A Three Dimensional Multi-Walled Carbon Nanotube based Thermal Sensor on a Flexible Parylene Substrate

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ABSTRACT—We present the first design, fabrication and testing results from a three dimensional Multi-Walled Carbon Nanotube based thermal sensor fabricated on a flexible Parylene-C substrate. Parylene-C is an inert, biocompatible, optically transparent, room temperature deposited polymer with a high mechanical strength, yet is rarely used as a flexible substrate. By utilizing a 2 mask process, we have manufactured a versatile microplatform for nanoscale assembly and then by utilizing dielectrophoretic assembly, incorporate MWNTs onto the platform in a 3D manner. The MWNTs are next encapsulated using a thin Parylene-C layer that acts as an environmental barrier and in addition keeps the MWNTs intact. The temperature Coefficient of Resistance of the MWNT sensor is measured to be between -0.21% and -0.66% per degree. The thermal sensor is compact, is very high density and could potentially be used for diverse temperature sensing applications such as in wearable textiles, on non planar surfaces and for in-vivo applications.

Keywords — Three Dimensional nanoassembly, MWNT, thermal sensor, Dielectrophoresis, Flexible parylene substrates

I. INTRODUCTION

Following their discovery in 1991 by Ijima [1], Carbon Nanotubes (CNTs) have attracted significant interest due to their very attractive mechanical and electrical properties. During the growth process, depending on the conditions in which they are formed, they assemble either as bundles consisting of individual cylinders (single-walled carbon nanotubes, SWNT) or as multi-walled co-axial tubules (multi-walled carbon nanotubes, MWNT). Individual nanotubes have a very high Young's Modulus (~1.2 TPa), stiffness and flexibility [2]. Accordingly, they could potentially be utilized in the flexible electronics industry based on these attractive properties as active devices or as interconnect materials.

Recently, various CNT based devices including gas sensors [3], pressure sensors [4], and transistors [5] are reported. Thermal sensors based using bundled Multi-Walled Carbon Nanotubes (b-MWNTs) are also demonstrated [6]. Furthermore, all these devices are fabricated on a planar two dimensional (2D) surface lacking the high density needed for future systems and also are manufactured on traditional silicon substrates. Moreover, sensors and electrical circuits fabricated on flexible substrates such as Polyimide (PI), Polyethylenenaphthalate (PEN) and Polyethylene terephthalate (PET) [4-5,7-8] have also been reported yet so far with the exception of Rodger [9], the use of a Parylene as a
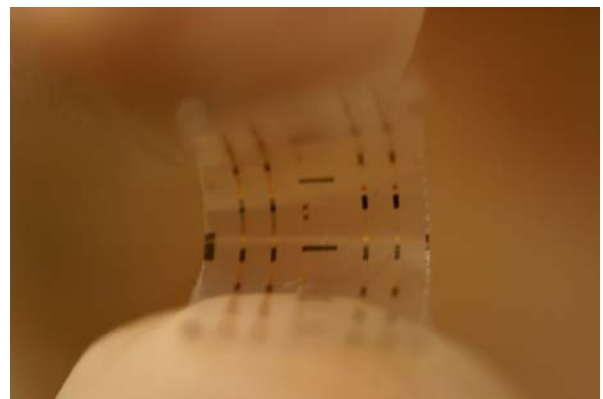

Fig. 1: MWNT thermal sensor array on a flexible parylene-C substrate

flexible substrate is not explored. Previously, we have demonstrated the three dimensional (3D) dielectrophoretic assembly technique for assembling gold nano particles [10] and Single-Walled-Carbon Nanotubes (SWNTs) [11]. In this paper, we present a MWNT based thermal sensor using 3D dielectrophoretic assembly technique on a Parylene-C flexible substrate (Fig. 1).

II. DIELECTROPHORETIC ASSEMBLY

Controlled placement of carbon nanotubes are needed for creating functional nano devices of technological importance. There are various means for incorporating CNTs on to micro platforms. Catalyst based CVD growth is one of the most common methods for selectively placing the CNTs. Yet a drawback of this approach is that CNT growth requires elevated temperatures (>700°C) and is not compatible with flexible devices since most flexible devices made out of polymers can not withstand such high temperatures. Another approach is to disperse the CNTs [19] on to wafers which is referred to as drop-casting, yet this approach lacks the control in selective and precise deposition of CNTs. In our approach, we have selected Dielectrophoretic assembly since it is a low temperature process compatible with flexible devices and moreover is amenable for batch manufacturing.

Dielectrophoresis has become a powerful method for manipulation, trapping and separating micro and nano particles. When a polarizable object is subjected to a non-uniform electric field, due to its interaction with the field, exhibits a translational motion which forms the basis of dielectrophoretic assembly [12]. Depending on the dielectric

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properties of the medium and particle, the exerted force on the nanomaterials will act towards (positive DEP) or away (negative DEP) from the regions where the electric field internsity is at a maximum. Even though dielectrophoresis occurs in both AC and DC electric fields, AC DEP is highly preferred since it allows manipulation and assembly of the nanostructures while minimizing and/or suppressing the electrochemical and particle migration effects present while using dc fields [13]. The Dielectrophoretic force exerted on the MWNT can be expressed by the following equation [6].

$$\left\langle F_{DEP}(t) \right\rangle = 2\pi ab^2 \varepsilon_m \, \text{Re}(K(\omega)) \nabla |E_{rms}|^2 \qquad (1)$$

In equation (1), ε_m is the absolute permittivity of the medium, a and b are the half-length and radius of the MWNT, and E_{rms} is the root mean square (rms) of the electric field. $K(\omega)$ (Clausius-Mosotti factor) and $L_{\parallel}$ (the approximated depolarization factor) are given as follows:

$$K(\omega) = \frac{\varepsilon_p^* - \varepsilon_m^*}{3\left[\varepsilon_m^* + \left(\varepsilon_p^* - \varepsilon_m^*\right)L_{\parallel}\right]} \qquad (2)$$

$$L_{\parallel} \approx \left(\frac{b^2}{a^2}\right)\left[\ln\left(\frac{2a}{b}\right) - 1\right] \qquad (3)$$

Here, ε_m^*, and ε_p^*, are absolute complex permitivities of the medium and MWNT. The electrostatic potential and the electric field lines around the 3D electrodes are illustrated in Fig.2. Since the DEP force acting on the MWNTs is positive, the CNTs will experience a pull towards the high field regions displayed by the arrow in Fig.2.
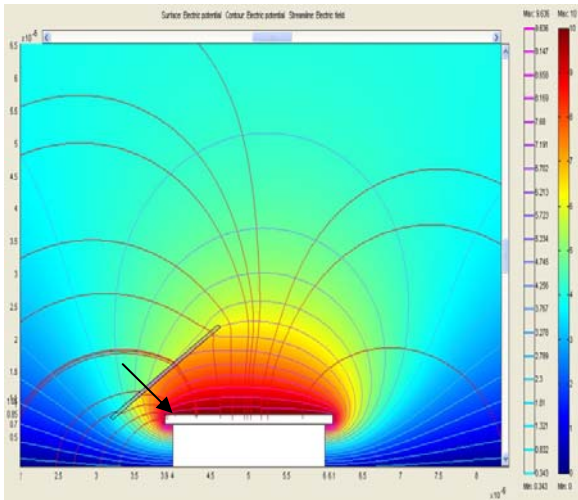

Fig 2: The electrostatic potential and field lines around the 3D electrodes

III. FABRICATION

A. Parylene as a flexible substrate

Flexible electronics are gaining popularity in applications where mechanical flexibility, large area, low cost and ease of fabrication are required. Polymer films such as PET, PEN and Polymide are widely used as substrate materials for most of the current flexible devices. Parylene, even though rarely explored, has attractive properties to be a competing technology as a substrate for flexible devices. Deposited at room temperature, parylene is a lightweight, optically transparent, mechanically strong and stress-free material which is compatible with integrated circuit fabrication processes. The melting point of Pa-C is about 290°C and it is also reported to have long term thermal stability [16]. Rodger et al [9] used Parylene type C (Pa-C) as a substrate to make flexible multi-electrode arrays for functional electrical stimulation in retinal prostheses. Since it is a biocompatible material, Parylene is utilized for patterning mammalian cells [15] and is also being explored as a biocompatible substrate for an on-chip micropump [14].

B. Fabrication of the micro electrodes for 3D assembly

The fabrication process for the 3D thermal sensor consists of a 3 mask process and is detailed in Fig. 3. The fabrication begins with the deposition of a 10 µm thick Parylene-C layer on a 3" silicon wafer at room temperature. This Parylene layer forms the flexible substrate which will be later peeled off from the silicon wafer. This peeling process for making flexible devices is much more straightforward and is simpler than present approaches where investigators have used sacrificial layers made of oxide or Aluminum, yet while removing the sacrificial layer, one exposes the sensor to various acids followed by rigorous rinse processes.
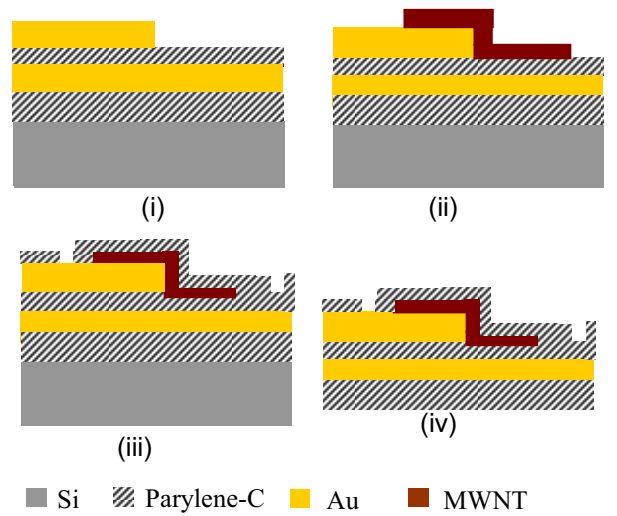

Fig. 3: Fabrication of 3D electrodes on a flexible parylene

The substrate thickness for a flexible device made out of parylene can vary between 5-20 µm, yet we have found out that as the Parylene film gets thicker (such as 20 µm), it becomes less flexible and yet if it is made thinner (such as 5 µm), then it fails during peeling and is not robust. Accordingly, we have selected a thickness of 10 µm for our flexible devices. Following the deposition of Parylene-C

substrate, we next deposit and pattern of the first metal electrode layer (Cr/Au, 200Å/1500Å in thickness) using a liftoff process. Then, a thin (0.7μm) and pin-hole free parylene-C dielectric layer is deposited that acts as an insulator between the 2 metal electrodes. The second metal layer (Cr/Au, 200Å/1500Å in thickness) is next deposited and patterned using the liftoff process (Fig.3(i)). These two metal layers serve as the electrodes for the 3D assembly of the MWNTs. Following this step, using the second metal layer as a mask, the parylene-C dielectric layer is etched away in an Inductively Coupled Plasma (ICP) Etching tool (Plasmatherm 790) using oxygen plasma. We then assemble tubes using a low temperature dielectrophoretic assembly process (Fig.3(ii)) the details of which is detailed in the following paragraph. Carbon nanotubes are highly sensitive to a broad class of chemical vapors and therefore this transduction mechanism can form the basis for a fast, low-power sorption-based chemical sensors [2, 18]. Accordingly, to isolate the CNTs from the environment and also to prevent contamination we have then encapsulated the 3D MWNT device with a thin and conformal Parylene-C layer. Contact holes are opened in this top Parylene layer utilizing oxygen plasma in the ICP reactor (Fig.3(iii)). Finally, the parylene C substrate containing the 3D thermal sensor is peeled off from the silicon wafer (Fig.3(iv)).
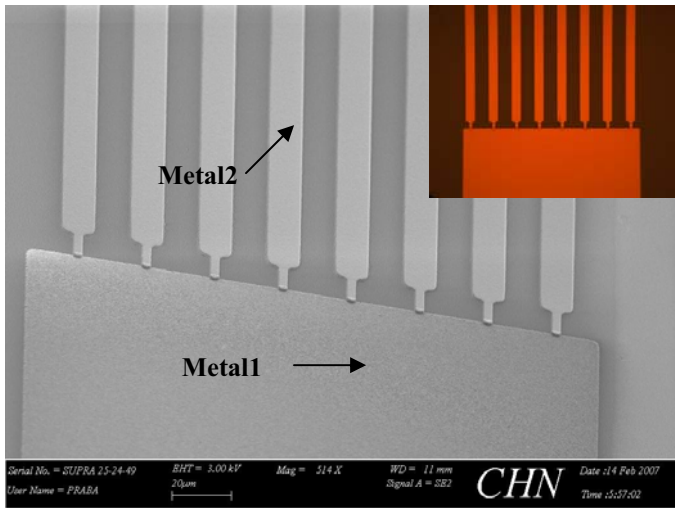

Fig. 4: SEM micrograph of 3D multifinger electrodes with optical image in the inset

C. Assembly process

Dielectrophoretic assembly is utilized while incorporating MWNTs into our 3D platform. In our experiments, we have designed and utilized multifinger electrodes design structure, where each finger has a width of 3μm and a length of 3μm at the tip. The fabricated multifinger assembly electrodes are shown in Fig.4. In our assembly process commercially available (Nanotechlabs, Yadkinville, NC, USA) MWNTs dispersed in an aqueous solution are utilized. As the first step in 3D assembly, we first apply an AC voltage with an amplitude of 10V peak-to-peak at a frequency of 10 MHz through a function generator (Agilent 33220A). After the

voltage is turned on, a droplet (2-3μl) of the MWNT solution is dispensed on to the chip containing the microelectrodes. After 20 seconds of assembly, the sample is blow dried and the power is turned off resulting in an assembled nanotube bridge between the electrodes seen in Fig.6. After I-V continuity measurements, a thin (1.0μm) parylene-C layer is deposited as the encapsulating layer. We then opened contact areas for measurements. The measured I-V curves before and after encapsulation is shown in Fig. 5 with a measured resistance of 21.18KΩ (before encapsulation) and 15.9KΩ (after encapsulation). It is interesting to note that the Parylene layer not only acts as a protective barrier, but also improves the two-terminal contact resistance of the 3D sensor. After the DEP assembly process, the MWNTs are attached onto the Au metal electrodes through van der Waals forces. Furthermore, we believe that the deposition of the top Parylene layer not only fixes the position of the CNTs, but also presses them against the Au metal and hence improves contact resistance between the metal and the CNTs. It is also likely that the parylene encapsulation increases the number of CNTs contacting the Au metal and hence improves the two terminal resistance of the structure and further experiments are underway to explain this behaviour. As seen in the SEM micrographs of Fig. 6 and Fig. 7, the nanotubes are mostly assembled around the sharp edges of the electrode where the electric field is maximum. The density of the assembled bundles can be controlled by varying the electric field which will be reported in a separate paper.
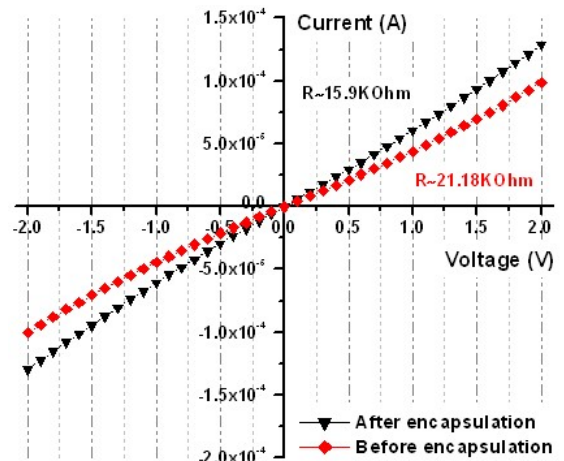

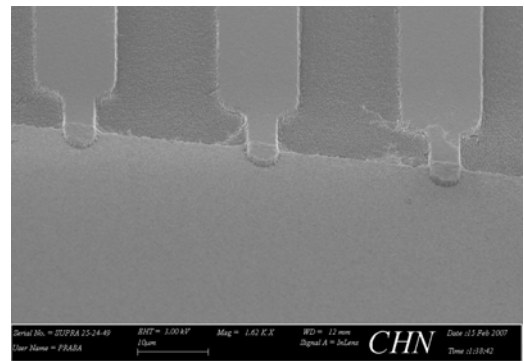Fig. 5: I-V measurements before and after the encapsulation

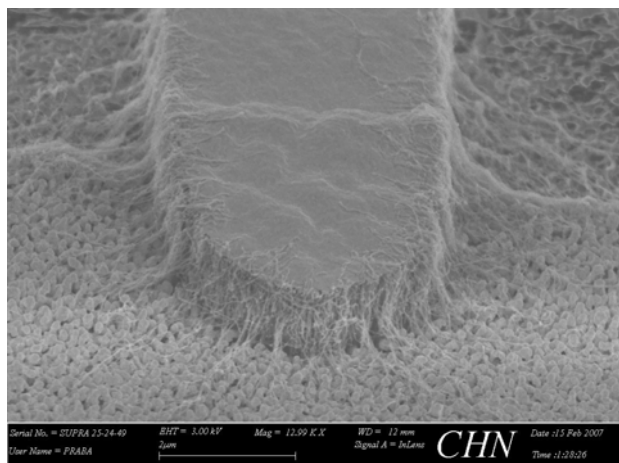Fig. 6: SEM micrograph of assembled MWNTs at 10V pp

Fig. 7: Close up SEM micrograph of assembled MWNTs

IV. RESULTS AND DISCUSSION

After fabrication, we have taken the sensor and performed temperature cycling. The 3D thermal sensor still situated on a silicon substrate for ease in testing (due to high thermal conductivity of si substrate) and is placed on a SUSS PM5 analytical probe system (with a heatable chuck) and we then measured the resistance while changing the temperature with the results illustrated in Fig. 8. The temperature is varied from 25°C to 75°C with 10°C increments. It is observed that MWNTs are sensitive to temperature and their resistance decreases corresponding to an increase in temperature. The temperature Coefficient of Resistance of the MWNT sensor is measured to be between -0.21% and -0.66% per degree. Then, several cycles of measurements were obtained from each device to ensure repeatability. Fig. 9 shows the temperature-resistance relationship repeated for 3 cycles.

It is important to note that the measured two-terminal resistance of the sensor slightly increased while the measurements were repeated; moreover the measured resistance stabilizes after about approximately several measurements. This could potentially be due to the fact that the nanotubes weakly adhere to the Au electrode and possibly detach during electrical measurements. Fig. 10 shows the repeated electrical measurement between 3D electrodes conducted after the two-terminal resistance of the sensor has stabilized. The Parylene encapsulation reduces this detachment but did not fully resolve the problem. The Parylene encapsulation makes the flexible MWNT sensor more stable and protects it from the environment. Non fluorinated Parylene such as Parylene C is known to have degradation at elevated temperatures in air or in an environment containing oxygen. It has been already studied that the oxidative chain scission in the parylene film mainly causes this thermal degradation. This discrepancy can be resolved by anti-oxidant treatment on the parylene film which increase the use temperature in the air [16]. Moreover,

Parylene HT, a new fluorinated variant of Parylene, provides thermal stability up to 450^0C [17] which enable the use of flexible Parylene substrate in applications where higher thermal stability is required. Therefore, Parylene with its excellent mechanical and thermal properties will find potential applications in flexible electronics applications.
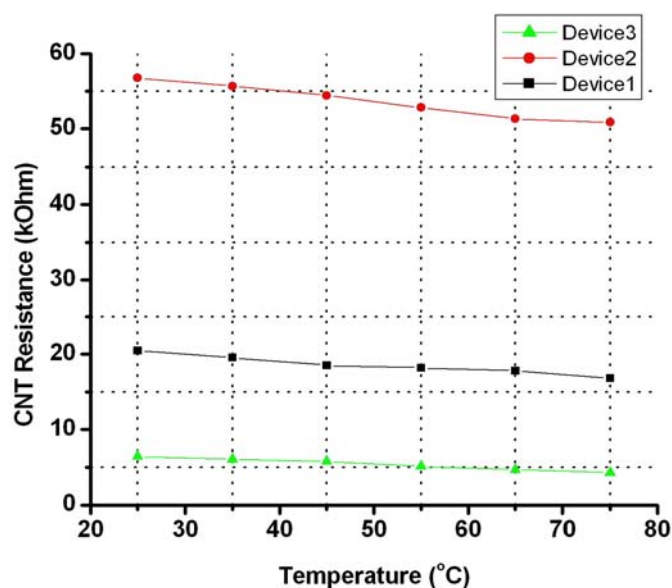

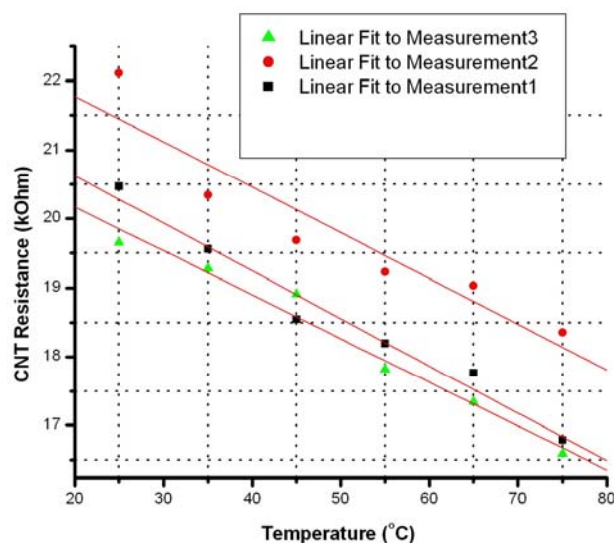Fig. 8: Temperature-resistance relationship of MWNTs sensors

Fig. 9: Temperature-resistance relationship of MWNTs sensor device1 in three consecutive measurements

V. CONCLUSIONS

In this paper, we demonstrate a MWNT based thermal sensor on a flexible substrate. Multi-Walled Carbon Nanotubes are utilized as the active layer of the thermal sensor. Utilizing dielectrophoretic assembly, the MWNT sensor was created in a 3D architecture at room temperature. Parylene C was used as a flexible substrate, dielectric and encapsulation layer. The fabrication process is quite simple and is amenable

to batch fabrication. The calculated TCR value from the MWNT thermal sensor device varied from -0.21 to -0.66%. This thermal sensor can be utilized in applications where flexibility is required such as electronic skin and wearable textiles.
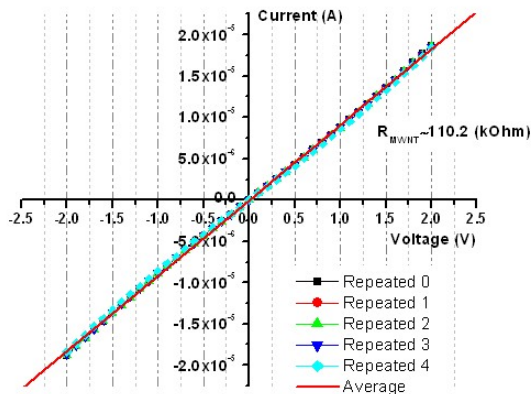

Fig. 10 Repeated electrical measurements

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