A Flexible Pressure Sensor With Sandwiched Carpets of Vertically Aligned Carbon Nanotubes Partially Embedded in Polydimethylsiloxane Substrates

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Abstract—This paper presents a flexible pressure sensor composed of two face-to-face electrodes of vertically aligned carbon nanotubes (VACNTs) carpets partially embedded in polydimethylsiloxane (PDMS) substrates. VACNTs were grown using atmospheric pressure chemical vapor deposition (APCVD) on a Si/SiO$_2$ substrate and transferred onto PDMS for partial embedment. This unique synthesis permitted a rapid and facile integration of a flexible and stretchable platform for the pressure sensor. The change of resistance occurs due to the external pressure applied orthogonal to the surface. The substrate was stretched to 180% and bent at bending radii of 87 mm and 105 mm. The pressure sensor exhibited the response times of 40 ms during loading and 60 ms during unloading. As a proof-of-concept, the sensor was attached on human skin; the heart rate, muscle flexing, and walking signals of an individual have been measured. In respect to durability, this sensor also showed a stable performance for 10,000 loading/unloading cycles with a resistance retention of 82% demonstrating its long-term use for repeated cycles toward practical applications.

Index Terms—Carbon nanotubes, flexible electrodes, pressure mapping, pressure sensor, stretchability.

I. INTRODUCTION

Recent research and development have enabled the manufacturing and integration of high-performance electronic systems on flexible substrates with promising prospect for e-skin, wearable, and bio-integrated applications [1]–[7]. These electronic systems incorporate a wide range of sensors, including electrophysiological, temperature, strain, and pressure sensors [8].

Pressure sensors are used to measure applied pressure via signal generation, which is often electrical. Silicon-based pressure sensors have long been realized commercially by well-established silicon micromachining technologies [9]–[13]. However, the rigid and brittle structure that constitutes the sensors can limit the functionality and applications of pressure sensors as wearable electronics [14], [15]. To this end, thin and flexible pressure sensors have been studied for flexible electronics and e-sk in applications [16]–[19]. Efforts have been made to develop pressure sensors on flexible substrates and to improve their performance (i.e., sensitivity, response time, pressure range, flexibility, and durability). Flexible pressure sensors are usually realized by replacing silicon with flexible substrates such as polymers, paper, or textiles [20]–[23]. In most cases, electrode materials are sandwiched between two flexible substrates. For the electrode materials, gold nanowires [24], silver nanowires [21], carbon nanotubes (CNTs), and graphene [25], [26] have been widely used, and various structures [27], [28] have been developed toward enhancing the performance of sensors. Several flexible
pressure sensors with CNTs as electrode materials exhibited the flexibility with up to 120% of stretching and bendability, with up to 90° bending angles [14, 19], [20]. A multi-functional stretchable sensor composed of orthogonal CNT-polyurethane sponge strips demonstrated the independent detection of omnidirectional bending and pressure [22]. Another pressure sensor comprised of hierarchical structures of aligned CNT/graphene and microstructured PDMS indicated a detection limit of 0.6 Pa and a response time of 16.7 ms [28]. Piezoresistive interlocked microdome arrays made of CNT-composite elastomer films detected various mechanical stimuli, including normal, shear, stretching, bending, and twisting forces [29]. Pattern transfer techniques have been commonly employed to fabricate electrodes towards flexible pressure sensors [30]–[35]. For example, graphite transferred onto PDMS using a two-step process by direct-write laser printing and patterned transfer resulted in flexible sensing resistors for fingertip pressure detection up to a range of 12 kPa [33]. Inkjet-printed CNTs of up to 35 layers transferred onto a PDMS substrate yielded a pressure sensor exhibiting the change in resistance with force up to 0.5 N [31]. CNT thin films fabricated by transferring mechanically drawn CNT sheets via metal stick directly onto a polyethylene naphthalate (PEN) substrate resulted in a flexible pressure sensor with a pressure detection limit less than 2 Pa [30]. Although aforementioned reports on flexible pressure sensors have demonstrated good mechanical flexibility and stable performance essential for realizing e-skin or wearable applications, there is room for improvement on both the complicated fabrication process and their performance.

Here we demonstrate a flexible pressure sensor using VACNT as the electrode materials and PDMS as a flexible platform. VACNTs are grown via atmospheric pressure chemical vapor deposition (APCVD) and then transferred onto partially cured PDMS. As a result, VACNTs are partially embedded in PDMS, ensuring that individual CNTs are strongly held by the fully cured PDMS. This enables the structure to sustain various strains. We measure the change in resistance due to the application of pressure orthogonal to the surface, while demonstrating the flexibility with stable performance. We determine that the fabricated VACNTs/PDMS structure achieves a high level of integrity under various strains. Detailed characterization on the durability and flexibility of the sensor is performed under various strains and for 10,000 loading/unloading cycles.

II. MATERIALS AND METHODS
A. Fabrication of Flexible Pressure Sensors
The fabrication of CNT/PDMS structure is similar to the process reported in our previous work [36]. VACNTs were grown via APCVD, and Raman spectroscopy confirmed VACNT quality, such that individual nanotubes are not affected by the lateral stretching of PDMS, as shown in our previous work [36]. Physical vapor deposition (PVD) was used to deposit 5 nm Al and 3 nm Fe as catalyst on the substrate of Si/SiO2. Following addition of catalyst, the substrate was placed in a quartz tube furnace for CNT growth via APCVD with a growth temperature increased to 750 °C while flowing 500 sccm Ar gas, and the furnace temperature was maintained at 750 °C for 15 min with 60 sccm H2 and 100 sccm C2H4. The CVD tube was then rapidly cooled to room temperature by opening the furnace cover, while maintaining Ar flow. The grown CNTs displayed a vertically aligned structure, composed of individual wavy nanotubes, mechanically cross-linked with one another. The grown CNTs on Si/SiO2 were transferred onto partially cured PDMS, as detailed in our previous work [36]. First, a liquid mixture of PDMS base and curing agent (Sylgard 184 Silicone Elastomer, Dow Corning) was mixed with a ratio of 10:1 and degassed under reduced pressure in a vacuum environment to remove gas bubbles. The liquid PDMS was heated on a hot plate at 65 °C for approximately 30 min to a state of partially cured PDMS. The curing condition of PDMS was optimized to wet fully the roots of individual CNT carpets upon the full curing of PDMS. To transfer the CNT carpet onto partially cured PDMS, as grown CNT on Si/SiO2 was placed face-to-face onto the partially cured PDMS, and PDMS infiltrated between each individual carbon nanotube, owing to the capillary effect and the viscoelastic property of PDMS. As a result, tips of interwoven CNTs were embedded into PDMS, and the CNT/PDMS was left in an ambient condition for 12 h to fully cure PDMS. After PDMS was fully cured, VACNTs were partially embedded in PDMS and the Si/SiO2 substrate was easily peeled away, resulting in a single CNT/PDMS electrode. Then, two CNT/PDMS electrodes were stacked face-to-face to fabricate the resistive-based flexible pressure sensor.

B. Characterization and Measurements
The scanning electron microscope (SEM) (Auriga Small Dual-Beam FIB-SEM, Carl Zeiss, Jena, Germany) was used to characterize the samples. The resistances of the sensors were measured using a potentiostat (236A, Princeton Applied Research, Oak Ridge, TN). The sensors were connected to the potentiostat and a voltage was applied to the sensor while the current was measured. A force testing system (Chatillon TCD110 Series) was used to apply various pressures to the sensor. A constant displacement rate of 0.5 mm/minute was applied, compressing the pressure sensor vertically (out-of-plane direction).

III. RESULTS AND DISCUSSION
Fig. 1a shows a schematic of the mechanics of the flexible pressure sensor. Fig. 1b–c show scanning electron microscope (SEM) images depicting the cross-sectional view of an area interfacing the two VACNTs/PDMS layers, where CNT carpets of upper and bottom layers make contact. Fig. 1d–e present digital photographs of a pressure sensor sample, showing the stretchability for wearable application. When an external pressure is applied orthogonal to the surface of VACNT carpets, the contact areas between individual CNTs embedded on both top and bottom PDMS substrates increase; the resistance of the contacting nanotubes then decreases because of the decrease of the electrical conducting length. The fabricated devices showed a broad range of pressure sensing from 26 Pa to 56 kPa, as shown in Fig. 2a, with capabilities in the sub-pressure regime such as screen touch (<1 kPa), the low-pressure regime such as daily.
activity (1–10 kPa), and also the medium-pressure regime such as object manipulation (10–100 kPa) [17], [27]. As shown in Fig. 2a, the recovery curve and response curve result in hysteresis due to interlocking of CNTs on opposing electrodes with increased pressure. As pressure is alleviated, individual CNTs maintain contact with CNTs of opposing electrodes during the recovery curve that were not present during the initial response curve. The long saturation period shown in Fig. 2a is attributed to the loading becoming stabilized.

Fig. 2. (a) Change of resistance in response to increasing and decreasing pressure loadings. (b) Response times under the pressure loading and unloading by instantaneously putting a weight on top of the pressure sensor manually.

The mechanical flexibility was tested by applying strains to the substrate and measuring the resistance change simultaneously. The experimental setup is shown in Fig. 3a, with initial state (no stretching) (top image) and with 50% stretching (bottom image). The amount of stretching is controlled by clamping both ends of PDMS into the system and physically extending one clamped end, while the other end remains fixed to introduce strain. As shown in Fig. 3b, the sample was stretched up to 180% until it reached the breaking point of the PDMS substrates. With the increase of tensile strains, some individual nanotubes may be separated from each other, increasing the overall resistance, especially at high stretching strains. Previously, a direct correlation has been observed with spacing of CNT arrays and the macroscopic electric field [37]. As strain is increased, a greater quantity and degree of stretching between individual CNTs likewise occurs, resulting in the observed trend herewith. Fig. 3c shows the measured resistances of a sensor at various stretching strains from 0% to 13% at different pressures of 0 Pa, 500 Pa, 509 Pa, 975 Pa, and 1783 Pa. As shown in Fig. 3c, there is no significant change in resistance with respective pressure values within this range of relatively lower stretching strains. We attribute this to intermingling contact maintained among neighboring CNTs at relatively low strain values, maintaining resistance values at respective applied pressures. As shown in Fig. 4a, various bending radii of 85 mm, 105 mm, and 200 mm were tested,
Fig. 3. (a) Photo image of tensile testing setup, showing the sensor with a stretching strain of 0% and 50%. (b) Changes in relative resistance (i.e., \(\Delta R/R_0\)) at various stretching strains from 0% to 180%. (c) Resistances of the flexible pressure sensor at various stretching strains from 0% to 13% at different pressures of 0 Pa, 500 Pa, 509 Pa, 975 Pa, and 1783 Pa.

with bending angles of 6.8\(^\circ\), 5.5\(^\circ\), and 2.9\(^\circ\), respectively, calculated using a 1 cm \(\times\) 1 cm sample. Different pressures were applied corresponding to weights of 0 g, 2 g, 5 g, and 20 g. Fig. 4b shows the schematic of the bending test of the sensor. The resistance of the sensor decreased with the increase of the applied loading but remained stable at various bending radii at equal loading, showing that the sensor was relatively robust against bending. Fig. 4c shows the relative resistance of a number of samples at different applied pressures of 0 Pa, 500 Pa, 1 kPa, 1.5 kPa, and 2 kPa. The variation in relative resistance for the pressure sensor is at 19.3%, 19.4%, 18.2%, and 17.0% at applied pressures of 500 Pa, 1 kPa, 1.5 kPa, and 2 kPa, respectively. We attribute this variation in relative
To test the long-term cyclic stability, the sample was tested using a force testing system (Chatillon TCD110 Series) for 10,000 cycles and applied load at a maximum of 20 N, as shown in Fig. 5a. Photographs of the experimental setup and equipment are shown in Fig. 5c–d. The pressure sensor sample had an electrode area of 1 cm × 1 cm, and a cross-sectional area of 0.5 cm². For clarity, Fig. 5a, a small
snapshots of the 10,000 cycles at different representative intervals, is shown. Each line on the graph (i.e., differing in color, as shown in the legend) represents the first 100 seconds at that initial cycle. For example, the first spike at “0 s” for the “7,000 Cycles” black line represents the 7,000th cycle. Each subsequent cycle of that black set represents the next cycle in that sequence (i.e., 7,001st, 7,002nd, etc.). After many cycles and accumulated pressure, the upper current values decreased, whereas lower current values increased, as shown in Fig. 5b. We attribute this change to the altering overall contact area between opposing electrodes following repeated cycles. As previously reported, compressive strain introduced parallel to VACNT electrodes increases electrical conductivity [38], and the application of lateral stretching via PDMS may not induce large strain to the CNT material itself. As pressure is applied, individual CNT buckle and the cumulative height of the electrode is lowered, resulting in local changes in contact surface area [39]. When contacting opposing electrodes of VACNT herewith, individual CNTs similarly undergo bending with a change of overall conductivity dominated by the change of contact areas.

To test the suitability of the fabricated sensor for an e-skin application, we attached the sensor on the skin of a person to obtain the pulse, muscle flexion, and step count (on sole of shoe), as shown in Fig. 6. We used the same sample that was used to obtain the pulse, muscle flexion, and step count for this experiment, demonstrating its potential ability to be used for wearable electronics. The experimental setup is detailed in the Materials & Methods section, similar to other experiments reported herewith. However, we used long wires connecting to the sample from the potentiostat to allow respective motion. The sensor was placed on the forearm of the person. As the person flexed the forearm muscle, the force caused by flexion produced higher pressure, increasing the measured current. Then the sensor was placed on the bottom of a heel of the person, and the sensor detected the walking signals. These capabilities demonstrate that this sensor has potential to be a promising wearable pressure sensor.

IV. Conclusions

We have demonstrated highly flexible pressure sensor enabled by opposing two VACNT layers, in which the tips of CNTs are partially embedded into PDMS, warranting a robust sensing performance under various mechanical strains. The device fabrication is extremely facile (i.e., two sandwiched electrodes each achieved by transferring directly grown CNTs onto partially cured PDMS), and the fabrication cost is also very low. The pressure sensor showed a broad sensing range from 26 Pa to 56 kPa, with capabilities in subtle-pressure regime such as screen touch (<1 kPa), the low-pressure regime such as daily activity (1–10 kPa), and also medium-pressure regime such as object manipulation (10–100 kPa). The response time of 40 ms enabled the pressure sensor to detect any biological ‘pressure’ signals real-time. This sensor also demonstrated stretching up to 180% and bending at different bending radii. The sensor showed a stable performance for 10,000 loading/unloading cycles with the resistance retention of 82%. This sensor detected the pulse signatures, muscle flexing, and step count/intensity, which is very promising for e-skin or wearable applications.

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References


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