Self-Welded Metal-Catalyzed Carbon Nanotube Piezoresistors with Very Large Longitudinal Piezoresistivity of ~ 4×10^{-8} Pa^{-1}

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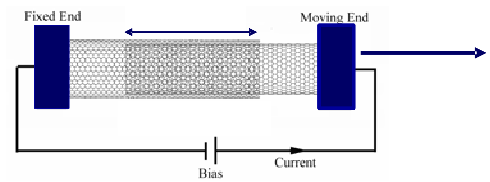
ABSTRACT

Self-welded double-walled and multi-walled carbon nanotube (DWCNT and MWCNT) bridges, grown using low-pressure metal-catalyzed chemical vapor deposition technique between silicon on insulator posts, were used as tiny piezoresistors to monitor vibration and bending/deformation of silicon cantilever beams for the first time. The weld strength of CNTs measured using atomic force microscope was larger than 100 nN/CNT and their full-scale resistance change was larger than 10^5 Ω.The effective longitudinal piezoresistivity of these CNTs was larger than 4×10^{-8} Pa^{-1} which is more than 10 times larger than that of Π_{44} in silicon.

Keywords: self-welded nanotube, nano-piezoresistor, nano sensors, strain gauge, CNT

1 INTRODUCTION

Capacitive and piezoresistive sensing techniques are main methods used in pressure sensors, accelerometers and other microfabricated sensors. As the device size decreases moving in the direction of nano-devices and systems, the capacitive sensing method becomes less sensitive because device areas shrink faster than the distance between different elements in most applications. The piezoresistive method also suffers for similar reasons. Thus, there is a genuine need for a nano-scale piezoresistor with large sensitivity to displacements in the nano regime. Moreover, owing to simplicity of growth and scalability (because it does not need electron beam lithography) a nano-scale CNT piezoresistor is also of great interest in bottom-up scalable growth and fabrication technologies. The effect of mechanical deformation on the electrical properties of carbon nanotube (CNT) has been studied and discussed in [1,2]. The results of one particular study [3] on the conductance between a CNT and a highly ordered pyrolytic graphite (HOPG) susbtrate demonstrated that the conductance of CNTs can be modulated by changing the lattice alignment between different interlayers, as shown in figure 1. The elongation of CNTs due to the telescoping effect was also reported using nano-manipulators in a TEM [4]. We also demonstrated that when the CNTs are stretched using an atomic force microscope tip, they become elongated [5]. Here we demonstrate the application of MOCVD CNT telescoping in piezoresistively detecting displacement.



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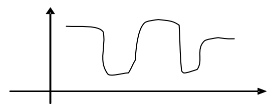


(b)

Figure 1 (a) Schematic of the double-walled CNT's conductance measurement. (b) The conductance demonstrates a periodic magnitude variation as a function of strain.

Piezoresistive pressure sensors based on CNT's that were post-processed have been reported in [6]. In their experiment, bundled carbon nanotubes were integrated by using dielectrophoretic (DEP) nanoassembly onto gold electrodes. In this approach the contacts between CNTs and gold electrodes are much weaker than the contacts achieved by direct CVD growth of CNTs. Hence, variations due to contact resistance in response to pressure and strain also contribute to the overall piezoresistance. Moreover, many CNTs are involved and the exact origin of piezoresistivity is not clear and it may be due to interactions in CNT-CNT and CNT-contact variations in response to strain. With our in-situ growth method, robust contacts can be formed between the carbon nanotubes and the electrodes and the contact resistance is reduced and is very stable (see the schematic in figure 2). Moreover, we can adjust our growth parameters to deposit a single CNT or a few CNTs to adjust the piezoresistive background.

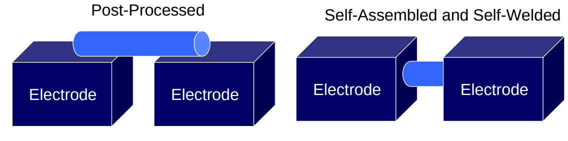


Figure 2 Comparison of post-processed and self-welded CNTs between the electrodes. Self-assembled and self-welded CNTs offer better contact integrity and scalability.

2 FABRICATION OF TEST STCRUTURE

The starting silicon-on-insulator (SOI) posts were defined using photolithography and deep-reactive ion etching as schematically shown in figure 3. The connecting posts were designed with 2 μm gap. They were oriented as opposed, matching pairs with their spacing ranging from 10 to 40 μm. Each post was connected to a larger area of silicon that had a 250 μm square platinum pad patterned on it. The height of pads is around 2 to 18 μm. The cantilever length is 600 to 1000 μm with width of 60 μm and thickness of 5 to 10 μm. At the end of the cantilever beam, there is another platinum pad to apply force or displacement for piezoresistivity measurement.

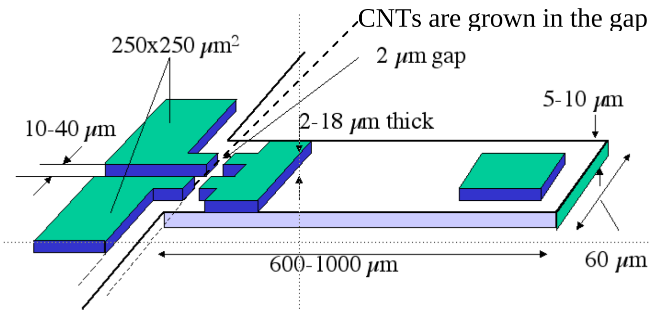


Figure 3. Schematic of a test device with piezoresistive sensing elements consisting of self-welded carbon nanotubes. As the cantilever beam tip is displaced, the gap (containing the CNTs) widens stretching the CNTs. The CNT resistance changes were monitored by performing I-V's of the contact posts or by monitoring the ac signal generated by the CNTs under dc current bias.

The above devices were pre-processed to deposit a thin layer of iron on a set of posts and a thin layer of amorphous carbon on the corresponding and opposing posts as schematically shown in figure 4. The iron layer (100 Å) was deposited off-axis in a thermal evaporator and both CVD amorphous carbon and sputtered carbon layers (50 Å) were deposited off-axis. Subsequently, these devices were loaded into a low-pressure chemical vapor deposition (LPCVD) chamber (figure 4b) and were thermally heated in an argon gas flow to 750-800 ˚C in 10^{-4} Torr. The heating cycle typically took around 5 minutes.

After the sample temperature reached 750 ˚C, the acetylene gas (50 sccm) was introduced through an opening located above the chip and CNT growth was carried out with both acetylene and argon gases flowing at 50 sccm for 15 minutes. Subsequently, the acetylene was turned off and the sample was cooled down to room temperature in the argon gas flow (50 sccm). The CNTs were then examined by scanning electron microscope, atomic force microscope (Nano-Scope IV) and they were electrically tested by current versus voltage technique (HP 4155B).

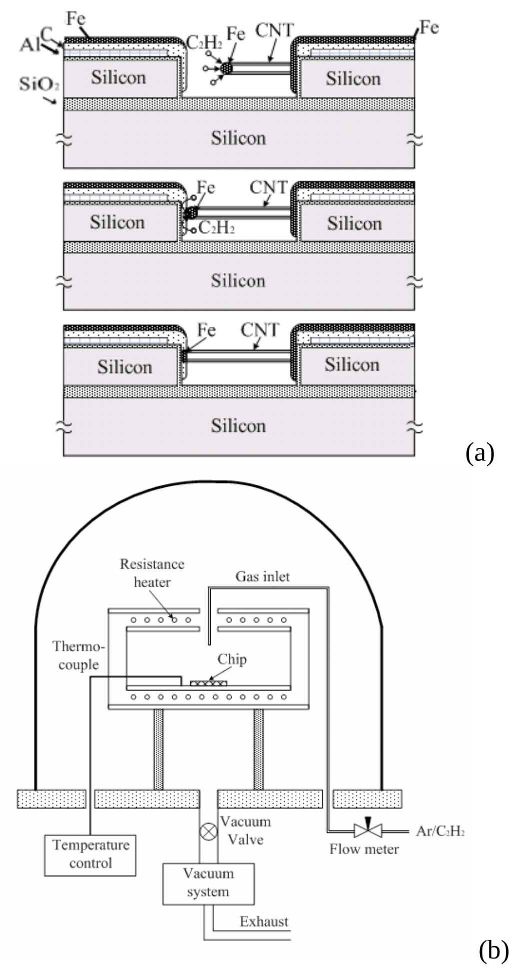


Figure 4 The sample temperature was controlled between 600 and 900 ˚C and the gas flow rates ranged between 0.1ml/min up to 100ml/min. CNT growth was carried out at 10^{-3}-10^{-1} Torr. a) Schematic of the welding process that may occur when the CNT tip grows against the carbon-coated silicon post. The iron particle located at the tip of the CNT becomes in contact with the carbon layer. The carbon atoms from this layer as well as the carbon provided by the gas drive the CNT tip into the carbon layer welding it with large bonding strength. b) Schematic of the low-pressure chemical vapor deposition chamber used for the CNT growth.

3 EXPERIMENT RESULTS AND DISCUSSION

The SEM of the microfabricated test device is shown in figure 5a where CNTs are grown in the gap between two sets of silicon-on-insulator posts that are located on the cantilever beam over its clamped end. When the cantilever beam bends, the gap between the silicon posts widens stretching the CNTs. The SEM of close-up view of the grown CNTs is shown in figure 5b. The CNTs grew horizontally and parallel to the substrate in the gap between the two silicon posts.

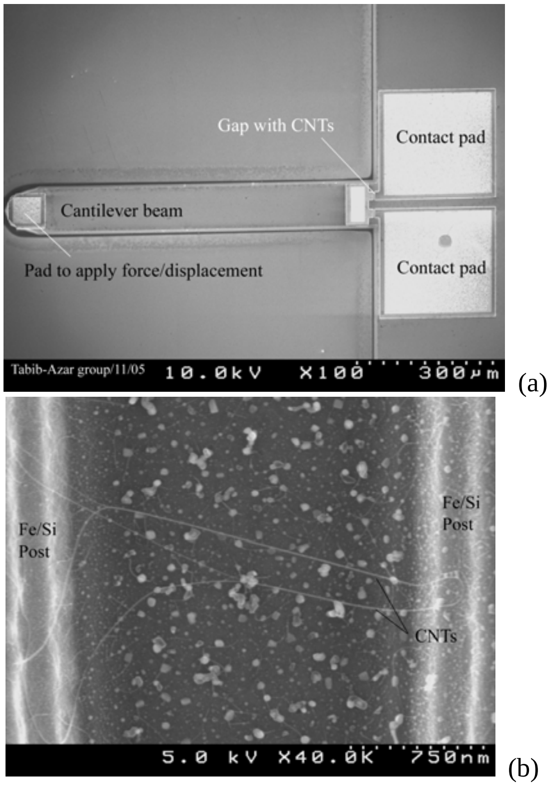


Figure 5 a) SEM of fabricated test device. b) SEM of the gap region with self-aligned and self welded CNTs.

It is also important to note that CNTs only grew between the posts and they are all suspended away from the substrate. Aspects of this behavior is reported in the past and explained by the gas flow patterns that exist around the raised posts. In our case, we believe that a combination of surface gas currents and van der Wall interaction are present. First we note that the CNTs in our case only grew inside the gap and not anywhere else. In [7] it was reported that the CNTs grew everywhere including the gap. In our case, the presence of aluminum contact regions precludes the CNT growth over the contacts. In these regions, as reported by us previously, aluminum acts as a CNT growth poison under certain conditions suppressing the CNT growth. One possible mechanism for this growth suppression is that at 750 ˚C, the aluminum is quite soft and starts dissolving the iron nanoparticles diminishing their catalytic ability. Second, we note that the CNTs also do not grow in other regions that are not covered with aluminum, for example on the walls of the raised SOI region away from the gap. This lack of growth, most probably is caused by the surface currents that generates strong boundary layer shear forces and currents that may "cool" down these regions below the CNT growth temperature. In between the gap regions, a stagnant volume may exist giving an opportunity for CNTs to grow. The surface current profiles, keep the CNT growth confined and directed and away from the bottom surface in these gap regions.

To examine the strength of this bond, the AFM technique was used to image, locate, and then apply a vertical force on the CNT to measure the bond strength. We used AFM probes with a 0.02 N/m spring constant and ultra-sharp tips. The tip was then positioned at the mid-point between two posts over the CNT and 110 nm vertical steps were successively applied while measuring the force using the AFM system. The resultant load deformation plot is shown in figure 6a. After AFM testing, the device was examined with SEM and it appeared that the CNTs were "stretched" rather than broken as also reported in other CNTs [8]. The SEM pictures of before and after AFM testing device are shown in figure 6b and 6c.

The load-deformation plot shown in figure 6a indicates that after the initial contact, the first 110 nm displacement resulted in a force of around 196 nN before the nanotube length was modified either due to telescoping effect or breaking during the second 110 nm displacement step. Self-welded silicon nanowires with similar structures broke at 75 nN level [9]. The initial slope of the load-displacement curve from figure 6a is 1.48 N/m. Taking the CNT diameter to be around 10 nm and its Young modulus around 1.25 TPa [10], the effective Hooke's constant at mid-point loading should be around 3.2×10^{-3} N/m. So the apparently large slope of 1.48 N/m is due to the maximum stress afforded by the welded CNT contacts on both ends.

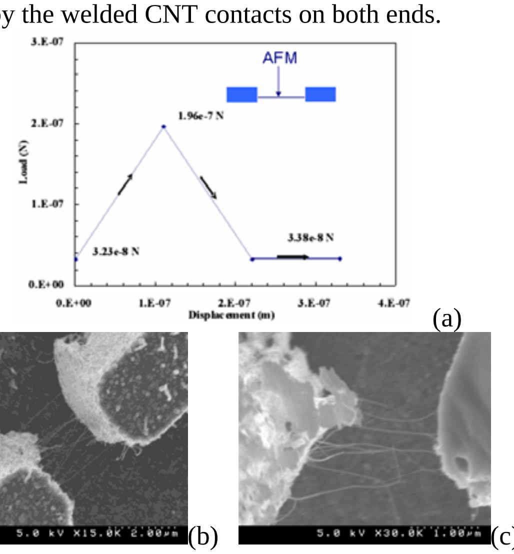
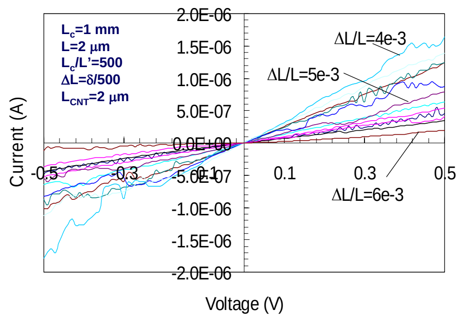


Figure 6. a) The load-displacement characteristics of one of the CNTs shown in figure 3 measured using atomic force microscope (AFM). The slope near the origin is 1.5 N/m. b) SEM of the device before the AFM testing. c) SEM of the device after the AFM testing. It appears that CNTs became elongated instead of breaking. This behavior is documented in multi-wall CNTs and it occurs dues to telescoping of the inner cylinders out of the outer cylinders in MW-CNTs.

A pressure sensing experiment was performed to validate the sensing ability of the CNT-based piezoresistor. The sensor was fixed on the probe station. By displacing the probe at the pad of the cantilever beam end, the pressure was introduced and applied and the corresponding resistances were monitored. The static I-Vs of the CNT bridges measured by displacing the cantilever beam tip are shown in figure 7a. Experimental results showed that the resistance across the CNT-gap was modulated by the telescoping of the inner shells of the multi-walled carbon nanotubes under tension. In figure 7b, the current is plotted at different voltages as a function of strain. Figure 8 shows the conductance modulation under different driving voltages applied to a loudspeaker that vibrated the device. The full-scale resistance change was larger than 10^5 Ω the above experiments. The effective longitudinal piezoresistivity of these CNTs was larger than $4\text{x}10^{-8}$ Pa^{-1} which is more than 10 times larger than that of Π_{44} in silicon.



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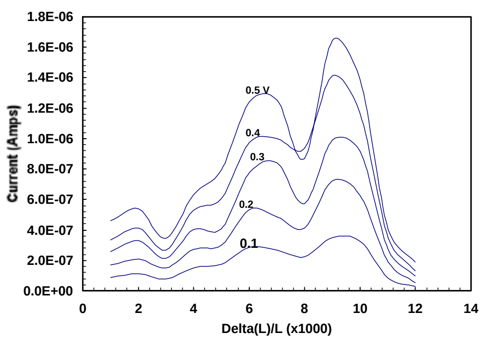

(b)

Figure 7 a) Current versus voltage of the device containing 4 CNTs. b) Current at different bias voltages as a function of CNT strains.

The vibration spectrum detected by measuring the ac voltage generated by the dc biased CNTs is shown in figure 8. The maximum displacement of the cantilever beam tip at 15 KHz was around 1 um, the cantilever length was 1000 um, its thickness was 1 um and the height of the contact post was around 1 um. The calculated longitudinal piezoresistivity was around $4\text{x}10^{-8}$ Pa^{-1}.

In summary, we described the fabrication process and electrical characterization of a novel self-aligned and self-welded CNT-based piezeresistor. By using LP-MOCVD, we have successfully integrated CNT sensing elements on the microfabricated structures. The piezoresistive effects of the device were preliminarily investigated by measuring the displacement-resistance dependency, which indicated that CNT-based sensors were capable of sensing input displacement variations. Based on these experimental results, we propose that self-aligned and self-welded carbon nanotubes are a novel material for fabricating micro piezoresistor, displacement sensor, which can also serve as alternative accelerometer, pressure sensor, and vibration sensor.

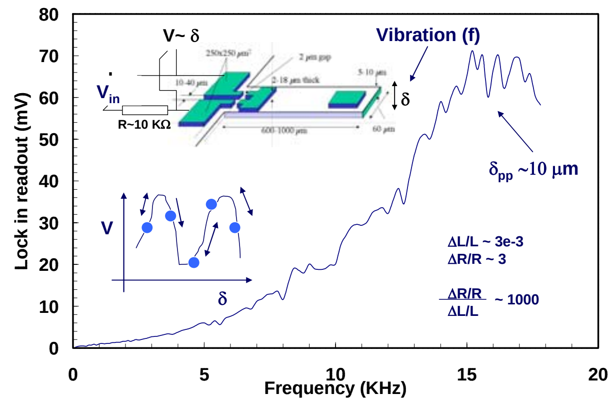

Figure 8 Vibration spectrum showing maximum displacement (10 μm) of the cantilever beam tip occurring at 15 KHz.

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