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Effects of chirality and impurities on the performance of carbon nanotube-based piezoresistive sensors

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A B S T R A C T

This paper presents a method to fabricate high purity, single chirality carbon nanotube (CNT) based sensor systems. Ultracentrifugation is initially used to create an 85% pure (6,5) CNT sample. This 85% pure sample has a gauge factor of -22.7 ± 0.5 which is significantly lower than the predicted gauge factor of 57 for a pure (6,5) CNT. However, this measured gauge factor closely matches the predicted gauge factor for the measured distribution of chiralities in the 85% pure sample. This indicates at a small number of impurities in the sensor can have a large effect on the strain sensitivity of the sensor. In order to increase the gauge factor of the 85% pure (6,5) CNT sample, an electrical breakdown technique is used to remove the low resistance and low gauge factor CNTs from the sensor. Using this technique it is possible to increase the gauge factor of the CNT-based piezoresistive sensor from -22.7 ± 0.5 to 34 ± 1. This result indicates that the majority of the impurities in the sensor can be removed during the fabrication process using the electrical breakdown technique.

Introduction

Single chirality carbon nanotube (CNT) based sensors have the potential to increase the sensitivity of numerous types of mechanical and chemical sensors. For example, theory suggests that the performance of CNT-based piezoresistive sensor systems could be improved by almost an order of magnitude if it becomes possible to accurately sort CNTs by chirality [1–5]. However, in order to reach this potential it is necessary to be able to fabricate single chirality sensor systems.

It is necessary to incorporate multiple CNTs of the same chirality into a parallel resistor network in order to optimize the performance of these CNT-based piezoresistive sensors systems. This is because this device architecture allows the high potential gauge factor of the single CNT to be maintained while increasing the carrier concentration to reduce the flicker noise in the sensor [6]. Therefore, by using this type of sensor architecture it is possible to increase the dynamic range of the CNT-based sensor by over two orders of magnitude as compared with single CNT sensors [7].

In this paper, we will present a method that can be used to fabricate high purity, single chirality parallel CNT resistor networks for CNT-based sensor systems. We will then use these sensors and the theoretical models developed in previous work to analyze the effects a small number of impurities can have in the performance of a single chirality CNT-based piezoresistive sensor network. In addition, we will demonstrate how the electrical breakdown of low resistance and low gauge factor CNTs can be used to remove impurities from and increase the strain sensitivity of CNT-based piezoresistive sensors.

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CNT enrichment

In order to analyze the accuracy and reliability of the theory and models presented in previous work [1], experiments were performed on enriched samples of (6,5) CNTs. From these models, (6,5) CNTs are predicted to have a gauge factor of 57. (6,5) CNTs were chosen because there has been a great amount of success in enriching (6,5) CNT samples from bulk samples [8,9]. The (6,5) CNTs were enriched from a solution of SWCNTs suspended in water with a sodium cholate surfactant [10]. The (6,5) CNTs were separated out using density gradient ultracentrifugation [11,12]. This method is used to first separate the metallic CNTs from the semiconducting CNTs and then to increase the (6,5) CNT concentration in the sample.

In order to determine the purity of the enriched (6,5) CNT sample, the absorption of the sample was measured over the ultraviolet (UV), visible (vis) and near-inferred (nIR) spectrums. From this absorption spectrum it is possible to determine the chiralities of the CNTs in the sample as well as the concentration of each type of CNT [13,14]. Based on the absorption spectrum, it was determined that the sample contained several other types of CNTs including (7,5), (7,6), (9,1), (6,4), (8,3), (8,4), and (9,2) CNTS as shown in Fig. 1.

From this absorption, the percentage of each type of CNT in the sample was calculated by integrating the area under each of the absorption peaks and dividing the area for each type of CNT by the total area under the curve. The percentage of metallic CNTs is estimated to be less than 1 part in 100,000. The results of this calculation are presented in Table 1 along with the gauge factor predicted from theory for each of the CNT chiralities. Overall, the sample contains 82.6% (6,5) CNTs.

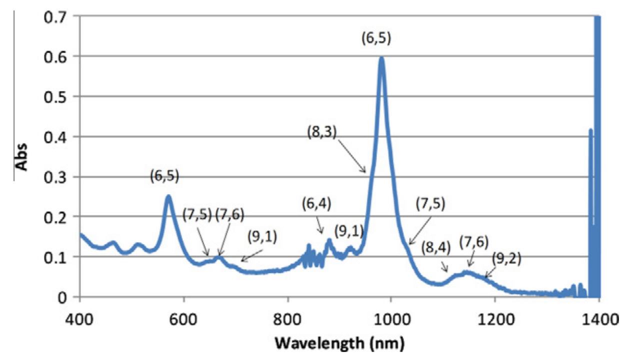

Fig. 1 – UV–Vis-nIR absorption spectrum for (6,5) enriched CNT Sample.

Experimental setup

A MEMS test structure was designed and microfabricated in order to measure the strain sensitivity of a carbon nanotube based resistor network. The test structure consists of a fixed–fixed flexure beam and electrodes connected to the base of the flexure. The outer four sets of electrodes are connected to polysilicon piezoresistors while the inner two electrodes are left empty so that CNTs may be connected across them. These central electrodes are spaced 1 μm apart. This architecture allows strain to be measured simultaneously and independently with the polysilicon and CNT piezoresistors. The center of the flexure has a locating hole where known weights may be placed, thereby loading the structure and straining the CNTs. For more details on the design, layout, and fabrication of the MEMS test structure please see Ref. [1].

CNTs were deposited onto these test flexures via dielectrophoresis. A droplet of a 3 μg/mL solution of SWCNTs in deionized (DI) water was placed on the middle electrodes of the test structure and a 5 MHz, 5 V peak-to-peak AC voltage was used to direct the deposition of the SWCNTs. After 5 min, the test structure was rinsed with DI water and dried. After the CNT deposition, the electrical contacts were coated in platinum using a focused ion beam and annealed at 525 °C for 30 min in order reduce the CNT-electrode contact resistance and produce Ohmic contacts [15].

A low noise sensor system was connected in order to measure the gauge factor of the CNT network [16]. The noise in the sensor electronics was more than an order of magnitude lower than the noise in the CNT sensor itself [17]. The CNT network was incorporated into a DC Wheatstone bridge in a quarter bridge configuration. An instrumentation amplifier was used to boost the signal from the bridge, which is nulled with a bias voltage and read by an Analog-to-Digital Converter (ADC).

Results for single chirality experiments

Measured gauge factor of enriched (6,5) CNT sample

Based on the high purity of the sample it might be expected that the CNT-based piezoresistors made from the enriched sample of (6,5) CNTs should behave like (6,5) CNTs in isolation since the number of (6,5) CNTs in the sample is at least an order of magnitude greater than any of the other types of CNTs in the sample. However, as shown in Fig. 2, the measured gauge factor for the enriched (6,5) sample is −22.7. This is significantly lower and of the opposite sign as the gauge factor of 57 that would be predicted from quantum mechanics based modeling for a pure (6,5) sample. This result indicates that even a small number of impurities can have a substantial impact on both the sensitivity and sign of the CNT-based piezoresistor.

In order to understand this result it is necessary to look at the component CNTs that make up the CNT-based piezoresistor created from the enriched (6,5) sample and to understand how the sensor operates. The CNTs can be modeled as independent, parallel resistors in a resistor network due to how the CNT-based piezoresistive sensor was fabricated. Based on this model, the voltage drop across each of the resistors is equal but the current is not. Therefore, the overall resistance of the sample is dominated by the CNTs with the highest current, which are the lowest resistance CNTs. In this sample, the lowest initial resistance CNTs are the (7,6), (7,5) and (8,4) CNTs. Both the (7,6) and (8,4) CNTs have positive gauge factors and thus increase resistance as the sample is strained. However, the (7,5) CNTs have a negative gauge factor and thus decrease in resistance when strained. Therefore, the presence of (7,5) CNTs in the sample might help to explain the measured negative gauge factor of the sample.

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Table 1 – Estimated chiral distribution of enriched sample from absorption spectrum.

CNT	Percentage (%)	Predicted gauge factor
(6,5)	82.60	57
(7,6)	5.60	48
(7,5)	1.70	−103
(9,1)	1.60	−348
(6,4)	1.00	−122
(8,4)	3.50	196
(9,2)	1.70	315
(8,3)	0.70	−252
Other	1.60	NA

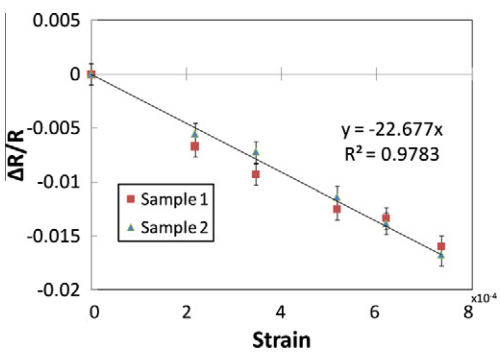

Fig. 2 – Measured $\Delta R/R$ vs. strain for enriched (6,5) CNT sample.

Monte-Carlo simulation for enriched (6,5) CNT sample

A Monte-Carlo simulation was created in order to determine the overall theoretical effect of the impurities in the enriched (6,5) sample. The Monte-Carlo simulation was setup for a random assortment of CNTs in a parallel resistor network with a probability distribution function equal to the measured probability distribution function of the CNT chirality content of the enriched (6,5) CNT sample. The strain sensitivity of each of the CNTs in the parallel resistor network was determined using the theoretical work presented in previous work [1].

Overall, the predicted results from the Monte-Carlo simulation of the enriched (6,5) CNT sample show that the gauge factor of the sample should be negative and the magnitude of the gauge factor depends on the initial strain on the sample. Based on the fabrication methods and molecular dynamics simulations of CNT interactions with a SiO_2 surface it is estimated that the initial pretension strain on the CNTs is approximately 0.2% [18]. This lever of pretension strain is consistent with previous results [1]. The results of the Monte Carlo simulation with an initial strain offset of 0.2% are given in Fig. 3 along with the experimental measurements from the piezoresistors fabricated with the enriched (6,5) CNT solution.

Overall, the results from the Monte-Carlo simulations are within experimental error of the experimental results for the enriched (6,5) CNT. The Monte-Carlo simulations predict the gauge factor of the enriched (6,5) CNT sample to be −22.3 while the experimentally determined gauge factor was −22.7 ± 0.5. This result shows that the presence of other types of CNTs in the enriched (6,5) CNT sample explains both the sign and the magnitude of the measured gauge factor for the enriched (6,5) CNT sample as well as its deviation from the theoretical gauge factor for a pure (6,5) CNT sample.

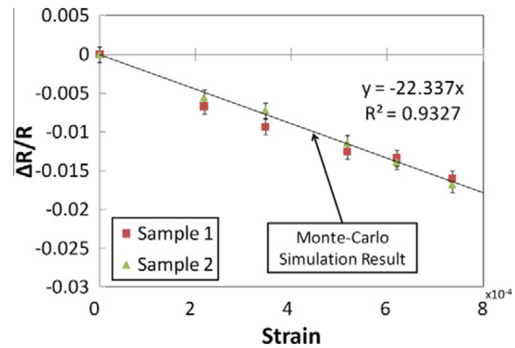

Fig. 3 – Measured results from enriched (6,5) CNT sample overlaid on theoretical prediction from Monte-Carlo simulations with 0.2% strain offset.

Electrical breakdown of CNTs in sensor

In order to produce sensors with the maximum strain sensitivity it is necessary to eliminate the low resistance and low gauge factor CNTs that limit the strain sensitivity of the sensor. As was shown in the previous section, a small number of these CNTs can have a large effect on the strain sensitivity of the sensor since most of the current in the parallel resistor network runs through these CNTs. This high amount of current causes the lower resistance CNTs to heat up much more than the higher resistance CNTs that comprise the majority of the CNTs in the sample. This Joule heating of the low resistance CNTs can be used to eliminate these CNTs through a process known as the electrical breakdown technique [19]. This technique takes advantage of the increased reactivity of CNTs at high temperature to create a rapid oxidation of the low resistance CNTs in the sample. This process creates a break in the CNT structure and eliminates the low resistance CNTs from the sample. The theoretically predicted resistances of each of the chiralities of CNTs in the enriched (6,5) CNT sample normalized to the theoretically predicted resistance of the (6,5) CNT are given in Table 2.

From these normalized resistances it is clear that at low strains, the (7,6), (7,5), (8,4) and (9,2) CNTs all have resistances that are at least an order of magnitude less than the (6,5) CNTs. Therefore, using the electrical breakdown technique it should be possible to eliminate these CNTs from the sensor. For large strains some of the CNTs increase in resistance and some of the CNTs decrease in resistance, changing the normalization between the (6,5) CNTs and the rest of the CNTs in the sample. For example, at 1% strain, the (7,6), (7,5) and (8,4) CNTs are still all an order of magnitude lower resistance than the (6,5) CNTs while the (9,2) CNTs are now higher resistance than the (6,5) CNTs. In addition, the (9,1) and (8,3) CNTs now have a resistance that is an order of magnitude lower in resistance than the (6,5) CNTs. Therefore, by performing an electrical breakdown at both low and high strains it should be possible to eliminate all of the CNTs in the sample except for the (6,5) CNTs and the (6,4) CNTs.

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Table 2 – Resistance normalized to (6,5) CNT resistance for CNTs in enriched CNT sample at various strain levels.

CNT	Diameter (nm)	Normalized resistance for a given strain			
		0%	0.2%	0.3%	1%
(6,5)	0.76	1	1	1	1
(7,6)	0.89	0.003	0.003	0.003	0.003
(7,5)	0.83	0.037	0.027	0.023	0.007
(9,1)	0.76	1.000	0.444	0.296	0.017
(8,4)	0.84	0.023	0.030	0.035	0.092
(6,4)	0.69	36.76	25.69	21.48	6.13
(9,2)	0.80	0.101	0.169	0.218	1.333
(8,3)	0.78	0.301	0.162	0.119	0.014

Results for electrical breakdown experiments

The electrical breakdown technique was used to eliminate some of the impurities from the sensor created from the enriched (6,5) CNT sample. First, electrical breakdown was performed on the enriched (6,5) sample with no load applied to the flexure. 17.7 v was applied between the two electrodes in order to cause the electrical breakdown of the (7,6), (7,5), (8,4) and (9,2) CNTs and to eliminate them from the sensor.

This low strain electrical breakdown was successful in increasing the gauge factor of the sensor from -22.7 ± 0.5 to -18.1 ± 0.4 as shown in Fig. 4. Overall this result is in good agreement with the result predicted from the Monte-Carlo simulations when the (7,6), (7,5), (8,4) and (9,2) CNTs are removed from the sample. These Monte-Carlo simulations predict that the gauge factor of the sensor will increase to -16.2 after the low-strain electrical breakdown, while the measured gauge factor is -18.1 ± 0.4. This overestimate of the sensor gauge factor is likely due to incomplete removal of the (7,6), (7,5), (8,4) and (9,2) CNTs during the low strain electrical breakdown. However, the increase in gauge factor does indicate that most of the low resistance CNTs were removed.

In order to further increase the gauge factor of the sensor, an electrical breakdown of low resistance CNTs was performed at high strain. In addition to the (7,6), (7,5), (8,4) and (9,2) CNTs removed in the previous low strain electrical breakdown step, it should be possible to remove the (9,1) and (8,3) CNTs with electrical breakdown at high strains. As shown

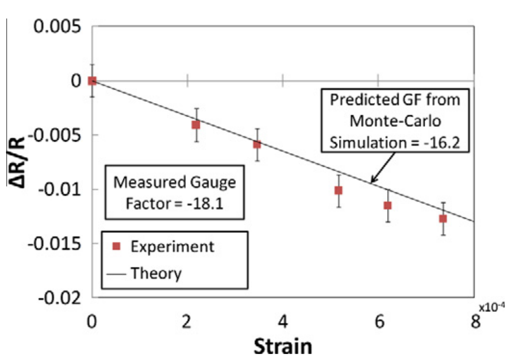

Fig. 4 – Measured results from low-strain electrical breakdown of enriched (6,5) CNT sample overlaid on theoretical prediction from Monte-Carlo simulations with 0.2% strain offset.

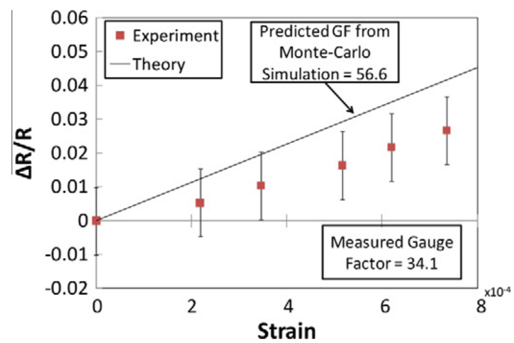

Fig. 5 – Measured results from high-strain electrical breakdown of enriched (6,5) CNT sample overlaid on theoretical prediction from Monte-Carlo simulations with 0.2% strain offset.

in Fig. 5, the gauge factor of the enriched (6,5) CNT-based piezoresistive sensor increased from -18.1 ± 0.4 for the low strain electrical breakdown sensor to 34 ± 1 for the high strain electrical breakdown sensor.

The increase in resistance and the change in sign of the gauge factor indicate that most of the low resistance and low gauge factor CNTs were removed during the two electrical breakdown steps. However, the Monte-Carlo simulations for the (6,5) enriched samples after the (7,6), (7,5), (8,4), (9,2), (9,1) and (8,3) CNTs are removed from the probability distribution function significantly overestimate the gauge factor of the sensor, as shown in Fig. 5. This indicates that the while the electrical breakdown technique was successful in eliminating most of the unwanted CNTs in the sample, it was not capable of completely removing all impurities from the sensor.

Overall, the results from this section show that the performance of the CNT-based piezoresistors created from enriched samples of single chirality CNTs can be significantly improved through the use of the electrical breakdown technique. This makes it possible to achieve markedly improved results from enriched samples even if the samples are not initially 100% pure.

Discussion and conclusions

CNT-based piezoresistors offer the potential to become versatile, high resolution sensing systems. Existing CNT-based piezoresistive sensor systems are competitive with metal and silicon strain gauges in terms of performance. In addition, theory suggests that the performance of CNT-based piezoresistive sensor systems could be improved by almost an order of magnitude if it becomes possible to accurately sort CNTs by chirality [11,20–22]. This would enable CNT-based piezoresistive sensors to overcome many limitations presently found in micro- and nanoscale sensor systems [23].

However, this work shows that a small number of low resistance or low gauge factor CNTs in the CNT-based sensor system can have a large effect on the performance of the sensor. Therefore, it is critical to be able to produce pure enriched samples of single chirality CNTs or to be able to remove these unwanted CNTs after the sorting process is finished. As shown in this chapter, it is possible to remove many of the unwanted CNTs from the sensor system using the electrical breakdown technique. Using this method it is possible to increase the sensitivity of the sensor system and to change the sign of the gauge factor from negative to positive. Using similar methods it should be possible to create CNT-based piezoresistive sensor systems with gauge factors in excess of 300. In order to accomplish this goal, however, it is necessary to improve the sorting techniques and the electrical breakdown technique in order to ensure that only the highest gauge factor CNTs are present in the sensor system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2012.08.011.

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