

# Morphology Control in Self-Assembled Monolayers Written by Dip Pen Nanolithography

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Here, we describe the effect of writing speed in dip pen nanolithography on the morphology (height and density) of self-assembled monolayers of alkanethiols on gold surfaces. The analysis of atomic force microscopy images of written monolayers shows that molecules assemble according to a nucleation and growth mechanism. Slow writing speeds lead to dense monolayers that can be used either to direct the self-assembly of metal nanoparticles or as masks for selective etching of conductive gold nanowires.

Recently developed lithographic methods have allowed for the fabrication of nanoscale features and devices that may have major implications in information technology and biosensing.<sup>1–3</sup> One of the most promising techniques, dip pen nanolithography (DPN), was developed by Mirkin and co-workers as a versatile method to deposit molecules on various surfaces using the tip of an atomic force microscope (AFM) as a transfer tool.<sup>1,4</sup> Since its discovery, many groups in the world<sup>5</sup> have been successful in using DPN for writing molecules on metal and semiconductor surfaces.<sup>6–10</sup> Applications of DPN include the fabrication of protein<sup>11,12</sup> and DNA arrays,<sup>13,14</sup> magnetic arrays,<sup>15</sup> metal nanoparticle based structures,<sup>12,16</sup> and masks for the etching of nanosized gold features.<sup>17</sup> Due to its enormous potential, DPN has attracted fundamental research on its enabling mechanism.<sup>18–21</sup> To date, most of the work has focused on understanding the phenomena

that allow the transfer of molecules from the tip to the surface. Here, we focus on the subsequent assembly of such molecules on the surface, showing that they can form homogeneous and dense self-assembled monolayers (SAMs) as long as they are given enough time to nucleate and grow. The analysis of atomic force microscopy height images of monolayers written via DPN proves that the writing speed determines the quality of the written SAMs. Applications of these findings for the efficient etching of nanowires are shown.

In DPN, molecules are adsorbed onto contact-mode AFM tips through a solution<sup>1</sup> or vapor deposition method.<sup>4</sup> When the tip is in contact with the surface, a water meniscus forms, favoring the transfer of molecules between the coated tip and the substrate.<sup>1,18–20</sup> The concentration gradient established between the coated tip and the surface drives diffusion of the molecules toward the substrate. The tip–surface contact time ( $t$ ) has been shown to affect the resolution of DPN;<sup>6,8,10,20,21</sup> in fact, when writing dots, a classical diffusion model has been used to show that the dot diameter grows linearly with  $t^{1/2}$ .<sup>6,8,10,20</sup> Relative humidity plays a role in the writing of hydrophilic molecules, because of the higher solubility in the water meniscus.<sup>19</sup> In the case of thiolated molecules on a gold surface, it has been shown that DPN can be used to write SAMs.<sup>1,4</sup>

SAMs of thiolated molecules on metal surfaces have been extensively studied,<sup>22,23</sup> and it has been established that they form through a multiple step mechanism.<sup>24,25</sup> The first step is always a fast adsorption on the surface, in which the molecules assume a flat-lying conformation. The second step occurs when the surface is almost completely covered; at this stage, new molecules can only bind to the surface by inducing a reorientation of the flat-lying molecules more normal to the surface. This step, nucleation, is characterized by the formation of isolated densely packed pockets. The third step consists of the growth of these pockets into a continuous and uniform film made of molecules all forming the same angle to the surface normal. This angle is the one that maximizes the density of the monolayer; indeed, the height of a monolayer is directly related to its density. While it is proven that

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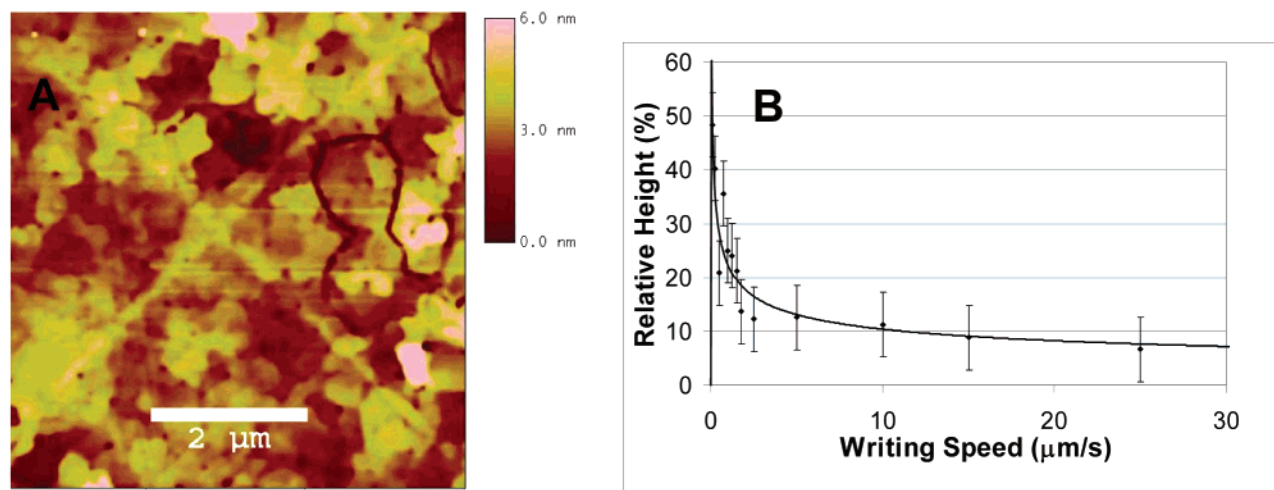
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**Figure 1.** (A) AFM height image of two crossing DDT molecular wires written via DPN on a gold on mica substrate in a single pass. (B) Plot of the relative height of DDT written patterns vs the writing speed. The points represent averages of the measured data, and the continuous line is a fit to  $v^{-1/3}$ . The 100% relative height is 1.7 nm for DDT, as found in ref 22.

DPN produces monolayers following such a mechanism,<sup>26</sup> it was unknown whether DPN allows for the control of the density of the patterned SAMs and consequently of the orientation of the written molecules. Here, we show that it is possible to stop the formation of the SAM at any point, starting from SAMs made of flat-lying molecules all the way to densely packed SAMs made of molecules almost normal to the surface.

To understand the relationship between DPN kinetics (i.e., writing speed) and monolayer formation kinetics, we investigated the height of the written SAMs. In particular, to include both monolayer density and molecular height in a single figure of merit, we introduced the concept of relative height, defined as the measured height of a monolayer divided by the height of the densely packed monolayer assembled on a large and flat surface. To ensure consistency when comparing the heights of monolayers, all our experiments were performed on the same type of surface, flame annealed Au(111) thermally evaporated on freshly cleaved mica. This type of substrate is composed of atomically flat terraces that have height mismatches of up to 2 nm. Height information of the written features on the substrate (see, for example, Figure 1A) was obtained using a feature of our microscope analysis software that allows for averaging the height of areas specified by the operator. Thus, the difference between the average height of the patterned areas and the averaged height of the surrounding gold substrate was measured. Internal controls were used to avoid errors or image artifacts and to quantify the error margins of our measurements. For instance, the height of the surrounding gold substrate was calculated in multiple spots of the image. For any given analyzed line, we calculated its height by selecting both the whole line and segments of it. We used data just in the case where all measurements agreed within 3 Å.

As shown in Figure 1, the height of dodecane thiol (DDT) monolayers written in DPN strongly depends on the writing speed (inverse of time). An explanation for this behavior is that, at high writing speeds, there is not sufficient time to allow for either the nucleation of dense islands or their growth. Conversely, when the tip moves slowly, the monolayer is allowed more time to nucleate and grow. To date, we have never seen complete monolayer formation upon writing with the tip passing over the

feature only once (i.e., single pass writing). The kinetics of this process are quite involved. The combined effect of the diffusion of molecules from the tip to the surface,  $t^{1/2}$ , together with the monolayer formation kinetics<sup>27,28</sup> is observed. Indeed, the height of the written features decays as  $v^{-1/3}$  ( $t^{1/3}$ ), where  $v$  is the writing speed. Diffusion dominates at high velocities (short times; when  $t^{1/3}$  is similar to  $t^{1/2}$ ), while the Langmuir kinetics of monolayer formation<sup>27,28</sup> become important at slow velocities (long times; when  $t^{1/3} < t^{1/2}$ ). We believe that a reasonable consequence of our result is that most of the SAM formation happens when the water meniscus is above the written feature.

Additional evidence for the proposed mechanism can be found in lateral force microscopy (LFM) images of features written with mercaptohexadecanoic acid (MHA, HS-(CH<sub>2</sub>)<sub>15</sub>-COOH). LFM images, commonly used to show DPN data, represent a map of the attractive forces between the tip and the substrate. It is well documented that such forces are lower in hydrophobic molecules and higher in hydrophilic ones when compared to the surrounding bare gold substrate.<sup>1,4</sup> LFM images of MHA wires patterned by DPN show high friction for wires written at slow speeds and low friction for those written at rapid speeds (Figure 2). The reason for this behavior is that, when quickly written, MHA monolayers consist of flat-lying molecules,<sup>29</sup> and thus, the AFM tip perceives the monolayer as being composed of mostly hydrophobic methylenes. At slower speeds, the written SAM is more dense, and thus, the AFM tip interacts primarily with the molecular end groups, the hydrophilic carboxylic acids.

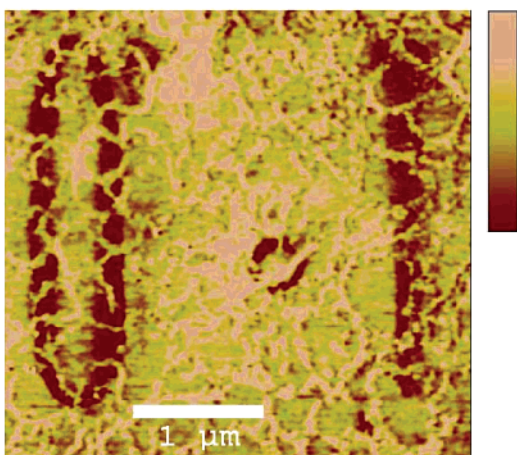
To further test our idea, we compared the kinetics of SAM formation in DPN for different molecules. These molecules were chosen to have similar diffusion rates but different rates of monolayer formation. First, we focused on comparing octadecanethiol (ODT, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>17</sub>-SH) to DDT (CH<sub>3</sub>-(CH<sub>2</sub>)<sub>11</sub>-SH) and octanethiol (OT, CH<sub>3</sub>-

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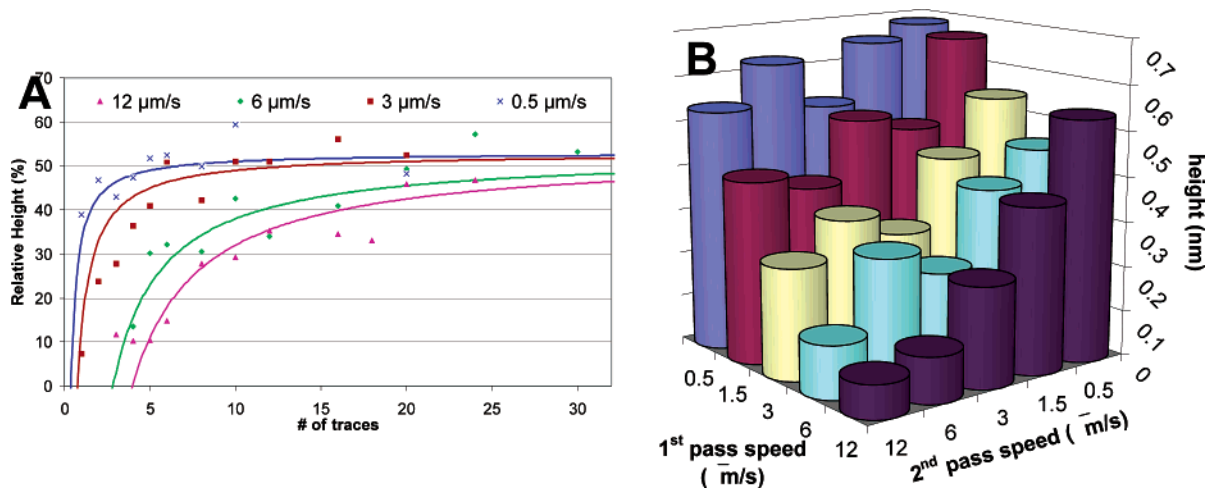
**Figure 2.** Lateral force microscopy image of two MHA lines written at  $0.25 \mu\text{m/s}$  (left) and  $3 \mu\text{m/s}$  (right). The lines appear as higher and lower friction, respectively, when compared to the surrounding gold surface. This is attributed to the fact that the left line is made of densely packed molecules; thus, the MHA carboxylic acid end groups compose the whole upper surface of the SAM and generate high frictional forces. The right line is made mainly of molecules lying flat on the surface; thus, its upper surface is mostly composed of the methylenes that are found in the middle of the MHA backbone.

$(\text{CH}_2)_7\text{-SH}$ ). It is known that shorter thiolated molecules form better monolayers more rapidly,<sup>24</sup> due to the fact that the energetic difference between an all-trans conformation and a conformation with one gauche defect gets larger as the molecule gets shorter. SAMs are composed of mostly trans molecules; thus, they form faster when starting from molecules that are already in such a conformation, that is, shorter ones. Compared to the case of ODT, we noticed that DDT forms shorter SAMs at higher speeds and longer SAMs at lower speeds (see the Supporting Information). At low writing speeds, the shorter molecule, DDT, forms SAMs with higher relative heights, that is, better packed. At high speeds, SAMs composed of flat-lying molecules will always form, but the ODT SAMs appear higher because of the conformational defects in the molecules that do not allow for perfect alignment to the surface plane. In the case of OT, writing was almost impossible due to the fact that the molecules

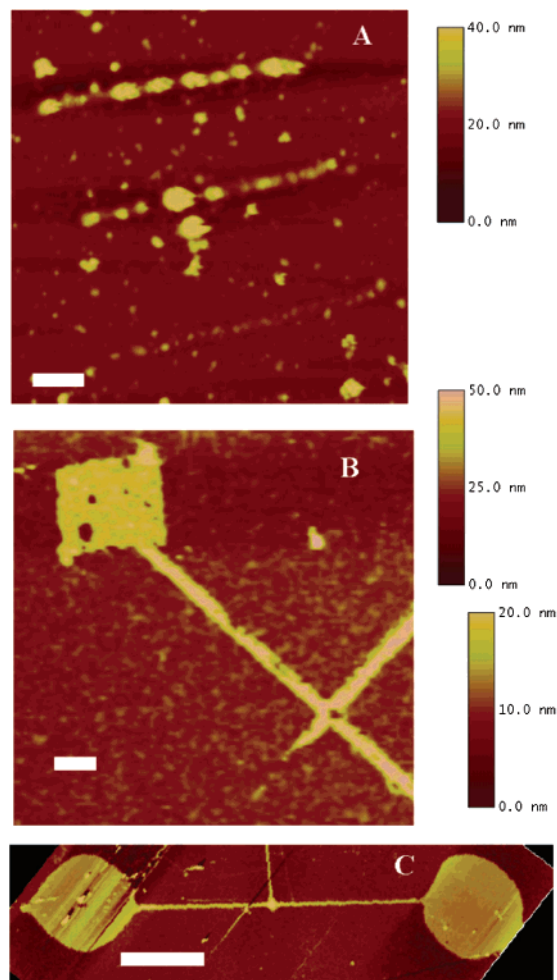
tend to crystallize either on the tip or on the substrate, showing that it is not easy to write in DPN with molecules that are too short. Results similar to those of the comparison of DDT and ODT were obtained when comparing MHA to mercaptoundecanoic acid (MUA,  $\text{HS}-(\text{CH}_2)_{10}-\text{COOH}$ ). It should be noted that alkanethiols achieve better relative heights when compared to carboxylic acid terminated molecules, probably due to the fact that the latter have slower kinetic rates of formation due to their headgroup interactions.

To better understand the mechanism of monolayer formation in DPN, we also analyzed AFM height images of features written in multiple passes. As shown in Figure 3A, the height of the lines written at different speeds plateaus at the same value at a high number of passes. At slow speeds, most of the monolayer formation happens in the first few passes and it looks like additional passes do not affect the height of the monolayer. The only observable effect is that the lines become wider and wider at every pass. At high writing speeds, the nucleation and growth keeps happening at every pass up to the moment when the plateau relative height is achieved. An additional insight in this writing mechanism has been studied; it looks at the height of features written in two passes in which the speeds of the first and the second pass are different. As shown in Figure 3B, when the first writing pass is slow, the monolayer height achieved is almost independent of the speed of the second pass. The faster the first pass, the more the height becomes dependent on the second pass speed, consistent with a nucleation and growth mechanism.

DPN can be used to write features that further direct the assemblies of other molecules or materials.<sup>11,13,14</sup> To further test the idea that writing speed determines molecular orientation, we studied the ability of DPN written monolayers to direct the assembly of suitably terminated nanoparticles. A densely packed monolayer has an upper surface homogeneously composed of the molecular end groups, while, at lower densities, the end group concentration varies along the surface. We used MUA coated nanoparticles as probes for the homogeneity of the carboxylic acid terminal groups in MHA monolayers. Such assembly can happen only through the interaction of the nanoparticles with the carboxylic acid end groups of the



**Figure 3.** (A) Plot of the relative height vs the number of traces for a series of ODT wires ( $5 \mu\text{m}$  in length) written via DPN. The curves are present to guide the eye when comparing lines written at different speeds. This plot shows that at a large number of traces the same relative height is achieved when writing at different speeds. (B) Height of ODT wires written in two traces plotted against the speed of the first and second trace. When the first writing trace is at a slow speed, most of the nucleation occurs in that stage; thus, the additional height gained during the second trace is almost independent of the writing speed. This shows that the growth occurs more rapidly than the writing speeds we tried.



**Figure 4.** (A) Tapping mode AFM height image of three lines of self-assembled Au nanoparticles on top of identically shaped lines of MHA written with DPN. The lines were written at 1  $\mu\text{m/s}$  (top), 3  $\mu\text{m/s}$  (middle), and 5  $\mu\text{m/s}$  (bottom). The nanoparticles are used as tools to detect the uniformity of the carboxylic acids on the upper surfaces of the written SAMs. It is evident that such uniformity is achieved only at slow writing speeds. Scale bar, 1  $\mu\text{m}$ . (B and C) Contact-mode AFM image of gold wires formed by patterning ODT on Au on Si, followed by etching the substrate to remove the Au from the unpatterned areas. The wire shown in part B is a 150 nm wide conductive gold wire. Scale bar in part B, 500 nm. The device shown in part C proves that we can write conductive wires as long as 30  $\mu\text{m}$ . Scale bar in part C, 10  $\mu\text{m}$ .

MHA monolayer. MUA coated nanoparticles, on average 3.8 nm in diameter, were assembled on wires written at different speeds by placing the substrate in an ethanol solution of such particles for 72 h. We found that they assembled selectively on patterns written at speeds lower than 10  $\mu\text{m/s}$ . Moreover, the slower the speed, the more uniform the coverage (as shown in Figure 4A), clearly confirming the nature of the underlying uniformity of the SAM orientation.

Controlling the morphology and the density of the written self-assembled monolayers in DPN has allowed us to find optimal writing conditions to fabricate conductive gold nanowires. It was recently shown that DPN could be used to produce resists for selective etching of gold films on silicon wafers.<sup>17</sup> This method consists of using written ODT monolayers as masks against gold etching in a ferrocyanide solution. In our experience, we have found that, to fabricate conductive metal wires, it is necessary to start with a SAM that is as dense as possible. In the case of less dense SAMs, wires that are either not percolated or with resistivities that are orders of magnitude higher than that of bulk gold are obtained. This is probably due to the etchant attacking at the boundary between dense nucleation centers and regions of flat-lying molecules. A 43  $\mu\text{m}$  long wire with a 1  $\mu\text{m} \times 20$  nm cross section obtained by etching a gold film protected by a dense ODT SAM written at 5  $\mu\text{m/s}$  with 20 retraces<sup>30</sup> showed a resistivity of  $3 \times 10^{-8} \Omega \text{ m}$ , just 30% more than that of bulk gold.<sup>31</sup> Additional evidence for the relationship between SAM density and resistivity to etching was obtained by writing single pass molecular wires at different speeds on the same substrate. After etching for 10 min, we analyzed the thickness of the remaining gold features and found that the average gold thickness decayed with increasing writing speed.

In conclusion, we have demonstrated that by controlling the writing speed one is able to control the morphology of the monolayers deposited via dip pen nanolithography. Specifically, the average height of such written monolayers decays with increasing writing speed, due to a nucleation and growth mechanism. The control of the morphology of the written SAMs has allowed us to write conductive gold nanowires with resistivities very close to that of bulk gold and to selectively self-assemble 3.8 nm nanoparticles on written MHA lines.

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**Supporting Information Available:** One figure showing a comparative plot of the relative height achieved by different molecules written via DPN on a gold surface at different speeds and a description of the experimental methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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