – 1.55 nm.

This successful assembly of SWNT networks opens a possibility to study their intrinsic properties and anisotropic behavior at the microscale. The assembled SWNT networks on the parylene-C substrate show desirable electrical properties that are promising candidates for the next generation of flexible devices. This work provides a simple and economical approach to realize patterned SWNT microstructures on flexible polymer substrates. The presented method is also scalable to wafer scale fabrication of SWNT-based flexible electronics including high performance flexible interconnects, sensors and FETs.

ACKNOWLEDGMENTS

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