Nanomanipulation and Lithography for Carbon Nanotube Based Nondestructive Evaluation Sensor Development

Buzz Wincheski, †Jan Smits, Min Namkung, ††JoAnne Ingram,
††Neal Watkins, Jeffrey D. Jordan †††Richard Louie,
NASA LaRC
Hampton VA 23681

†Lockheed Martin Engineering and Sciences Corporation, ††Swales Aerospace, †††Pacific Lutheran University

Abstract

Carbon nanotubes (CNTs) offer great potential for advanced sensor development due to the unique electronic transport properties of the material. However, a significant obstacle to the realization of practical CNT devices is the formation of reliable and reproducible CNT to metallic contacts. In this work, scanning probe techniques are explored for both fabrication of metallic junctions and positioning of single-walled CNTs across these junctions. The use of a haptic force feedback interface to a scanning probe microscope is used to enable movement of nanotubes over micron length scales with nanometer precision. In this case, imaging of the surface is performed with light or intermittent contact to the surface. Increased tip-to-sample interaction forces are then applied to either create junctions or position CNTs. The effect of functionalization of substrate surfaces on the movement and tribology of the materials is also studied. The application of these techniques to the fabrication of CNT-based sensors for nondestructive evaluation applications is discussed.

Introduction

With the ever-increasing demands being placed on today's structures and materials, there is an equally increasing need for the development of advanced nondestructive evaluation sensors (NDE).

CNT devices capable of measuring strain and magnetic fields while carrying structural loads offer great potential as the foundation of the next generation of structural health monitoring systems. Current fabrication techniques of CNT devices employ electron beam lithography, scanning probe nanolithography, nanomanipulation, and self-assembly techniques.

Both electron beam and scanning probe nanolithography have been used to produce metallic contacts with length scales on the order of tens of nanometers. Such sizes are required to connect single-walled carbon nanotubes (SWCNTs) to conventional microlithography circuit elements. SWCNTs are deposited on the surface using various methods such as exposure to a CNT dispersed solution or spraying with an atomizer. CNT positions are then verified using a scanning probe microscope. This process, while functional, relies on the random distribution of CNTs on the substrate surface.

Two other techniques being explored include the use of a patterned self-assembled monolayer (SAM) which can either enhance or deter CNT adherence [1, 2], and nano-manipulation via the NanoManipulater, a haptic force feedback interface coupled to the scanning probe microscope (SPM). The NanoManipulator enables the mechanical movement of CNTs by switching from imaging (tapping) mode to an increased tip-to-sample force contact mode, enabling modifications to be carried out. [3-5]

All of these different fabrication methods share a common goal of CNT positioning capabilities which facilitate CNT device development.

Scanning Probe Lithography

Because of its ability to resolve features on the atomic scale, the SPM is integral to nanotechnology. In one application, the SPM is used to modify conventional microcircuits into a nano-circuit by creating a small gap on a conductive trace for a CNT to span.

In this technique, a diamond tipped cantilever is used to both image and modify the surface by varying the tip-to-sample force. As shown in Figure 1, conductive traces from a thin film circuit were imaged in contact mode with a force of 5 μN. Once a location was selected for modification, the SPM was switched into line scan mode, repeatedly scanning the same line. During this time the imaging force was increased to 50 μN and scanning continued until the trace was completely cut. The tip-to-sample force is then reduced and the complete trace rescanned to verify the effectiveness of the cut [7].

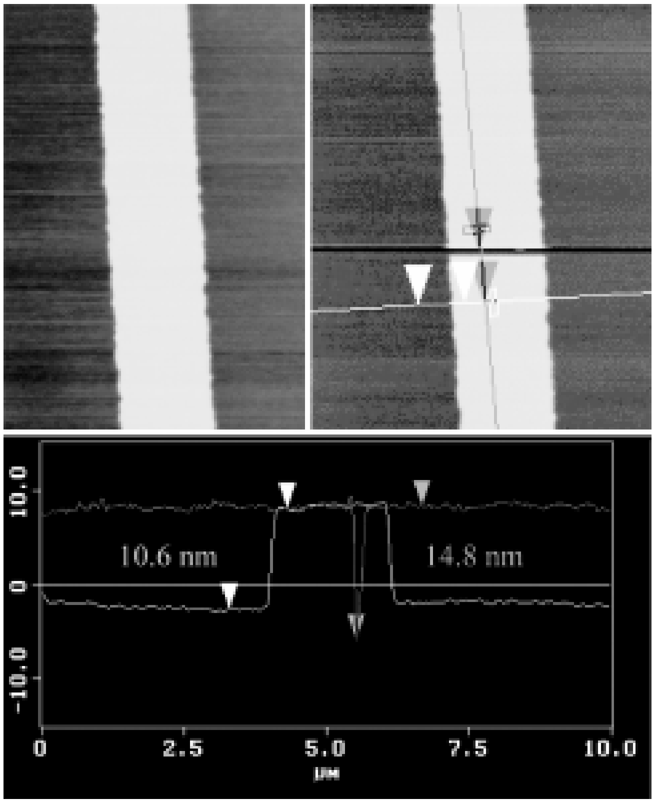


Figure 1. *Image taken with diamond tip cantilever on Digital Instruments Nanoprobe IIIa. Top left shows gold in white on a Si substrate. Right, is the same trace which has been cut using the Diamond tip. Vertical and horizontal lines measure topography, shown in graph. Note the depth of cut is greater than the height of the conductive trace.*

Electron Beam Lithography / CNT Deposition

Electron beam lithography is used to fabricate thin film circuits using either a one or two layer resist [6]. Feature sizes can be produced with length scales of tens of nanometers, allowing electrical contacts of a reasonable size to be made to the CNTs. CNTs are attached to such contacts by depositing CNTs on the surface before or after the lithography process. The CNTs are first dispersed, at low concentrations, using solvents such as DMF, toluene, or IPA, by sonication for several hours. The CNT material is then deposited onto the surface by either immersing in a CNT dispersion or spraying with an atomizer, Density of deposited tubes can be controlled by either immersion time or quantity sprayed onto the substrate. Figure 2 shows a completed CNT device element in which a SWCNT rope has been deposited across contacts defined by electron beam lithography.

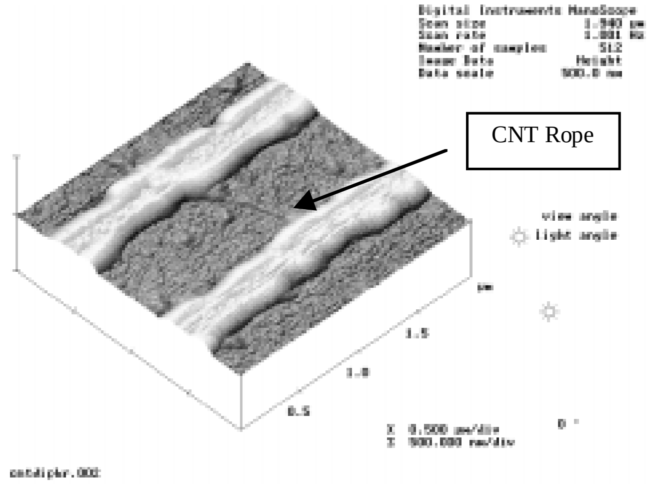


Figure 2. *Simple SWCNT device consisting of two metallic traces 200nm wide and 500nm spacing. Note the nanotube running between the traces.*

Self Assembled Monolayer

In recent publications, it has been shown that self-assembly techniques offer a great potential for the positioning of CNTs. [1, 2] CNTs can be immobilized on a surface via electrostatic interactions between the nanotubes and surface-bound moieties. The strength of this interaction greatly depends on the nature of the terminal groups on the substrate. Silicon wafers were coated with a thin layer of either methyl- or amino-terminated groups using self-assembly techniques. CNTs have previously been shown to adhere strongly to amino-terminated surfaces and weakly to methyl-terminated surfaces. Combining these two observations leads to a scheme for CNT placement and alignment on a substrate.

Silanization chemistry is a well-established technique for depositing monolayer coverage via organosilane reactions with hydroxyl groups on the silica surfaces, producing layers with known terminal groups. Silicon wafers were silanized using 3-aminopropyltriethoxysilane (APTES) to produce amino-terminated surfaces. APTES first reacts with surface adsorbed water in a hydrolysis reaction to produce 3-aminopropylsilane triol. This species can then condense with hydroxyl groups, either other APTES molecules or surface-bound hydroxyl groups, leading to attachment of an amino-terminated chemical linker. Similar reactions occur using octadecyltrichlorosilane (OTS) leading to the attachment of trimethylsilyl (TMS), a methyl-terminated group. A summary of the reactions is shown in Figure 3.

NanoManipulation

It has previously been shown that multi-walled CNTs, can be easily displaced or strained using the NanoManipulator without significant distortion of the nanotube topography [4]. According to M.R. Falvo et al., the multi wall CNTs are much stiffer and respond to the increased tip to sample force by rolling then sliding [3]. The same instrumentation can also be applied to the

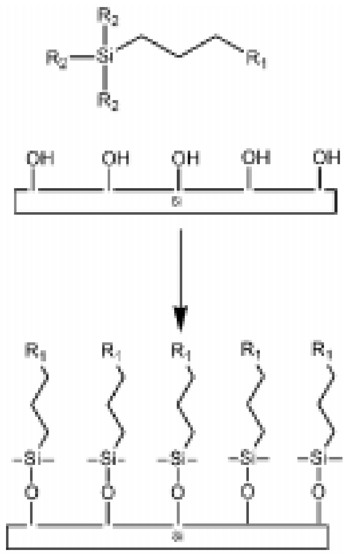


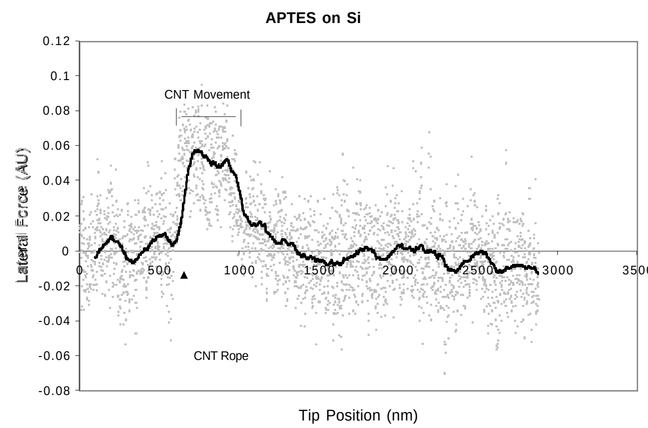
Figure 3. *(A) Structure of organosilane. For APTES,* R_1 *=* NH_2 *and* R_2 *=* OCH_2CH_3 *and for OTS,* R_1 *=* $(CH_2)_{14}CH_3$ *and* R_2 *= Cl. (B) Surface bound hydroxyl groups on silicon substrates. (C) Chemical linker after silanization with APTES or OTS.*

positioning of SWCNTs. Using the NanoManipulator (3rd Tech), interfaced with an Explorer SPM (ThermoMicroscopes), modifications were made to CNT ropes on different surfaces using a Nanodevices magnetic force cantilever operating both in imaging (tapping) mode and contact (manipulation) mode. Lateral force manipulation measurements were taken in the direction of a left to right line scan only. Studies were conducted to determine the effects of CNT manipulation on functionalized SAM-coated Si substrates.

It has been observed that SWCNTs are difficult to move while maintaining the integrity of the CNT ropes, which vary in length and diameter. Difficulties lie in the resolvable size and inter-dynamics of the CNT ropes. In this case, CNT ropes (3-15nm diameter) composed of several SWCNTs (1.4nm diameter) respond differently to the direct force applied by the SPM tip than the multi-wall CNTs reported by M.R. Falvo et. al.

Application of force by the SPM tip to the ropes normal to their long axis, yields different deformations on each of the different SAMs. After each modification of the surface/rope the sample was imaged. On the CNT repulsive TMS surface, ropes were deposited by spraying dispersed tubes on the substrate. Ropes on this surface ranged 5-15nm in diameter. Deformation of the rope typically followed a pattern consisting of an initially large lateral force which is maintained for a distance of approximately 300 – 500nm, followed by a decay period after which the lateral force returns to its zero state. On APTES, tubes would quickly adhere to the surface when the substrate was immersed in a toluene solution containing dispersed CNTs. The CNT ropes on this surface were on average smaller in diameter ranging from single tubes up to 8nm in diameter. Manipulations were conducted on larger CNT ropes to increase the signal-to-noise ratio. Manipulations differed from the TMS sample by having a shorter duration of the initial force and little to no decay period on the average manipulation. Figure 4 displays lateral force measurements for tube movement on APTES and TMS SAMs.

In addition to the differences in the modification data, the post-modification images taken on each sample show significant differences in how the CNTs move. On TMS, large portions of the tube were displaced, as opposed to the APTES samples were tube movement is localized to the area directly in contact with the probe tip. The surface modifications corresponding to the lateral forces depicted in the top of Figure 4 are shown in Figure 5 and are typical results for SWCNT ropes deposited on an APTES surface.



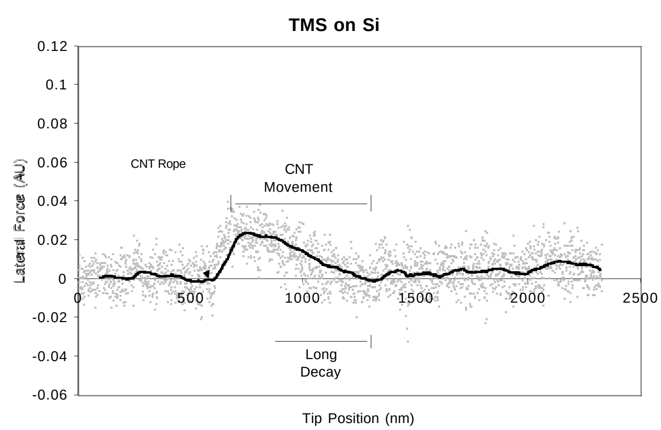


Figure 4. *Lateral force data from CNT modification, APTES above and TMS below. Note the lower force and long decay in TMS data.*

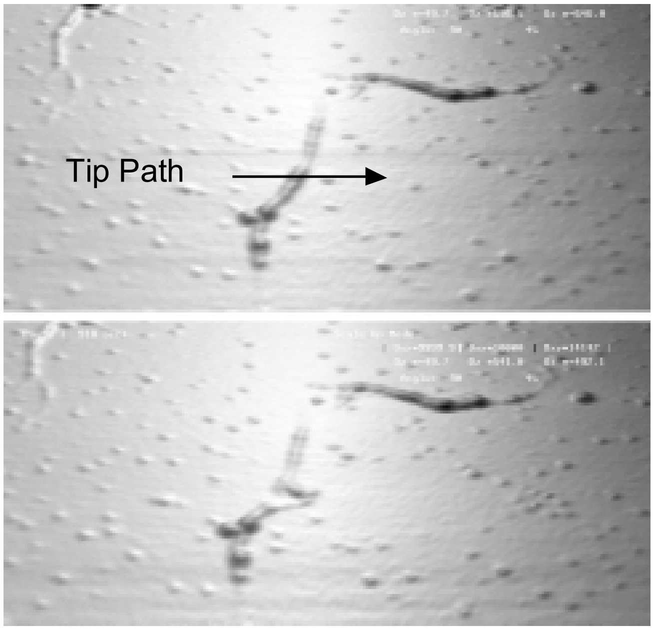


Figure 5. *CNT rope on APTES coated wafer. Tip path is indicated in top picture. The resulting modification can clearly be seen in the post-modification image below.*

Summary

SWCNTs offer great potential for next generation NDE sensors due to their unique electronic transport and load carrying capabilities, enabling the development of multifunctional structures with embedded structural health monitoring. In an effort to realize this goal, fabrication techniques for CNT-based NDE sensors have been studied. In this work we have explored techniques for the fabrication of single nanotube devices, focusing on scanning probe microscopy methodologies. Diamond tipped scanning probe nanolithography, force feedback carbon nanotube manipulation, and lateral force microscopy have all been presented as critical tools for the study, understanding, and fabrication of reliable CNT NDE devices. Coupling these techniques with electron beam lithography and functionalization of substrate surfaces using self-assembled monolayers has the potential to lead to breakthrough gains in vehicle performance and structural health monitoring.

References

1. Ji Liu, Michael J. Casavant, Micheal Cox, D.A. Walters, P Boul, Wei Lu, A.J. Rimberg, K.A. Smith, Daniel T. Colbert, Richard E. Smalley, Chemical Physics Letters, 303, 125-129, (2000).
2. K.H. Choi, J.P. Bourgoin, S. Auvray, D. Esteve, G.S. Duesberg, S. Roth, M. Burghard Surface Science, 462, 195-202, (1999).
3. M.R. Falvo, G. Clary, A. Helser, S. Paulson, R.M. Taylor II, V. Chi, F.P. Brooks, Jr., S. Washburn, and R. Superfine, Mocrosc. Microanal. 4, 504-512, (1999).
4. M. Guthold, M.R. Falvo, W.g. Matthews, S. Paulson, S. Washburn, D. Erie, R.Superfine, F.P. Brooks, Jr., R.M. Taylor II, 3rd Tech web site: www.3rdtech.com.
5. M.Guthold, G. Matthews, A. Negishi, R.M. Taylor II, D. Erie, F.P. Brooks Jr., R. Superfine, Surf. and Interface Anal. 27, 437-443 (1999).
6. Handbook of Microlithography, Micromachining, and Microfabrication, volume 1: Microlithography, ed. P. Rai-Choudhury, Chapter 2. SPIE (1997).
7. B. Wincheski, S.M. Paik, and M. Namkung, in Nanospace 2001: Exploring Interdisciplinary Frontiers, IAIR, (2001).