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Vertically aligned multiwalled carbon nanotubes for pressure, tactile and vibration sensing

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Abstract

We report a simple method for the micro–nano integration of flexible, vertically aligned multiwalled CNT arrays sandwiched between a top and bottom carbon layer via a porous alumina (Al2O3) template approach. The electromechanical properties of the flexible CNT arrays have been investigated under mechanical stress conditions. First experiments show highly sensitive piezoresistive sensors with a resistance decrease of up to ∼35% and a spatial resolution of <1 mm. The results indicate that these CNT structures can be utilized for tactile sensing components. They also confirm the feasibility of accessing and utilizing nanoscopic CNT bundles via lithographic processing. The method involves room-temperature processing steps and standard microfabrication techniques.

(Some figures may appear in colour only in the online journal)

1. Introduction

Carbon nanotubes have superior electrical and mechanical properties with high electrical conductivity, supercompressibility, bending elasticity, structural flexibility and high aspect ratio, as well as chemical inertness. These make them an attractive material for pressure, vibration and tactile sensors. Free-standing films of vertically aligned carbon nanotubes have highly compressive behavior, up to 85%. The nanotubes can collectively form zigzag buckles that return to their original length in a fully elastic way upon load release [1]. They are optimal devices for highly sensitive pressure sensing of various surfaces as a result of mechanical strength and high elasticity. Nanotubes exhibit extreme structural flexibility and can be repeatedly bent through large angles and strain without structural failure [1]. Fundamental studies of mechanical properties and pressure sensitivities of individual CNTs or composite materials with dispersed CNTs were performed by several groups [2–6]. The selective deposition of single CNTs is a complex and costly process. It also involves composite materials with small sensitivities employing disordered CNTs with limited applicability due to their non-uniformity of length, diameter and density of the individual CNTs.

Mechanical properties of CNTs in the form of dense vertically aligned arrays have also been investigated [1, 7–12], whereas [7, 9–11] have additionally characterized the resistance change with mechanical pressure. The vertical SWCNTs in [9] were 600 nm long and showed a conductance enhancement of 12% at \( \Delta l/l = 1/3 \). Large CNT blocks showed an increased electrical conductivity of ∼4% at a compressive strain \( \Delta l/l = 1/10 \) [7]. The piezoresistive pressure sensor in [10, 11] used a multiwalled CNT forest (height ∼500 µm [10]) supported by a deflectable polymer membrane as the sensing element. Positive gauge pressures decreased the sensor resistance by 6% at 60 kPa [10]. The source of piezoresistive effects of CNT forests has been

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related to the change in distances between individual CNTs due to the applied lateral stress. In [12] branched treelike carbon nanotubes (height \( \sim 7 \mu m \)) on silicon membranes were applied for interdigital capacitive pressure sensors. The capacitance decreased from 7.5 to 3.8 pF at an applied pressure of 1 atm. Skinlike sensors were recently reported in the literature [13] based on planar nanotube electrodes in an elastic matrix (not vertically aligned) with detectable pressure of 50 kPa and capacitance change of 15% at 1 MPa. The micro–nano integration of vertical well-aligned CNT structures is still a challenging topic [15].

Our studies presented herein extend the above-mentioned studies on vertically aligned CNTs as pressure sensors to a significant extent. The investigated structures are composed of microsized 3D aligned CNTs in a matrix configuration with unique sensitivity up to 35% at \( \Delta l/l = 1/10 \) and high special resolution <1 mm. The vertically multiwalled carbon nanotube arrays reported here have high area density and are particularly useful for applications involving mechanical deformation. Due to its flexible mechanical structure the CNT array is bendable and this should allow mounting on a variety of flexible substrates. Furthermore, it makes use of simple micro–nano integration. This work demonstrates pressure and vibration sensing using such devices. Individually addressed devices were built using the developed process. The device dimensions are adjustable and defined by photolithography for high spatial resolution.

2. Fabrication process

2.1. CNT growth

Porous alumina with parallel, hexagonally arranged, cylindrical pores was used as a nanostructured template. The pore diameter (4–200 nm) and template height (2–100 \( \mu m \)) can be varied by controlling the anodization potential, electrolyte and anodization time of the electrochemical oxidation [14]. Vertically aligned, multiwalled nanotube arrays were produced by non-catalytic chemical vapor deposition (CVD) inside and outside the alumina pores, having an average pore diameter of 160 nm. A CVD reactor with induction heating was used and CNTs were grown at a deposition temperature of 750 °C by using a homogeneous flow of propylene (C\(_3\)H\(_6\)) for 10 min. Argon was used as carrier gas and growth resulted in the formation of a carbon layer on the top, on the bottom and inside the pores (forming the carbon tubes) of the alumina template. The carbon nanotubes had homogeneous length, diameter and density (6 \( \times \) 10\(^6\) mm\(^{-2}\)). The resulting CNT network channel contains mainly metallic paths. Figure 1(a) shows a typical side view of an as-grown CVD CNT array with an array height of \( \sim 50 \mu m \). The CNTs are linear all along the pores. Details of CNT growth can be found elsewhere [15, 16].

2.2. Micro–nano integration

The sensor architecture consists of parallel carbon nanotubes, which merge into the top and bottom carbon layers perpendicular to the tube axis. The grown CNT structures were used for the fabrication of thin, flexible, skin-like pressure sensors for tactile sensing. The CNT arrays were used while still being embedded in Al\(_2\)O\(_3\). The electrical contact of the structure takes place before the acid-based removal of the alumina. This allowed us to use the CNT/alumina composite by ensuring both higher mechanical stability for the following photolithographic processes and also protection of the tubes through the template. Several process steps were necessary for the micro–nano integration. First, both sides of the complete CNT arrangement were sputtered with 100 nm Au to realize the contacts to the carbon layers and the CNTs (figure 2(a)).

A continuous surface metallization served as lower contact while the smaller contacts on the top defined the second electrode and the resolution of the sensor matrix. The analysis of the spatial sensitivity required the complete
decoupling of individual sensor cells in order to eliminate any cross-sensitivities. The top metallization and carbon layer were structured by optical lithography and subsequent etching (figure 2(b)). Designs with $2 \times 2$ and $3 \times 3$ matrix configurations with $\sim 40 \, \mu\text{m}$ contact diameter and $300 \, \mu\text{m}$ center-to-center separation were used to determine the spatial resolution. A straightforward electrode formation at both ends of the CNTs was possible due to the integrated carbon layers on the top and bottom of the tube arrangement. Afterward, the samples were passivated by $\sim 1 \, \mu\text{m}$ thick polymer by spin coating the top side (figure 2(c)). A second photolithography process was used to open contact regions by oxygen plasma etching (figure 2(d)). These were connected to larger gold bonding pads of $400 \, \mu\text{m} \times 400 \, \mu\text{m}$ size (figure 2(e)). Finally, a wet chemical etching process was used to remove the $\text{Al}_2\text{O}_3$ template surrounding the contacted CNTs, which resulted in a negative carbon copy of the original template and allowed completion of top and bottom contact fabrication. Free-standing vertically aligned uniform CNTs could be obtained in this way (figures 1(a) and (b)). The back contact was glued on a conductive, flexible and adhesive support material to perform the pressure measurements.

The distribution of CNTs after oxygen plasma etching of the top carbon layer is given in figure 3. The fabricated devices vary from the ideal model given in figure 4(a). The initial device resistance can vary even without exercising any additional pressure due to the existence of additional current paths. The pressure sensor makes use of the relative resistance change, which is less influenced by the uniformity of CNT distribution.

Figure 4(a) shows a simplified schematic diagram for contacting. A $2 \times 2$ matrix chip is given in figure 4(b). Only the indicated CNT contacts ($\varnothing 40 \, \mu\text{m}$) have an opening in the polymer layer on the top of the sample (see figure 4(b)) and were connected to the larger gold bonding pads on the top of the polymer layer of $400 \, \mu\text{m} \times 400 \, \mu\text{m}$ size. The metal wires on the bonding pads were fixed far from the CNT contacts. This initial configuration was sufficient to determine the spatial resolution. Further optimization of the wiring is possible with a grid of resistances for future ‘skin-like’ applications (see figure 4(c)).

The complete structure is monolithic and flexible and can be produced in a size of up to several square centimeters depending on the original template size. Increased CVD

Figure 3. (a) Surface of the 3D CNT layer after deposition of the gold electrode and plasma etching of the carbon layer. (b) CNT distribution after complete removal of the top carbon layer (higher magnification).
growth time results in thick walled carbon tubes, whereas higher temperature growth produces more crystalline, graphite-like structures. The high density \((6 \times 10^6 \text{ mm}^{-2})\) and 50 \(\mu\text{m}\) long carbon tubes have a large surface area, permitting enhanced interaction with neighboring CNTs. An important application of the developed pressure sensor is artificial tactile components with sensitivity equivalent to that of human fingers [17].

### 3. Measurements

#### 3.1. Function of the pressure sensor

The use of the \textit{in situ} grown top and bottom carbon layers allows a flat arrangement of individual contact points with high sensor surface density and thus leads to a high spatial resolution of the sensor matrix. The flexible matrix element is a sensitive, stable, 3D sensor \((x, y, z)\) for mounting on arbitrary surfaces (figure 4(d)). The piezoresistance of the contacted CNT was evaluated. The sensors can be easily adapted to 2D and 3D curved surfaces that enable spatial resolved monitoring of forces interacting with it. Upon mechanical pressure on the CNT bundle, there are three effects that lead to piezoresistive effects (figure 5). Normally, the conductance of individual (semiconducting) CNTs decreases under compressive stress, and is associated with a change in length or curvature of the CNTs and significant local deformation of the band structures in the individual CNTs [5, 18] (see figure 5(a)).

The second reason is the CNT/metal contact modification [19], which is manifest as a conductance decrease (figure 5(a)). The dominant sensing mechanism in the proposed configuration (figure 4(a)) is of a completely different physical nature (figure 5(b)). At certain compressive strain levels, the mechanical deformation of the CNT arrays causes an increase of CNT bundle conductance. The bent CNT bundle touches its neighboring free-standing tubes and presents some lateral cross-tube coupling, which generates additional current paths in the vertical direction (parallel to the CNTs) and increases the conductance of the sensor element (figure 5(b)).

The resistance change in the \(x\)- and \(y\)-directions with respect to pressure is of the same degree and cannot be distinguished without an evaluation of the neighboring contacts. The vertical force (\(z\) direction) can be detected separately for each contact with a single point measurement, as long as no superposition of forces in \(x\) and \(y\) directions occurs.

#### 3.2. Pressure sensing

The entire bottom contact and large Au bonding pads on the top side were used for connecting the nano- and micro-parts of the pressure sensor. A home-built loading platform using a needle was used to define the displacement and compression of the CNTs. The loading stage consists of a micropositioner part with a needle and a piezoelectric stage providing the actuation (figure 6(a)). It is actuated by a piezoelectric element through the continuous kicking action of a PZT. The displacement resolution of the current platform was limited by the piezoelectric stage to 150 nm. Figure 6(a) shows the setup used for compressive tests. The needle at the micropositioner stage is pressed into the CNT array, whose substrate is fixed to the moving part.
Figure 5. Working principle of the nano-pressure sensor element. The mechanical deformations result in change of the band structure and CNT/metal contact resistance (a). The CNT bundle contacts the neighboring free-standing tubes (b). Mechanism (a) causes a decrease while mechanism (b) leads to an increase of the CNT sensor conductance.

Figure 6. (a) A home-built loading platform using a needle to define the displacement and compression of the CNTs. (b) Displacement dependent resistance change of the nano-pressure sensor.

Figure 7. Setting of defined force in the nano-pressure sensor array by a Frey filament mounted at a calibration robot arm. The entire demonstrator has a size/area of about 0.25 cm$^2$ (5 mm $\times$ 5 mm). (a) Region with the pressure sensor and Frey filament.
Table 1. Device conditioning.

<table>
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<tr>
<th>Maximum voltage (V) for preconditioning</th>
<th>1</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device resistance (Ω)</td>
<td>33</td>
<td>38</td>
<td>53</td>
<td>345</td>
<td>625</td>
<td>1205</td>
<td>2085</td>
<td>7140</td>
</tr>
</tbody>
</table>

Figure 8. Illustration of reproducible measurements of the piezoresistivity (a) and relative resistance change of the sensor element versus position of the Frey filament (b). Contour plot of the spatial pressure sensitivity of the nano-pressure sensor measured with a Frey filament at 32 mN (c).

of the PZT kicking stage in the direction perpendicular to the array surface. The resistance–displacement curves under compression loading of 50 μm tall CNT arrays are shown in figure 6(b). The mechanical deformation of the CNT networks generated additional current paths and increased the vertical conductance of the CNT pressure sensor element. The results indicate that the electrode beam presents first non-linear characteristics followed by linear behavior under higher compression. The measurements showed a reproducible displacement dependent resistance decrease in the range of ∼35% per cent upon 5 μm displacement (figure 6(b)). Upon application of different compressive strain levels there is a significant change in the conductivity with a recovery after strain removal. Multiwalled CNTs (MWCNTs) have unique reversible electrical conductivity and compressive strain responses. The MWCNTs in our work showed small initial cross-tube coupling among neighboring tubes and are stiffer compared to single-walled CNTs (SWCNTs). The pressure can also be applied from the bottom side with uniform single contact. The pressure from the bottom can force a contact of the CNT bundle with the neighboring free-standing tubes similar to the pressure from the top side.

The obtained characteristics and sensitivities were also evaluated by considering the initial resistance of a single sensor element. The resistance of the fabricated pressure sensors depends on the contact size, growth condition (graphitization), tube diameter and wall thickness and had values ranging from 30 Ω to >10 kΩ. Less graphitic and thin-walled CNTs have higher resistance and flexibility for mechanical sensors. The initial resistance also increased with smaller contact size. The increase of additional current paths at applied pressure is higher for smaller contact pads. Therefore, sensors with smaller contact pads lead to higher sensitivity. Devices with small top contact diameter (40 μm) were fabricated and characterized particularly for tactile sensing. An opening in the polymer layer served for connecting the small contacts to the larger gold bonding pads of 400 μm × 400 μm. We have obtained for these devices a resistance of >100 Ω.

Devices with larger contact size (∼100 μm) and smaller initial resistances could be preconditioned by high current densities to achieve a pronounced increase in the resistance and thus improved sensitivity. Highly conductive CNTs in the CNT bundle are modified or burned at higher applied voltages (5–10 V). The device resistance remained stable in the following low voltage measurements (see table 1 for device conditioning). Here the contact with neighboring CNTs (without conditioning and in the presence of high conductivity) has a pronounced resistance change and therefore high sensitivity to external mechanical stresses.

3.3. Tactile sensing

Following the first measurements with the home-developed measurement systems the piezoresistivity and spatial resolution of the sensors were tested in detail with an industrial
Figure 9. (a) A home-built platform for CNT sensor vibration up to 10 kHz. (b) Vibration frequency dependent resistance change of the nano-pressure sensor.

robot arm at Battenberg ROBOTIC laboratory. The force was set by a so-called Frey filament mounted at a calibration robot arm (figure 7). The local and spatial sensitivity were measured close to the sensitive area of the nano-pressure sensor array. The Frey filament used buckled at a defined force of 32 mN and was applied to the nano-pressure sensor multiple times in the same way. The results of repeated pressure measurements are shown in figure 8(a).

The introduction of a small 32 mN force leads to a resistance decrease of ∼0.7 kΩ for an initial resistance of 12.7 kΩ (figure 8(a)). This corresponds to a relative change of ∼6%. Repeated measurements showed good reproducibility of the observed changes in resistance. The standard deviation of the resistance change was only 13 Ω for ten measurements. This meets the intended use of nano-pressure sensors as a sheet-like probe element to simulate the function of a human finger. The introduction of ‘macroscopic’ forces (1 N) on the surface of the nano-pressure sensor destroyed the nano-pressure sensor. The response time of the CNT sensor element and thus resistance change was smaller than the time for loading and unloading the sample. No fast pressure change tests were performed. Figure 8(b) shows the resistance change versus the position of the Frey filament.

Based on these results the Frey filament (32 mN) was used at different sensor surface positions. The resistance change decreased continuously from the most sensitive contact region and had no influence at ∼500 µm distance from there. The spatial accuracy for the fabricated sensor was ∼1 mm. Figure 8(c) shows the contour plot of the spatial pressure sensitivity, where the x and y axes refer to the position of the filament. The resistance change is shown in color. The determined surface dependence reflects the high spatial sensitivity of the nano-pressure sensor at 32 mN. The resolution (<1 mm) obtained by the Frey filament measurements is not much limited by the top surface contacting. It will be more limited by the thickness and elasticity of the used polymer layer, which can transfer some lateral forces toward the contacted CNT bundle.

A recent publication has analyzed the uniaxial compression of vertically aligned carbon nanotubes [20]. It was found that at high compressive strains periodic softening events correspond to the appearance and evolution of individual buckling events. However, it was presumed that vertically aligned CNTs with higher density would produce smaller amplitude buckles due to the increased number of tube-to-tube interactions and therefore decreased deformation. Furthermore, materials made with larger diameter tubes (and thicker walls) would have larger wavelength buckles. Elastic loading with some bending instead of buckling of CNTs is expected for such devices (high density and large diameter MWCNTs) and applied compressive strains (<10%). Simulations of the resistance changes e.g. for different CNT diameters as well as distances of the CNT within an array structure have to be performed to fully understand these effects.

3.4. Vibration sensing

A home-built measurement platform was also used to characterize the CNT arrays by measuring their vibration when placed on a Teflon holder. This allows the characterization of the CNT sensor configuration in the absence of direct load and strain. A rectangular plate (6 mm × 3 mm; thickness 1 mm) made of Teflon was fixed in the center to the subcone of an ordinary speaker with free-standing ends. With the speaker turned face up, the CNT sensor configuration was placed and contacted with gold bonding wires on the horizontal Teflon plate. A schematic diagram of the experimental setup is shown in figure 9(a). A sinusoidal oscillation was generated by a signal generator and was used as input to the speaker. The input signal amplitude was kept constant and the oscillation frequency was changed from 10 to 10 000 Hz. The fundamental frequency of self-excited vibration of the attached Teflon plate was measured at 4 kHz (figure 9(b)) and changed with the Teflon holder size. The estimated resonant frequency of the fabricated CNT itself is much higher. The vibration of the Teflon holder leads to bending of the mounted CNT sensor and contacting of the free-standing (non-contacted) neighboring CNTs. These new paths increase the conductivity and decrease the device resistance by 30%
at an input signal of 0.15 V. The vibration amplitude of the speaker diaphragm was ~15 μm at 50 Hz and decreased with higher frequency.

4. Conclusions

Micro–nano integration of vertical well aligned MWCNT arrays was successfully realized for pressure, tactile and vibration sensing. The 50 μm-long CNTs were very linear and merged into the top and bottom carbon layers perpendicular to the tube axis. Measurement setups suitable for sensitivity investigations and spatial resolution evaluation were realized. First experiments show the possibility of realizing highly sensitive piezoresistive sensors with a resistance decrease in the range of ~35% and 6% for the home-made piezoelectric measurement setup and the Frey filament system, respectively. The study showed good reproducibility and initial spatial resolution of <1 mm. The CNT sensor configuration was also used as vibration gauge on an oscillating Teflon plate and showed a resistance decrease of ~30% at an input signal of 0.15 V. A configuration of this type can be used for the measurement of indirect forces. The sensor array is monolithic, flexible and can be produced in a size of up to several square centimeters. It can be implemented in future systems for the measurement of 3D compressive forces on any curved surfaces and can be employed for the simulation of human tactile sensitivity.

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