

# “Dip-Pen” Nanolithography on Semiconductor Surfaces

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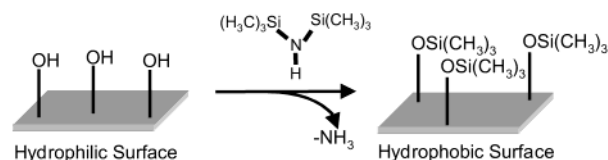
**Abstract:** Dip-Pen Nanolithography (DPN) uses an AFM tip to deposit organic molecules through a meniscus onto an underlying substrate under ambient conditions. Thus far, the methodology has been developed exclusively for gold using alkyl or aryl thiols as inks. This study describes the first application of DPN to write organic patterns with sub-100 nm dimensions directly onto two different semiconductor surfaces: silicon and gallium arsenide. Using hexamethyldisilazane (HMDS) as the ink in the DPN procedure, we were able to utilize lateral force microscopy (LFM) images to differentiate between oxidized semiconductor surfaces and patterned areas with deposited monolayers of HMDS. The choice of the silazane ink is a critical component of the process since adsorbates such as trichlorosilanes are incompatible with the water meniscus and polymerize during ink deposition. This work provides insight into additional factors, such as temperature and adsorbate reactivity, that control the rate of the DPN process and paves the way for researchers to interface organic and biological structures generated via DPN with electronically important semiconductor substrates.

## Introduction

Dip-Pen Nanolithography (DPN)<sup>1–3</sup> allows one to fabricate one molecule thick nanostructures with micron to sub-100 nm dimensions on solid substrates. With the DPN methodology, an organic molecule, such as a thiol, is used as “ink” and is transported from the tip of an atomic force microscope (AFM) through a water meniscus onto a gold surface. This technique has been used to generate structures with line widths as small as ~10 nm and separations of as little as 5 nm.<sup>2</sup> Thus far, all reported examples have dealt exclusively with the “gold paper”–“thiol ink” combination, or the use of metal salts as inks and an appropriately biased silicon substrate to electrostatically drive the salts to the surface and reduce them to form metallic and semiconductor lines.<sup>4</sup> However, in principle, the DPN approach for patterning organic nanostructures can be extended to any substrate, provided one can identify suitable inks through an understanding of the surface modification chemistry of the substrate of interest<sup>5</sup> and the compatibility of such inks with the meniscus ink-transport medium.

In a DPN experiment, the molecules chosen as “inks” and the substrates serving as the “paper” typically react with each other in a facile and predictable manner to yield reproducible and stable patterns. Herein, we report a successful strategy for using DPN to write organic structures directly onto semiconductor substrates, Scheme 1.<sup>6,7</sup> Utilizing hexamethyldisilazane (HMDS) as the “ink” in a conventional DPN procedure, we can write features with less than 100 nm line widths onto

## Scheme 1



Si/SiO<sub>x</sub> and oxidized GaAs. HMDS is widely applied in semiconductor-based photolithography protocols as a resist adhesion promoter layer.<sup>7</sup> The silazane end reacts with oxide surfaces, resulting in the immobilization of trimethylsilyl (TMS) groups on the surface and the concomitant elimination of NH<sub>3</sub>, Scheme 1. HMDS was chosen rather than trichlorosilanes and trialkoxysilanes to avoid polymerization of the ink in the meniscus.<sup>8</sup>

## Experimental Section

Si/SiO<sub>x</sub> (100) wafers (4 in. diameter; 3–4.9 ohm/cm resistivity; 50–500 μm thickness) were purchased from Silicon Quest International, Inc (Santa Clara, CA) or WaferNet, Inc (San Jose, CA) and used as received, or cleaned in O<sub>2</sub> plasma for 5 min prior to patterning. The patterning quality was qualitatively unaffected regardless of the Si/SiO<sub>x</sub> wafers' pretreatment. GaAs (100) wafers (2 in. diameter; ≥375 ± 20 μm thickness) were purchased from Marketch International (Port Townsend, WA) and were n-type (Si doped) with carrier concentrations of 5 × 10<sup>17</sup> to 2 × 10<sup>18</sup> cm<sup>-3</sup>. Prior to each experiment the GaAs wafers were oxidatively etched in a solution of H<sub>2</sub>O:H<sub>2</sub>SO<sub>4</sub> (8:2; v/v), washed with ethanol, and dried with N<sub>2</sub>.

Hexamethyldisilazane (99.9%), 1,3-diphenyl-1,1,3,3-tetramethyldisilazane (99.9%), di-*n*-butyltetraphenyldisilazane (99.9%), and 1,3-divinyl-1,3-diphenyl-1,3-dimethyldisilazane (99.9%) were purchased from Gelest, Tullytown, PA, and used without further purification. Acetonitrile (ACS grade) was obtained from Fisher Scientific. HMDS is moisture sensitive, and the reaction of water with the silazane could potentially compete with the writing process. However, <sup>1</sup>H NMR spectroscopy showed no measurable degradation of the HMDS (~10<sup>-5</sup> M) when it was brought in contact with ~5-fold excess of water for

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(1) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. *Science* **1999**, *283*, 661.

(2) Hong, S.; Zhu, J.; Mirkin, C. A. *Langmuir* **1999**, *15*, 7897.

(3) Hong, S.; Mirkin, C. *Science* **2000**, *288*, 1808.

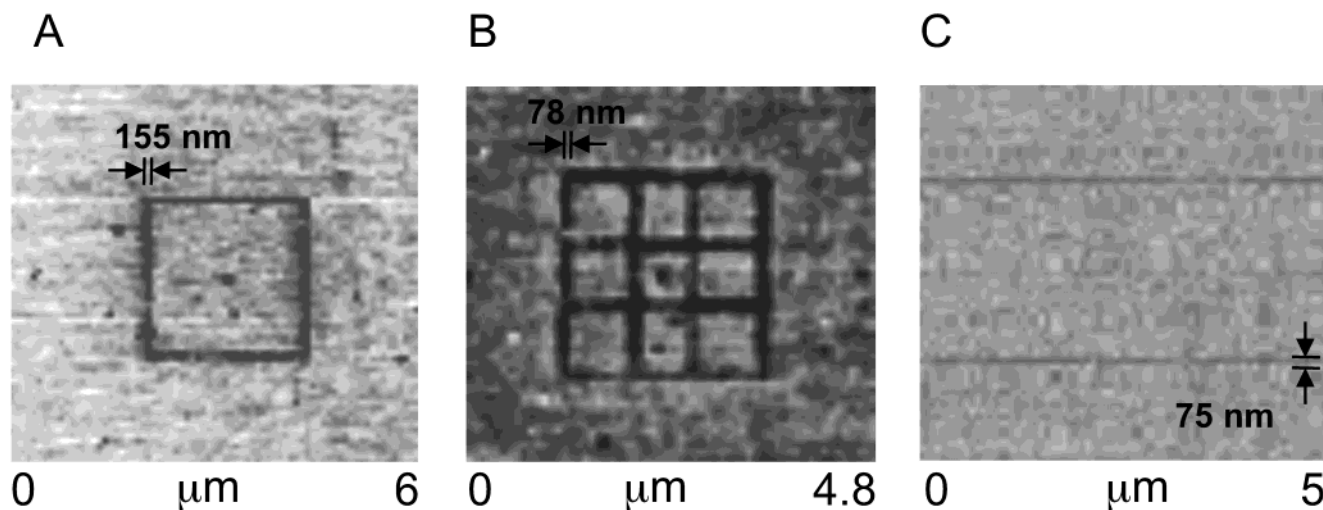
(4) Li, Y.; Maynor, B. W.; Liu, J. *J. Am. Chem. Soc.* **2001**, *123*, 2105.

(5) Blackledge, C.; McDonald, J. D. *Langmuir* **1999**, *15*, 8119.

(6) Pereira, G. J.; De Silva, M. L. P.; Tan, I. H.; Gouvea, D. J. *Mater. Chem.* **2000**, *10*, 259.

(7) Dammel, R. *Diazonaphthoquinone Based Resists*, 1st ed.; SPIE Optical Engineering Press: Bellingham, WA, 1993.

(8) Hong, S.; Mirkin, C. Unpublished results.



**Figure 1.** Lateral force microscopy (LFM) images of DPN-generated TMS monolayer patterns on semiconductor surfaces. All LFM images were recorded at a scan rate of 4 Hz. In all cases lighter contrast areas (higher friction) correspond to the hydrophilic ( $-OH$  group rich) semiconductor surface and darker areas (lower friction) are due to the deposited silazane via DPN: (a) square TMS pattern ( $2.4 \mu\text{m}$  edge width) on  $\text{Si}/\text{SiO}_x$  with a writing speed of  $0.08 \mu\text{m/s}$ ; (b) a TMS grid on  $\text{Si}/\text{SiO}_x$  substrate ( $2.4 \mu\text{m}$  edge width) with a writing speed of  $0.04 \mu\text{m/s}$ ; and (c) a parallel line pattern on oxidized GaAs with a writing speed of  $0.02 \mu\text{m/s}$ .

10 min. This time is twice as long as a typical writing period. Note that extra care was taken to keep all “inks” dry when not used for writing, since they react with ambient moisture over longer periods of time ( $>5$  h).

All the data described herein were taken using a ThermoMicroscopes CP AFM driven by customized software and conventional  $\text{Si}_3\text{N}_4$  cantilevers (ThermoMicroscopes sharpened Microlever A, force constant =  $0.05 \text{ N/m}$ ). Prior to writing, tips were soaked in a 3:1  $\text{CH}_3\text{-CN}:\text{HMDS}$  (v/v) solution for 60 s and blown dry with compressed difluoroethane. Unless otherwise noted, all patterning experiments described herein were conducted under ambient conditions at 30% relative humidity and  $23^\circ\text{C}$  with a tip–substrate contact force of  $0.5 \text{ nN}$ . Subsequent imaging of the generated patterns was done under the same conditions. The temperature of the substrate was measured using a Digi Sense Thermocouple Thermometer purchased from Cole-Parmer.

## Discussion

**HMDS DPN Writing on Semiconductor Surfaces.** Prior to the DPN procedure the surface of each semiconductor was hydrophilic as evidenced by water contact angles of  $40^\circ$  and  $36^\circ$  for  $\text{Si}/\text{SiO}_x$  and oxidized GaAs, respectively. The transformation of surface OH groups in the form of well-defined and pre-programmed patterns was achieved by delivering the HMDS on the AFM tip to the surface, Figure 1. Typically, if a simple alkyl silane is used as a surface modification agent, a base is used to catalyze the reaction. For this reason, silazanes work particularly well in these types of surface modifications because they have a built-in amine base.<sup>7</sup>

HMDS surface modification conditions for large area  $\text{Si}/\text{SiO}_x$  substrates have been previously studied. Typically, gas-phase HMDS is delivered (temperature  $> 150^\circ\text{C}$ ) to an oxidized silicon wafer during the modification procedure,<sup>7</sup> but ambient temperature conditions and liquid HMDS also have been used to effect surface modification.<sup>9</sup> The latter is not the choice in the semiconductor industry because of its high cost, inefficiency, and the difficulty of working with the HMDS in the liquid rather than gas phase. However, in a DPN experiment where the meniscus controls the effective tip–substrate contact area, HMDS can be deposited on such surfaces with precise control over pattern shape and feature size.

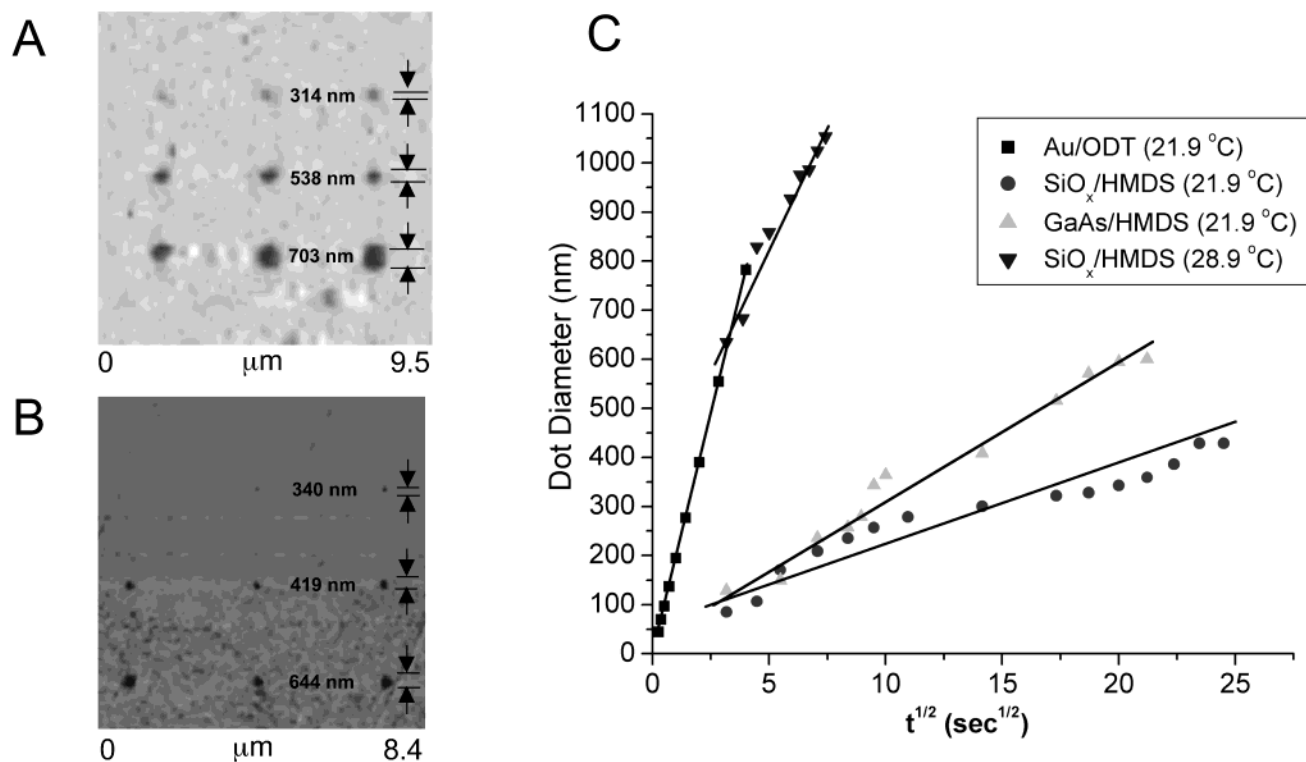
In a typical patterning experiment, a tip coated with HMDS was brought into contact with either the oxidized GaAs or  $\text{Si}/\text{SiO}_x$  surface. A single square feature (Figure 1A) and a grid of squares (Figure 1B) can be traced by raster scanning the tip (scan speed ranged from  $0.02$  to  $0.4 \mu\text{m/s}$ ) across an arbitrarily chosen region of the semiconductor surface. Immediately after this deposition step, a lateral force microscopy (LFM) image (scan rate of 4 Hz) of the patterned section within a larger scan area allows one to distinguish patterned from unmodified substrate. The patterned areas exhibit relatively lower lateral force (dark) than the unmodified areas (light), due to the replacement of the OH groups with the TMS groups. Thus far, we have successfully deposited lines with widths as small as  $50 \text{ nm}$  and as large as  $10 \mu\text{m}$  via DPN on the  $\text{Si}/\text{SiO}_x$  surfaces. In general, line widths increase with longer tip–substrate contact times, and the resolution of the patterning is dependent upon scan speed, as evidenced from the comparison between the lines in parts A and B of Figure 1. In addition, the generated patterns were unaffected by three successive acetonitrile rinses, as determined by AFM, which suggests irreversible adsorption of the TMS groups on the oxidized surface. Furthermore, we performed surface FTIR on  $\text{Si}/\text{SiO}_x$  samples with monolayer square features of  $10 \mu\text{m} \times 10 \mu\text{m}$  patterned via DPN and microcontact printing. In both cases, three bands were observed at  $860$ ,  $848$ , and  $831 \text{ cm}^{-1}$ , which are assigned to the methyl vibration modes of the surface-bound  $\text{Si}(\text{CH}_3)_3$  groups.<sup>10,11</sup> Oxidized GaAs can be patterned in a similar manner to generate line and dot features with comparable dimensions, Figures 1C and 2B. Finally, in addition to HMDS, we investigated 1,3-diphenyl-1,1,3,3-tetramethyldisilazane, di-*n*-butyltetraphenyldisilazane, and 1,3-divinyl-1,3-diphenyl-1,3-dimethyldisilazane as possible inks, and discovered that they also can be used to pattern semiconductor surfaces via DPN.

**Kinetics of HMDS DPN Writing.** The two different semiconductor substrates also were used to study the diffusion properties of HMDS during the DPN procedure, Figure 2. In a typical experiment, the tip coated with HMDS was brought into contact with the oxidized surface (either  $\text{Si}/\text{SiO}_x$ , Figure 2A, or

(10) Slavov, S. V.; Sanger, A. R.; Chuang, K. T. *J. Phys. Chem. B* **2000**, *104*, 983.

(11) KBr diluted spectra of HMDS show stretching frequencies at  $870$ ,  $847$ , and  $756 \text{ cm}^{-1}$ .

(9) Anwender, R.; Nagl, I.; Widenmeyer, M. *J. Phys. Chem. B* **2000**, *104*, 3532.



**Figure 2.** Diffusion properties of HMDS on (a) Si/SiO<sub>x</sub> surface and (b) oxidized GaAs. Each plot shows the LFM image after the tip has been in contact with the surface for 50, 100, and 200 s (top to bottom row, part a) and 30, 50, and 300 s (top to bottom row, part b). All LFM images were recorded at a scan rate of 4 Hz. (c) Plot of the feature diameter as a function of  $t^{1/2}$  for HMDS on Si/SiO<sub>x</sub> (21.9 and 28.9 °C), HMDS on oxidized GaAs (21.9 °C), and ODT on Au (21.9 °C). Data on Au were taken from ref 12 for comparison at 21.9 °C. The uncertainty of measuring the dot radius is  $\pm 5$  nm.

GaAs, Figure 2B) for successively longer periods of time. In addition to demonstrating that uniform dots can be generated under ambient conditions, our experiments show that the writing times required for this molecule on both surfaces are much longer than those for thiol-based "inks" on Au substrates under nearly identical experimental conditions.<sup>12</sup> The dot size exhibits the expected  $t^{1/2}$  dependence, in accord with the model used thus far to describe the DPN process, Figure 2C.<sup>1,2,14</sup> The model suggests that both the diffusion coefficient and the "sticking coefficient" of the ink will play major roles in controlling the speed of the patterning process

At room temperature, the reaction rates of the silazane with both oxidized semiconductor substrates are much slower than those for alkanethiols with gold, hence the writing speed under these conditions with the silazane will typically be slower than for the thiol on gold system. However, the writing speed can be increased by adjusting the temperature of the substrate and HMDS-coated tip during the DPN procedure. For example, attempts at facilitating the HMDS transport rate to an oxidized silicon substrate by illuminating the sample stage area of the AFM instrument with a fiber optic lamp (150 W) for 200 s result in a significant increase in the rate of deposition ( $\sim 2$ ), Figure 2C. We report the temperature of the semiconductor substrate only, since measuring the temperature of the tip (which we suspect is much higher) would require us to disturb our optical feedback system. The writing time needed to generate features is dramatically decreased, when the temperature of the substrate and ink is elevated from 21.9 °C to 28.9 °C. This is,

in part, due to increased diffusion rates of the ink to substrate, and it is known that silazanes react faster with oxide surfaces at elevated temperatures.<sup>15</sup>

### Conclusion

This study is significant for the following reasons. (1) It shows that DPN can be used to directly pattern organic structures onto Si/SiO<sub>x</sub> and GaAs. Both of these are electronically important substrates and the ability to interface organic and biological nanostructures with these substrates via DPN will open up a variety of avenues for making functional devices. (2) The choice of a silazane as the ink allows one to avoid complicating polymerization reactions in the meniscus and takes advantage of the intramolecular base to facilitate the chemisorption process. (3) It provides insight into some of the factors that control the DPN process and shows that temperature is a variable that can be used to regulate the speed of the process. Moreover, if speed of chemical patterning is an important issue, as it will be with any serial process, the results herein point toward the importance of understanding the fundamental parameters that govern the chemical (ink) transport process in the DPN experiment for further optimization and generalization.

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(12) Weinberger, D. A.; Hong, S.; Mirkin, C. A.; Wessel, B. W.; Higgins, T. B. *Adv. Mater.* **2000**, *12*, 1600.

(13) Hong, S.; Zhu, J.; Mirkin, C. *Science* **1999**, *286*, 523.

(14) Jang, J.; Hong, S.; Schatz, G. C.; Ratner, M. A. *J. Chem. Phys.* **2001**, in press.

(15) Anwander, R.; Nagl, I.; Weinberger, D. A.; Engelhardt, G.; Groeger, O.; Clemens, P.; Roser, T. *J. Phys. Chem. B* **2000**, *104*, 3532–3544.