REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-03-

0310

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REF
	30 JULY 2003	FINAL REPORT 01 MAY 02 - 31 OCT 03

4. TITLE AND SUBTITLE
DURIP: Surface-Templated Assembly and Conductivity Study of Molecule-Based Electronic Nanostructures

5. FUNDING NUMBERS
F49620-02-1-0192
61103D
3484/US

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4015 Wilson Blvd., Room 713
Arlington, VA 22203-1954

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
Approve for Public Release: Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

We built dip-pen nanolithography (DPN)-based molecular patterning system comprised of a commercial atomic force microscope (AFM) and environmental control systems (Figure 1). The equipment has been utilized for two major projects: 1) integration of the DPN process with conventional micorfabrication processes and 2) study of electron transport in individual molecules. Even in short one year period, we were able to achieve several major research results which can have a significant impact on nanoscale sciences and technology. These include: 1) surface-templated assembly of carbon nanotubes, 2) dip-pen nanolithography on inert surfaces, and 3) conductivity study of DNA and other organic molecules. These results have been published or will appear in various prestigious journals such as Nature and Physical Review Letters.

20030818 004

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLAS	UNCLAS	UNCLAS	

Title: DURIP: Surface-Templated Assembly and Conductivity Study of Molecule-Based Electronic Nanostructures.
Type of report: Final Technical Report
Name of the principal investigator: Seunghun Hong
Period covered by the report: 05/01/2002 ~ 04/30/2003
Name and address of the recipient's institution: Florida State University, 118 North Woodword Ave., Tallahassee, FL 32306-4166
Sponsor ID#: F49620-02-1-0192

I. Introduction

We built *dip-pen nanolithography (DPN)-based molecular patterning system* comprised of a commercial atomic force microscope (AFM) and environmental control systems (Figure 1). The equipment has been utilized for two major projects: 1) integration of the DPN process with conventional micorfabrication processes and 2) study of electron transport in individual molecules.

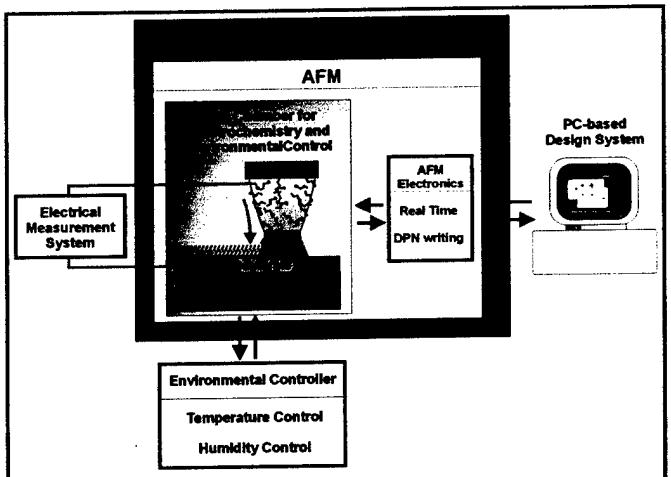


Figure 1. DPN-based molecular patterning system.

Even in short one year period, we were able to achieve several major research results which can have a significant impact on nanoscale science and technology. These include: 1) surface-templated assembly of carbon nanotubes, 2) dip-pen nanolithography on inert surfaces, and 3) conductivity study of DNA and other organic molecules. These results have been published or will appear in various prestigious journals such as *Nature* and *Physical Review Letters*. The manuscripts are enclosed with this report.

II. Significant Scientific Achievements Resulted from the Equipment

A) Surface-Templated Assembly of Carbon Nanotubes: *Nature, accepted* (2003)

Nanoscale electronic devices made of carbon nanotubes (e.g. transistors, sensors) can be much smaller and more versatile than any conventional microelectronic chips, while the lack of a mass-production method has been holding back their practical applications. Inspired by biomolecular self-assembly, we developed a novel self-assembly method for the wafer-scale fabrication of millions of carbon nanotube circuits with a single-nanotube-level precision. This method may enable industrial-level production of nanotube-based devices such as faster computer chips and high-density sensor arrays.

This method utilizes organic molecular marks on the substrate to guide the self-assembly of individual single-wall carbon nanotubes (SWCNTs) (Figure 2a). In the *surface functionalization* step, we create two distinctive surface regions coated with either *polar* (e.g. $-NH_2$, -COOH) or *non-polar* (e.g. $-CH_3$) chemical groups by directly depositing proper organic molecules (e.g. self-assembled monolayer molecules) via dip-pen nanolithography (DPN) or

microcontact stamping techniques. When the substrate is placed in SWCNT suspensions, SWCNTs are attracted toward the *polar* regions, and they *self-assemble* to form pre-designed structures. Here, direct deposition methods such as DPN and stamping allow us to functionalize substrates without intermediate chemical steps, which minimize surface contamination.

A key discovery in this project is the existence of a *lateral-directional force* on SWCNTs *near the boundary between polar and non-polar molecular regions* (Figure 2b). This force, which presumably originates from electrostatic interactions, *rotates* the SWCNTs toward the *polar* region and keeps them inside the region (inset). Previous methods such as Lieber's flow cell technique utilized external forces to precisely align nanowires along desired directions to assemble *a few* carbon nanotubes. However, it can be extremely time-consuming to align *multiple randomly-oriented* nanotube circuits using external forces. In our process, individual polar molecular marks attract and align SWCNTs along pre-determined directions without utilizing any external forces. Now, we can assemble any SWCNT-based structures simply utilizing *polar molecular patterns with proper shapes.*

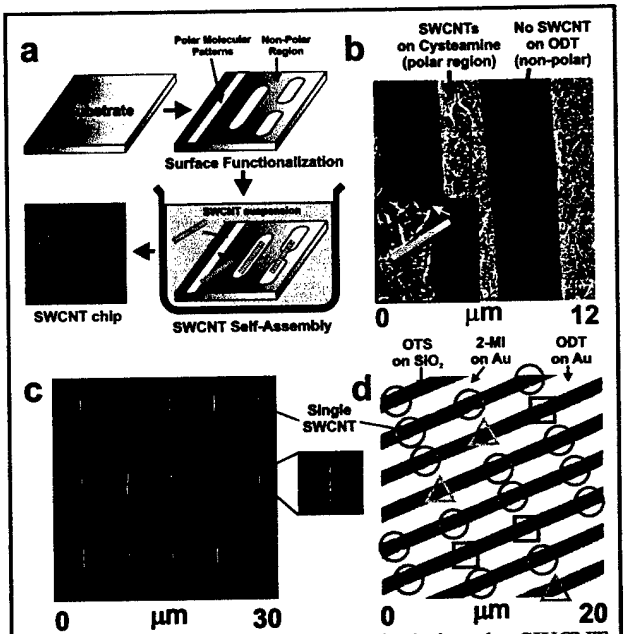


Figure 2. a, Schematic diagram depicting the SWCNT assembly process. **b,** SWCNTs near the boundary between polar and non-polar (1-octadecanethiol (ODT)) molecular patterns on Au. **c,** Array of individual SWCNTs on Au surface. The friction force image (inset) shows a single SWCNT (dark line), 2-mercaptoimidazole (2-MI) (bright area), and ODT (dark area) regions. **d,** Array of junctions with 0(Δ), 1(O), and 2(□) SWCNTs between Au electrodes.

Utilizing this strategy, we are able to assemble individual SWCNTs onto molecular patterns on flat surfaces (Figure 2C) as well as on electrode structures (Figure 2D). On flat surfaces current yield is over 90%. On electrode structures, the yield is about 70%, which is only limited by the size distribution of SWCNTs in the suspension. This yield is expected to improve as the purification process advances in the future.

B) Dip-Pen Nanolithography on Inert Surfaces: *Physical Review Letters 90*, 115505-1 (2003)

Recent development of dip-pen nanolithography provides an ideal tool for the rapid fabrication of molecule based functional devices. The DPN process is a direct deposition technique that utilizes an atomic force microscope tip as a pen, molecular substances as ink, and solid substrates as paper. As the AFM tip is translated

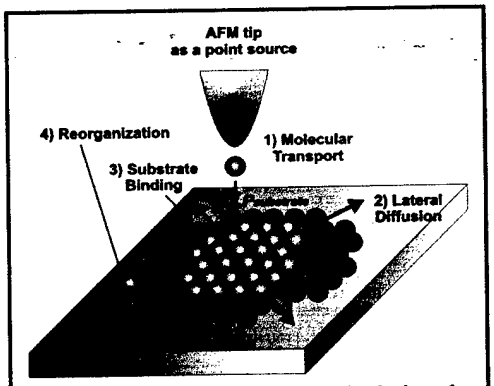


Figure 3. Schematic diagram depicting the dip-pen nanolithography process.

relative to the sample, the deposited ink forms a patterned, self-assembled monolayer (SAM) on the substrate. A number of variables, including relative humidity, temperature, and tip speed, can be adjusted to control ink transport rate, feature size, and linewidth. The DPN technique permits lithography of unprecedented resolution. Considering that conventional direct deposition technology such as an ink jet printer has a minimum feature size of ~ 10μm, current resolution of DPN (~15nm) means a revolution of direct printing technology.

Until now, DPN has been demonstrated in the case when the molecules strongly anchor to the surface via chemical or electrostatic bindings. However, as the applications of DPN expand, we can expect the cases when the binding between the deposited molecules and substrates is very weak (Figure 3). Examples include *biomolecules on inert surfaces* and *molecules on carbon nanotubes*. Recently, we were able to deposit organic molecules without strong chemical bindings via the DPN technique. In this case, we have observed an *anomalous surface diffusion* (Figure 4). In this experiment, AFM tip coated with desired molecular species is held at a fixed position in contact with the substrate so that molecules diffuse out onto the substrate, and various size *dot* patterns are formed depending on the contact time (Figure 4A and C). Figure 4 shows various diffusion results from two different molecules: 16-mercaptohexadecanoic acid (MHA) on Au and dodecylamine (DDA) on mica. In case of normal diffusion, ink molecules diffuse in radial directions from the AFM tip and form a circular pattern (Figure 4A). However, dodecylamine on mica shows fractal-type growth kinetics (Figure 4C). This is the first observation of anomalous diffusion in nanoscale direct deposition processes. This result indicates that anomalous diffusion can be problematic in case of DPN writing on inert surfaces. Patterns generated with DDA molecules via DPN process is shown in Figure 4D. Due to the anomalous diffusion, the patterns are significantly distorted. The pattern by a normal diffusion process is also presented for comparison (Figure 4B). A possible solution for this anomalous diffusion can be simply minimizing the surface diffusion during the patterning process. For example, to generate large size patterns, multiple small dots or thin lines should be utilized rather than large dots or thick lines.

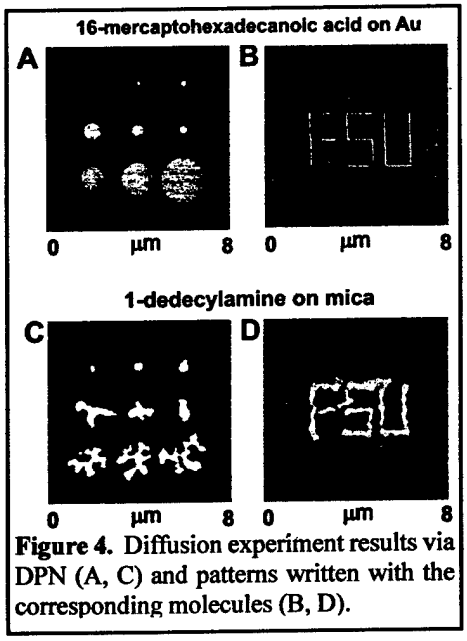


Figure 4. Diffusion experiment results via DPN (A, C) and patterns written with the corresponding molecules (B, D).

C) Conductivity Study of DNAs and Other Organic Molecules: *MRS Symposium Proceedings* for the symposium titled, "Bio-Inspired Nanoscale Hybrid Structures" (2003)

Towards *bio-* and *molecular electronics*, many researchers have been investing extensive efforts to study the electrical properties of DNA and other organic molecules. However, the measurement of electric conduction in small organic molecular wires is still extremely difficult, and the conduction mechanism in DNA molecules is still controversial. If one could find an experimental tool that allows one to reliably characterize short molecular nanowires like conventional "I-V stations" in microelectronics labs, he/she can remove one significant bottle neck which has been holding back the development of molecular electronics.

In this work, we applied the conductance microscope (CM) technique to characterize well-defined organic molecular patterns generated via *dip-pen nanolithography* (DPN) or *microcontact printing*. The conductance images from the sample with two different molecular patterns allow us to reliably measure the *relative conductance* of two different organic molecular species.

Figure 5 shows the basic experimental set up of CM. In the measurement, the conducting AFM tip is in direct contact with the surface, and the electric current between the AFM tip and conducting substrates are measured at each point on the substrate allowing us to take a conductance map. If the conducting surface is covered with different organic molecular species, one can measure the *relative conductivity* of those organic layers by measuring the current map at a fixed bias voltage. The measured current I can be written as,

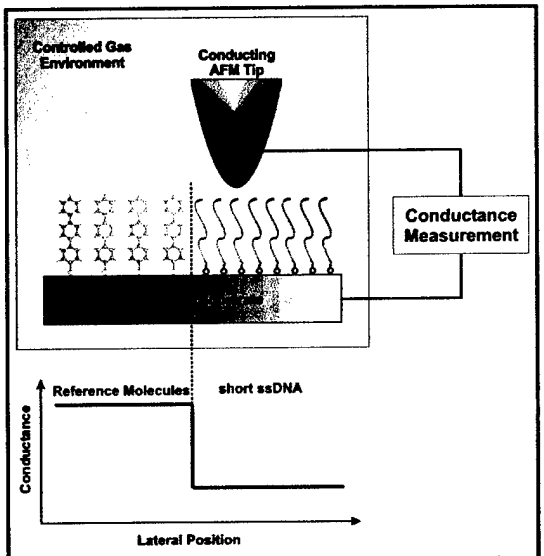


Figure 5. Schematic diagram depicting the relative conductance study of ssDNA molecular layers via the CM method on patterned molecular surfaces.

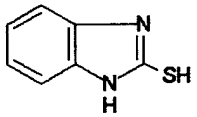
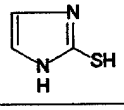
$$I = A \times N \times C \times V$$

where A is the contact area between the tip and the substrate, N is the number density of molecular wires, C is the conductance of individual molecular wires, and V is the bias voltage. Since the same tip is utilized on two different molecular regions, the ratio of measured currents I_1/I_2 from two different molecular patterns is,

$$I_1 / I_2 = (N_1 \times C_1)/(N_2 / C_2)$$

Significantly, this ratio is a function of only intrinsic properties of organic molecular layers, and it is independent of external variables such as the tip shape or contact area which are usually extremely difficult to measure. The number density of most of self-assembled monolayer is usually well known, or it can be measured by various methods. Eventually, the CM on molecule patterned surfaces can allow us to reliably measure the *conductance ratio between various molecular species*.

Table 1 shows the list of molecules that were studied.

Molecules (Abbreviations)	**Formula**
10-mer Thiolated Thymine (ssDNA)	5'-TTT TTT TTT T/3 Thio MC3-D/-3'
Cystamine Dihydrochloride (Cys)	$H_2NCH_2CH_2SSCH_2CH_2NH_2 \cdot 2HCl$
2-Mercaptobenzimidazole (MBI)	
16-Mercaptohexadecanoic Acid (MHA)	$HSCH_2(CH_2)_{13}CH_2COOH$
2-Mercaptoimidazole (MI)	

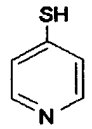
4-Mercaptopyridine (MP)	
1-Octadecanethiol (ODT)	$CH_3(CH_2)_{16}CH_2SH$

Table 1. List of organic molecules used in the experiment.

Figure 6 shows the CM images taken *at the same location* at various relative humidity (12, 20, 40, and 60 %). The brighter regions represent higher conductivity areas. The results show that MHA layer is conducting better than ODT layer. The conductance averaged over 6 different rectangular regions in the figure shows almost identical contrast with a variation of less than 15% under different humidity conditions. This implies that the effect of adsorbed water is not significant, and conductance microscopy can provide relatively reliable *relative conductance* data over a large range of humidity conditions.

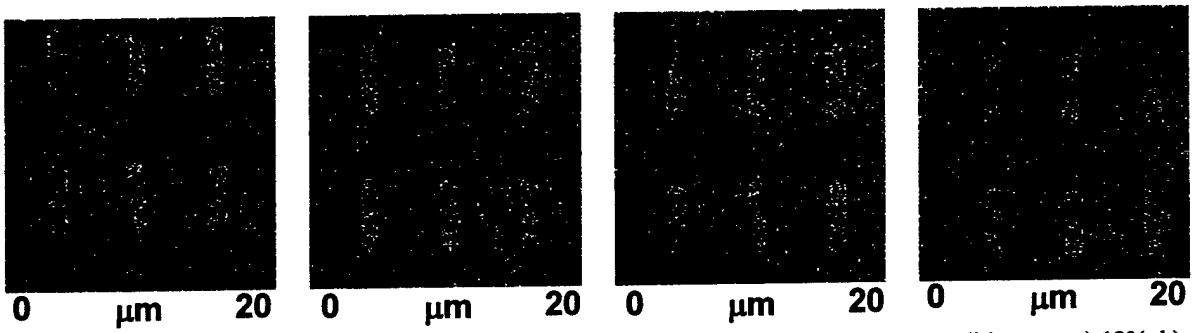


Figure 6. CM images of ODT (bright rectangles) and MHA (dark areas). Relative humidity conditions are a) 12%, b) 20%, c) 40% and d) 60%, respectively. 0.25 V sample bias is applied.

We utilized CM to study the relative conductance of very short reference molecular patterns. The results show that MP, Cys, and MHA are conducting better than ODT as summarized in Table 2.

Finally, we applied the CM technique to study the relative conductivity of ssDNA molecular layers and reference molecules. Five samples were made, MI/ssDNA, MBI/ssDNA, MP/ssDNA, Cys/ssDNA, and MHA/ssDNA.

We can clearly find that the MBI and MHA molecules are conducting better than ssDNA (Figure 7). The measured conductance contrast from MBI/ssDNA and MHA/ssDNA samples are 72nA and 30nA, respectively. The data shows *the conductance ratio of 2.6 for MBI/ssDNA and 2.0 for MHA/ssDNA*. Particularly, MHA could be a good upper limit for the conductivity of our ssDNA. We could not observe the clear conductance contrast from Cys/ssDNA, MI/ssDNA, and MP/ssDNA even though existence of the patterns can be confirmed by the lateral force microscopy (LFM) images. The results are summarized in Table 2.

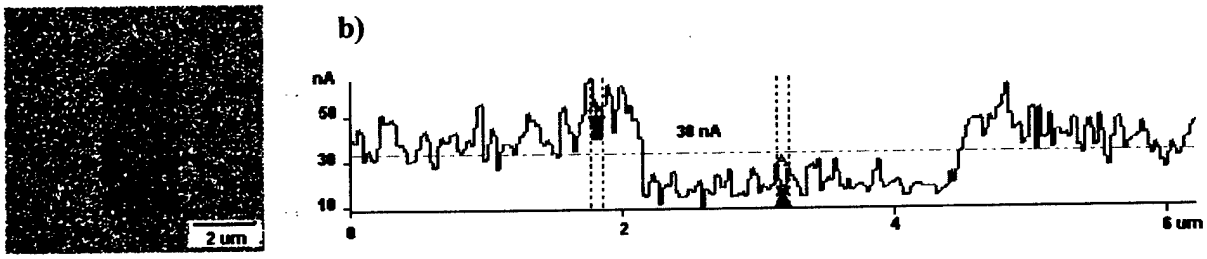


Figure 7. (a) CM image on MHA (bright area) and ssDNA (dark area), and (b) the cross-section averaged over the vertical line inside the rectangular area in (a) (2.0 V sample bias).

MHA molecules are usually considered *insulating* molecules because it does not contain delocalized π-electrons and it also has a very large HOMO-LUMO gap. The experimental results implies that ssDNA with 10T bases is a poor conductor, which is qualitatively consistent with theoretical prediction and some experimental results.

It should be cautioned that the measured ratios in Table 2 provide only information about ensemble averaged value of the relative conductivity of *molecular layers*. To find out the conductance of *individual molecules*, one has to know other information such as the *number density* of molecular layers. However, the number densities of many molecular species are well-known, or it can be measured via various other techniques. The ssDNA experiments demonstrate that, after proper considerations, the CM on patterned surfaces can provide direct measurement of the electrical conduction in biological and chemical molecular species.

Patterned Molecules (mp)	**Back Filled Molecules (mf)**	**Conductance Ratio (I_{mp}/I_{mf})**	**Current Difference ($I_{mp} - I_{mf}$)**	**Sample Bias**
ODT	MP	<1/10	-100 nA	+0.2 V
ODT	Cys	~1/8	-85 nA	+0.2 V
MBI	ssDNA	~2.6	72 nA	+2.0 V
MHA	ssDNA	~2.0	30 nA	+2.0 V

Table 2. Comparison of electrical conductivity of several molecular nanowires.

III. Publications Resulted from the Equipment

Journal

1. "Massive self-assembly for integrated carbon nanotube circuits," S. Rao, L. Huang, W. Setyawan, S. Hong ***Nature***, accepted (2003).
2. "Anomalous Surface Diffusion in Nanoscale Direct Deposition Processes," P. Manandhar, J. Jang, G. Schatz, M. Ratner, S. Hong ***Physical Review Letters 90***, 115505-1 (2003).

Proceedings

1. "Conductance Microscopy for Electric Conduction Study of Bio-Inspired Hybrid Nanostructures under Ambient Conditions," W. Setyawan, S. Rao, S. Hong ***MRS Symposium Proceedings*** (2003).

Book Chapter

1. "Nano-Deposition of Soft Materials," in the book titled *"Encyclopedia of Nanoscience and Nanotechnology," to appear* (American Scientific Publishers, 2003).

IV. Presentations Resulted from the Equipment

1. "Conductance Microscopy for Electric Conduction Study of Bio-Inspired Hybrid Nanostructures under Ambient Conditions," W. Setyawan, S. Rao, S. Hong, Materials Research Society Meeting, Boston (2002)
2. " Rapid Prototyping of Hybrid Nanoscale Devices via Dip-Pen Nanolithography", S. Hong, Nanoimprint and Nanoprinting Technology Conference, San Francisco (2002).
3. "Precision Positioning and Alignment of Multiple Carbon Nanotubes via

Surface-Templated Assembly Process," S. Rao, L. Huang, S. Hong, American Physical Society Meeting, Austin (2003).
4. "Surface-Templated Assembly of Synthetic Nanostructure-Based Devices," S. Hong, Nanomanufacturing Conference, Boston (2003).