Single Wall Carbon Nanotube-Based Structural Health Sensing Materials

A. Neal Watkins[*], JoAnne L. Ingram[**], Jeffrey D. Jordan[***], Russell A. Wincheski[***], Jan M. Smits[****], and Phillip A. Williams[*****]

[*]NASA Langley Research Center, MS 493, Hampton, VA 23681, a.n.watkins@larc.nasa.gov
**Swales Aerospace, Inc.
***NASA Langley Research Center
****Lockheed-Martin
*****National Research Council Postdoctoral Associate

ABSTRACT

Single wall carbon nanotube (SWCNT)-based materials represent the future aerospace vehicle construction material of choice based primarily on predicted strength-to-weight advantages and inherent multifunctionality. The multifunctionality of SWCNTs arises from the ability of the nanotubes to be either metallic or semi-conducting based on their chirality. Furthermore, simply changing the environment around a SWCNT can change its conducting behavior. This phenomenon is being exploited in order to create sensors capable of measuring several parameters related to vehicle structural health (i.e. strain, pressure, temperature, etc.) Construction of the structural health monitor is accomplished using conventional electron-beam and photolithographic techniques in order to place specific electrode patterns on a surface. SWCNTs are then deposited between the electrodes using an electrophoretic alignment technique. Prototypes have been constructed on both silicon and polyimide substrates, demonstrating that surface-mountable and multifunctional devices based on SWCNTs can be realized.

1 INTRODUCTION

Since their discovery in 1991 by Iijima [1], carbon nanotubes have attracted a growing amount of attention due to their remarkable strength and conductive properties [2]. Single wall carbon nanotubes (SWCNTs) are one of the strongest known materials with a Young's modulus of approximately 1 TPa (about 10 times as strong as steel) making it a material of choice for the next generation of structural materials. SWCNTs can exhibit either semiconducting or metallic behavior based on the chirality of the tube while ballistically transporting electrons and maintaining their spin state down the length of the tube [2]. Due to this property, SWCNTs have been used to fabricate several nanoscale devices, such as field-effect transistors [3,4] and molecular logic devices. Sensors with SWCNTs as the active element have also been constructed for a variety of gaseous analytes [5,6].

Because of these unique mechanical and electrical properties, SWCNTs seem to be the material of choice for future aerospace vehicle construction material. Not only does using advanced materials incorporating SWCNTs lead to more efficient, lighter aerospace designs, but their inherent multifunctionality could lead to designs which are "self-sensing"; sensor skins capable of probing the environment around the vehicle could be designed so that they are part of the vehicle itself. Several advantages to this approach are readily apparent. First, the added cost of adding external sensors and devices is alleviated, as is the intrusiveness of the added sensors to the performance of the vehicle (i.e. added weight, changing the flow characteristics, etc.) Second, since SWCNT-based devices can be made extremely small, then a variety of different sensors can be placed in a very small area, and conceivably in places on a vehicle not currently amenable to adding external devices.

This work describes the construction and testing of prototype sensors based on SWCNTs for measuring parameters related to vehicle structural health, specifically strain. The sensors have been constructed using standard electron beam and photolithographic techniques to pattern electrodes on both silicon and flexible plastic substrates. SWCNTs were then deposited and aligned using an eletrophoretic technique [7-9], creating electrical bridges between the electrodes. It has been demonstrated using an atomic force microscope (AFM) tip that the conductance through a SWCNT can change with an applied strain [10], and this is the mechanism for the proposed sensor.

2 EXPERIMENTAL

2.1 Materials

Purified SWCNTs produced using the HiPCO process [11] were purchased from Carbon Nanotechnologies, Inc., and used as received. Toluene (ACS reagent grade, 99.5%), hydrofluoric acid (HF, 48% in water), sulfuric acid (H_2SO_4, ACS reagent grade), and hydrogen peroxide (H_2O_2, 30%) was purchased from Aldrich and used as received. Rapid-curing polyimide precursors solution (PI2525) was

purchased from HD Microsystems and used as received. Oxidized silicon wafers (500 nm SiO_2 thickness) were purchased from TTI Silicon.

2.2 Sensor Fabrication

Before use, the oxidized silicon wafers were cleaned by immersing in a solution of 70:30 H_2SO_4:H_2O_2 for 30 minutes at 100°C ("piranha" solution, *Caution: strong oxidizer, may explode*) to remove any organic contaminants present. After cleaning, the wafers were rinsed with de-ionized water four times, ethanol four times, and finally dried under a stream of nitrogen.

Sensor construction on silicon wafers was accomplished by using conventional photo- and electron-beam lithography to deposit circuit elements followed by SWCNT deposition. First, a layer of photoresist was deposited on the surface by spin coating at 3000 rpm for 30 sec. Large circuit elements (e.g bond pads, wires, etc.) were defined by illuminating with UV through a custom designed photomask. Following development of the photoresist, an adhesion layer of chromium or titanium (10 nm) and a thin layer of gold (20 nm) were evaporated onto the surface. Two sets of electrodes are then defined using electron-beam lithography. The first set of electrodes is used to deposit and align the SWCNTs. To create the first set of electrodes for depositing and aligning the SWCNTs (or alignment electrodes), a thin layer of poly(methyl methacrylate) (PMMA) was deposited onto the pattern by spin coating at 3500 rpm for 30 seconds. The electrodes were then defined using an electron beam. The typical width of each electrode was approximately 1 μm, and the separation between the electrodes was 3 μm. Deposition and alignment of the SWCNTs was accomplished using an electrophoretic technique. First, a small amount of nanotubes was dispersed in toluene by ultrasonication for 24 hours. Because the concentration of nanotubes in the suspension was small, only a slight discoloration occurs. Several drops of this solution were then placed on the sample so that the surface was covered. Two spring-loaded pins were then used to make contact with the pads and an AC voltage was applied to the pads to generate an electric field. Typical conditions for deposition were 10 V_{PP} at 5 MHz for 6 minutes. Following deposition of the SWCNTs, the second set of electrodes was patterned using the same procedure as the alignment electrodes. These interdigitated electrodes (connection electrodes) are aligned perpendicular to the alignment electrodes with a separation of 500 nm and are used to make an electrical connection across the aligned nanotubes.

Sensor construction on the flexible, plastic substrates was accomplished by coating a cleaned oxidized silicon wafer with a thin film (~12 μm) of PI2525 by spin coating at 2000 rpm for 30 seconds. After spinning, the film is cured in air by heating to 200°C at 4°C/min, holding at 200°C for 30 minutes, heating to 300°C at 2.5°C/min, and holding at 300°C for 60 minutes, followed by a gradual cooling to room temperature. All patterning and SWCNT deposition is performed using the procedures listed for the silicon substrates. After deposition of the connection electrodes, the polyimide film is removed from the silicon surface by dissolving the oxide layer using a 1% HF solution. To prevent the nanotubes from being dislodged during the removal process, the polyimide coated silicon surface is held by forceps so that only an edge of the surface is exposed to the HF. As the HF dissolves the oxide layer, capillary forces draw the HF up behind the polyimide layer, resulting in removal of the polyimide film while protecting the nanotubes from the HF solution. After removal of the film, the polyimide substrate is gently rinsed with de-ionized water to remove any residual HF.

3 RESULTS AND DISCUSSION

The lithographic patterns employed for these devices were designed to maximize the concentration and alignment of SWCNTs in a relatively small area. An optical micrograph of the larger gold wires and alignment marks for e-beam lithography deposited using photolithography is shown in Figure 1A, and an atomic force microscope (AFM) topography image showing the alignment electrodes is shown in Figure 1B. Finite element simulation of the potential and electric field near an alignment electrode is show in Figure 1C, and shows that this design is ideal for concentrating and aligning nanotubes in a relatively small area. The potential on the surface decreases rapidly a short distance away from the electrode, while the electric field is strongest at the tip and oriented toward the second electrode. The addition of the connection electrodes *after* the SWCNT deposition step helps to ensure adequate electrical contact for probing the nanotubes, as the electrodes are formed on top of the nanotubes on the surface. They also provide an anchor for the nanotubes, thus minimizing slippage on the surface. An AFM topography image showing deposited SWCNT bundles and connection electrodes is shown in Figure 1D. The nanotube bundles can be clearly seen to span between the two alignment electrodes, and only where the electric field is strongest (i.e. between the two tips of the alignment electrodes). It can also be seen that despite the low concentration of nanotubes used for deposition, some spurious bundles are still deposited during this process. However, they are typically away from the electrodes and cause no interference with the measurements.

Electrical connection between the connection electrodes and the immobilized SWCNTs was investigated using a conventional four-point measurement technique. The measured current as a function of applied voltage is shown in Figure 2, exhibiting the expected linear behavior with a calculated resistance of 10.5 kΩ. The relatively small resistance indicates that the immobilized bundle may contain several individual nanotubes, thus lowering the resistance. With careful control of the deposition conditions

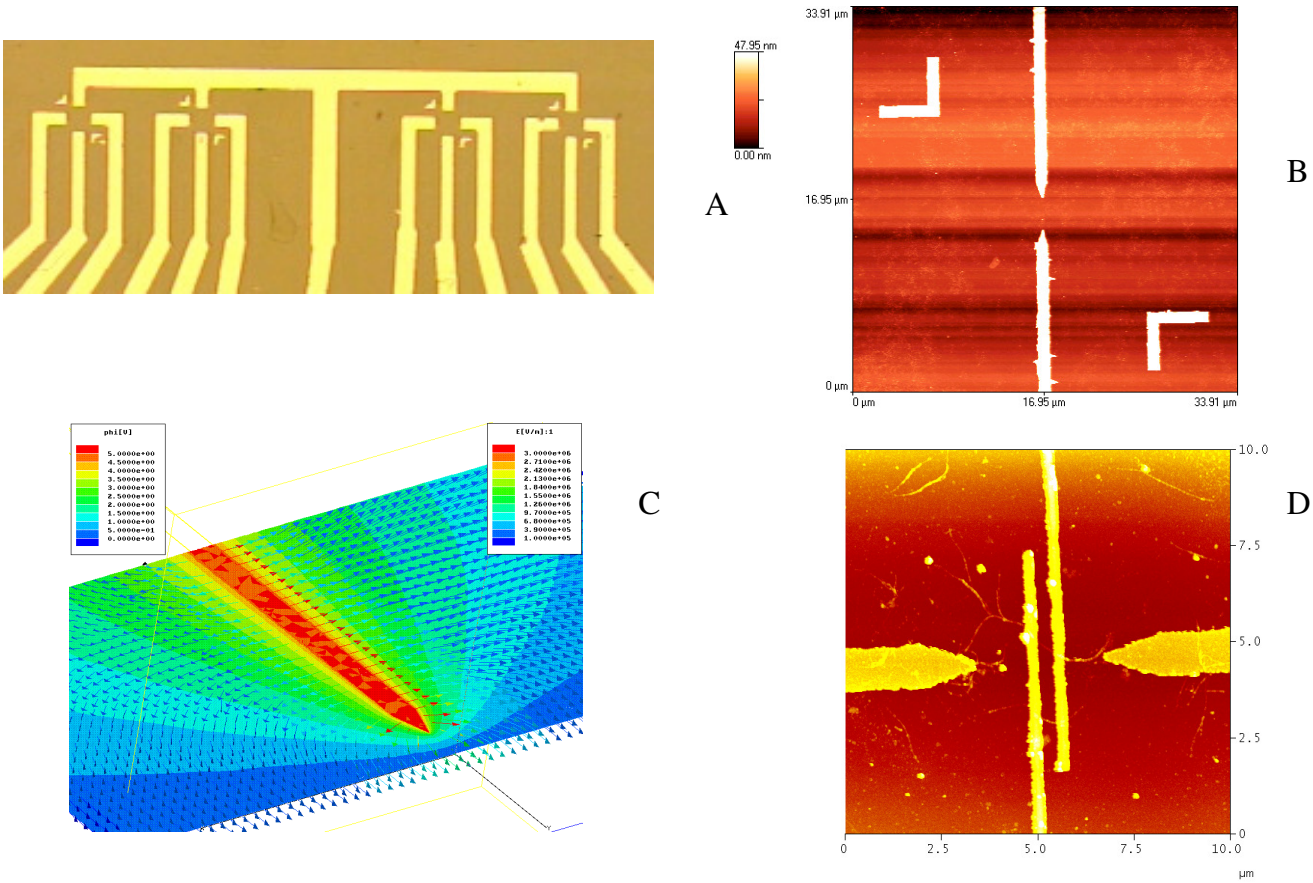

Figure 1. Procedure for designing SWCNT-based structural health monitor. A) Optical micrograph showing large gold wires and alignment marks deposited using photolithography. B) AFM topography image showing alignment electrodes deposited using electron beam lithography. C) Finite element simulation of the potential and the electric field near an alignment electrode. D) AFM topography image showing a deposited and aligned SWCNT bundle and the deposited connection electrode.

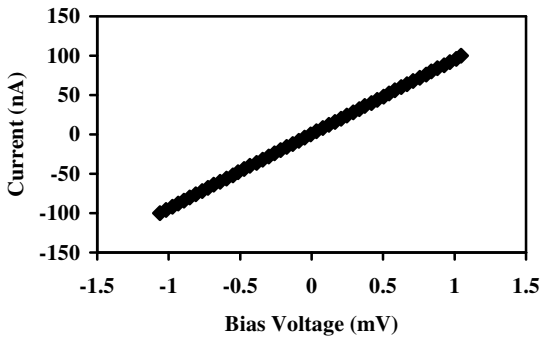

Figure 2. Typical I-V curves measured through a pair of connection electrodes with deposited and aligned SWCNT bundles bridging them. The measurements were obtained using a conventional four point measurement technique, and the calculated resistance of the bundles is ~10.5 kΩ.

(concentration, applied voltage, alignment electrode separation, etc.), smaller bundles and even individual nanotubes can be deposited, resulting in measured resistances of several hundred kΩ.

To determine the efficacy of this approach for creating sensors, an early prototype was mounted in an environmental chamber, and the resistance of the nanotubes was measured using a Manipulated Nanoprobe System. The resistance was monitored as the temperature was increased from 100 K to 350 K. The results are shown in Figure 3 and indicate a transition of some of the nanotubes in the immobilized bundles from semiconducting at low temperature to metallic behavior at higher temperatures. To investigate this design for measuring strain, the sensor will be mounted on an aluminum beam and placed in a load frame. In order to determine the actual strain applied and correlate the response of the sensor, conventional strain sensors will also be applied in the same area.

4 CONCLUSIONS

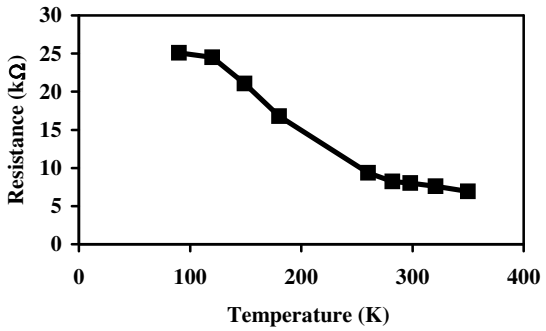

Figure 3. Measured resistance through aligned SWCNT bundles as a function of temperature.

A prototype design for using SWCNTs as sensors has been presented. The sensor is designed using conventional e-beam and photolithography techniques to pattern alignment and connection electrodes. SWCNTs are deposited and aligned from a suspension using an electrophoretic technique. This design was chosen so that the concentration and alignment of the nanotube bundles occurs in specific, controllable places, and has been demonstrated to be sensitive for temperature. Tests are currently underway to determine its sensitivity to applied strain. Finally, these sensors are small, robust, and can be easily manufactured on flexible, plastic-based substrates. These advantages will make a SWCNT-based sensor that is surface-mountable and multifunctional (large arrays capable of measuring many different parameters) a near-term achievable goal.

REFERENCES

[1] S. Iijima, Nature, 354, 56-58, 1991.

[2] M. Dresselhaus, G. Dresselhaus and P. Avouris, Eds., "Carbon Nanotubes: Synthesis, Structure, Properties and Applications," Springer-Verlag: Berlin, 2001.

[3] S.J. trans, A.R.M. Verschueren and C. Dekker, Nature, 393, 49-52, 1998.

[4] R. Martel, T. Schmidt, H.R. Shea, T. Hertel and P. Avouris, Appl. Phys. Lett., 73(17), 2447-2449, 1998.

[5] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho and H. Dai, Science, 287, 622-625, 2000.

[6] P.G. Collins, K. Bradley, M. Ishigami and A. Zettl, Science, 287, 1801-1804, 2000.

[7] X.Q. Chen, T. Saito, H. Yamada and K. Matsuhige, Appl. Phys. Lett., 78(23), 3714-3716, 2001.

[8] L.A. Nagahara, I. Amlani, J. Lewenstrin and R.K. Tsui, Appl. Phys. Lett., 80(20), 3826-3828, 2002.

[9] J. Smits, B. Wincheski, J. Ingram, N. Watkins and J. Jordan, "Controlled Deposition and Applied Field Alignment of Single Walled Carbon Nanotubes for CNT Device Fabrication," presented at the Materials Research Society Conference, December 2-5, 2002 and published in the proceedings.

[10] A. Maita, Nature Materials, 2, 440-442, 2003.

[11] P. Nikolaev, M.J. Bronikowski, R.K. Bradley, F. Rohmund, D.T. Colbert, K.A. Smith and R.E. Smalley, Chem. Phys. Lett., 313(1-2), 91-97, 1999.