

Site-Specific Dual Ink Dip Pen NanolithographyTM

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Summary: The ability to deposit different materials with nanoscale precision at user-specified locations is a very important attribute of dip pen nanolithography (DPN[®]). However, the potential of DPN goes beyond simple deposition since DPN used in conjunction with lateral force microscopy (LFM) allows site-specific investigations of nanoscale properties. In this work, we use two different inks, 16-mercaptohexadecanoic acid (MHA) and 1-octadecanethiol (ODT) to show site-specific dual ink DPN enabled exclusively by our proprietary software. A diamond-dot pattern was created by using a layer-to-layer alignment (LLA) algorithm, which enables a MHA pattern (diamond) to be written concentric with another ODT (central dot) pattern. This simple demonstration of multi-ink DPN is not specific to alkanethiol ink systems, but is also applicable to other multi-material patterning, interaction, and exchange studies. SCANNING 31: 122–126, 2009. © 2009 Wiley Periodicals, Inc.

Key words: Dip pen nanolithography, nanofabrication, DPN 5000, MHA, ODT, scanning probe, multilayer lithography

Introduction

The ability to deposit materials at the nanoscale with a broad range of “inks” under ambient conditions is a key aspect of Dip pen nanolithography[®] (DPN[®]) technique. In DPN (Piner *et al.* 1999) an atomic force microscope (AFM) tip is used to deposit materials of interest (inks) at specific locations on the substrate as shown in Figure 1.

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Whether the desired nano-architecture is physical or chemical, there are two approaches to building nanostructures: top-down or bottom-up. DPN enables both these approaches to nanofabrication by using a silicon nitride AFM tip to direct-write inks on suitable substrates. Further, precision nanoscale deposition is a fundamental requirement for much of current nanoscience research, and depositing a variety of materials as nanoscale features at precise locations is a challenging requirement for nanoscale processing systems. DPN is an inherently additive AFM-based technique that operates under ambient conditions, making it suitable to deposit wide range of biological, organic, and inorganic materials, at specified locations. As such, DPN can overcome many obstacles to flexible nanoscale pattern creation.

Demonstrations of DPN had its origins in depositing alkanethiol-based materials (inks) on a gold substrate at non-specific locations. However, with a push toward parallelization (Haaheim and Nafday 2008) and with a goal of accurate deposition of multiple inks, the ability to place inks at specific sites on the substrate becomes important. In order to achieve site-specific DPN needs, we have developed the DPN 5000TM DPN platform, which allows precision placement of materials based on a computer-aided design (CAD) pattern creation software toolbox. The toolbox allows multiple patterns to be drawn in InkCADTM, which is our proprietary DPN and pattern registration software. In InkCAD, users can create the patterns in one or more layers inside the 90 × 90 μm AFM scanner range. Each pattern (in every layer) has independent pattern creation properties such as tip speed/line width (for line features), tip dwell time/dot radius (for dot features), set-point, lift tip after pattern lithography, which can be specified by the user. The layers themselves can be individually aligned with respect to each other, thus allowing precise recording and translation of the ink-coated tip between layers. This precise tip translation between multiple layers is achieved using a layer-to-layer alignment (LLA) algorithm in InkCAD. Using the layered pattern design approach one can design patterns in multiple layers and with the help of the LLA algorithm in

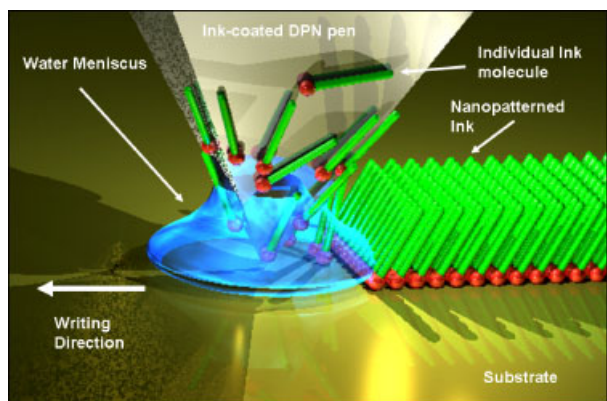


Fig 1. Schematic representation of the DPN technique (Reproduced with permission from John Wiley & Sons, Inc. (Scanning, Haaheim and Nafday 2008).

InkCAD achieve precise DPN results between patterns in different layers. Precise positioning in DPN is important for a number of reasons, i.e. performing site-specific exchange studies with combinatorial libraries of nanostructures (Ivanisevic *et al.* 2002) investigate nanoscale ink transport (Hampton *et al.* 2006) multiplexed lipid and biomolecule studies for templating (Sekula *et al.* 2008; Lenhert *et al.* 2007) and combining nanolithography with electrochemical desorption and deposition (Mullen *et al.* 2008; Seo and Borguet 2006) to document a few.

The earliest attempt to use DPN with multiple inks with a view to create combinatorial libraries was demonstrated by Ivanisevic *et al.* (2002). In this work four different thiol-based inks were written on a gold surface with DPN. These ink regions were subsequently imaged with an inked AFM tip (similar to what is commonly performed in DPN) to perform site-specific ink exchange studies and to determine the stability of the four inks with respect to each other. This study also demonstrated writing of one ink (16-mercaptohexadecanoic acid, MHA) on a region of already deposited ink (1-octadecanethiol, ODT). Such ink-on-ink DPN (Fig. 2) was later used by Hampton *et al.* (2006) for investigating nanoscale ink transport related to the water meniscus. Figure 2 shows the deposition of ODT (dark lateral force microscopy (LFM) contrast) over the MHA “plus-shaped” region (bright LFM contrast). However in both cases, the deposition of the second ink (MHA in Fig. 2A and ODT in 2B) was off-center by a few hundred nanometers. This offset between region centers might not be important for the Hampton study, which only required the MHA and ODT inks to be in contact with each other; however, in the case of areas (inks) that are in the realm of the nanoscale, a few hundred nanometers of offset can cause the inks to be deposited side-by-side instead of on top of each other. Multiple thiol ink DPN was also demonstrated by using a *single* AFM tip by controlling the relative

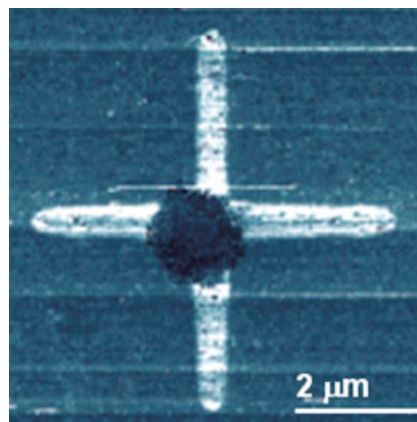


Fig 2. LFM image of ODT ink (dark contrast) patterned on MHA “+” shaped region (bright contrast). Reproduced with permission from the American Chemical Society (JACS, Hampton *et al.* 2006).

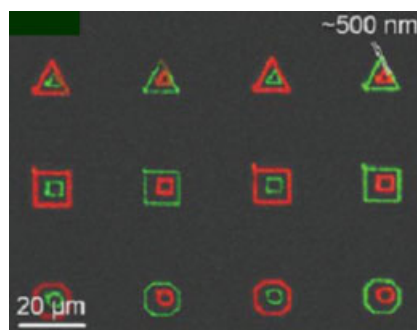


Fig 3. Fluorescence microscope image of DPN of two different proteins (red and green) patterned using the multilayer pattern creation approach. Reproduced with permission from Wiley Interscience Small, Sekula *et al.*

humidity of the patterning environment (Nafday *et al.* 2006). Further, the work of Sekula *et al.* (2008) has also demonstrated multiple lipid patterning as shown in Figure 3, where two different proteins (red and green) were written with DPN on the subcellular scale.

Patterning regions of different inks on top of each other with no off-centering is indeed a difficult task, partly due to the generic scanner positioning imprecision and partly due to the irregular spreading of the one ink when it comes in contact with the ink that is already patterned. In order to isolate the latter effect, we show precise positioning of ODT region inside a MHA diamond pattern rather than patterning on another ink.

Experimental Methodology

Preparing MHA-Inked AFM Tips for DPN

MHA (90% pure, ACS grade) was purchased from Fisher Scientific (Waltham, MA). A 2 mM

MHA solution was prepared in ethanol and cantilevers were manually dipped in the solution for about 10 s followed by another dipping in pure ethanol for about 5 s. This was repeated three times to ensure a uniform MHA coating. The cantilever was then allowed to dry under ambient conditions after which they were ready for DPN.

Preparing ODT-Inked AFM Tips for DPN

ODT (99% pure) was purchased from Fisher Scientific. ODT was deposited onto an “A”-type tip. The tips were attached to the back-side of metal tin cap using double-side sticky tape and common Post-it notes (3M Inc., St. Paul, MN). The powdered ODT (~50 mg) was then carefully sprinkled over the tips using weighing paper, taking care not to come in contact (wear gloves) with the ODT powder. The metal tin was then kept in an oven and heated to 70°C for 2 h. After 2 h, the oven was allowed to cool overnight. A second cycle of heating at 70°C for 2 h was then performed. These cantilevers were then ODT inked and ready for DPN.

Preparing Gold Substrates for DPN

Silicon substrates were freshly cleaned with pure ethanol followed by deionized water. A 10 nm thick adhesion layer of titanium followed by a 25 nm thick layer of gold were then evaporated on these clean substrates followed by a 1 h cooling step under vacuum. After removal, these substrates provided an ideal gold surface for DPN.

Results and Discussion

LLA Procedure in InkCAD

In order to write two different inks in two separate layers, NanoInk has a LLA routine in InkCAD. In this routine, two layers can be aligned with respect to each other with nanoscale precision enabling different inks (one or more in each layer) to be written in close proximity (or on top of each other). This dual-layer, dual-ink DPN procedure can be extended to writing multiple layers (more than two) with multiple inks. The LLA technique can be leveraged by either using multiple cantilevers (each cantilever has a different ink) on the same array or by using two different single cantilevers sequentially (write with one ink in one layer first and then write with the other ink in the second layer). In this work, we demonstrate dual-ink DPN (ODT in one layer and MHA in the second) where the first layer was

patterned with ODT and MHA was patterned in the second layer. This ink-on-ink lithography approach performed in a single automated pass has significant advantages when nanoscale precision and bottom-up architecture building are desired.

Before making any patterns, the ink diffusion rate from the inked tip has to be calibrated for good pattern size control. The process of calibrating the inked tip writing should ideally be carried out before any pattern creation in InkCAD and pattern lithography, as calibrating the ink diffusion will help to specify the tip speeds (tip dwell times) in the actual pattern. A calibration as shown in Figure 4A is created with known tip dwell times (dots) and tip speeds (lines), and the sizes of actual pattern written with the ink (Fig. 4B) is then measured. This pattern size vs. tip speed (dwell time) calibration is then stored and this information is then transferred to the pattern while actual lithography.

The multi-layer pattern is designed in InkCAD using the InkCAD structure design window as shown in Figure 5. The basis of the entire routine is to create one pattern at a location with one type of ink and then image that pattern with a tip that will

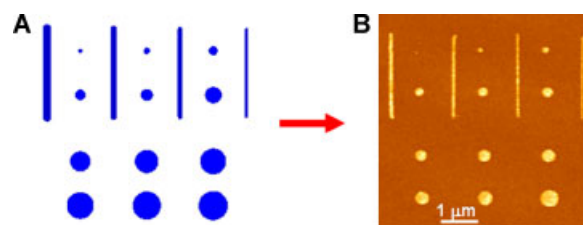


Fig 4. (A) An actual calibration pattern with dot and line features designed before actual pattern creation. The dot patterns are created with tip dwell times specified from 1 to 50 s while the lines have specified tip speeds ranging from 0.05 to 0.15 $\mu\text{m/s}$. (B) LFM image of the same calibration pattern created with MHA ink.

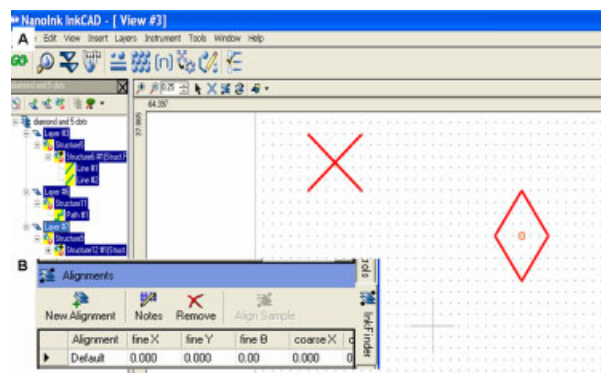


Fig 5. (A) InkCAD structure design window showing a dot and a diamond pattern created in two different layers. The X pattern is the alignment marker used to align the dot to the diamond. (B) The left inset at the bottom shows the start of the LLA routine in InkCAD.

write the second pattern (this tip will be coated with a different ink). In order to avoid “smudging” the first pattern was written with ODT, with the MHA-inked tip we introduced an alignment *X* pattern. Figure 5A shows the pattern designed in three separate layers—the first layer is the dot pattern, the second layer is the *X* alignment pattern, and the third layer is the diamond pattern around the dot. The tip dwell time of the dot is 150 s while the tip speed for drawing the diamond is 0.05 $\mu\text{m/s}$. The tip speed for the alignment *X* pattern is 0.1 $\mu\text{m/s}$.

Figure 5B shows the “InkCAD window at” start of the LLA routine, which is performed after making sure the inked tips are actually writing with MHA and ODT. The dot pattern in the first layer and the *X* marker is written simultaneously with the desired ink (ODT in this case) and instead of imaging the ODT patterns, the LLA routine is invoked as shown in Figure 5B. In this routine, the original positions of the ODT patterns (the dot and the alignment *X*) are stored in the first part of the LLA routine. Then the ODT tip is withdrawn from the gold substrate and the tip inked with the other ink (MHA in this case) is mounted. Since the original ODT pattern location is stored, the second part of the LLA routine is invoked, which is imaging the ODT *X* pattern with the MHA mounted tip. Imaging and finding the pattern with a differently inked tip enable writing a pattern with the new ink at the previous location on the substrate. This alignment is performed by matching the feature on the substrate (as seen in the video monitor) saved in the first step to the same feature that is now located by pointing at the same feature on the video screen. This constitutes a microscale alignment as there can be nanoscale differences in the *X*, *Y* co-ordinates even though the pointer is clicked on the same feature on the substrate. In order to perform a nanoscale alignment the *X* feature made with ODT is now imaged with the MHA-inked tip (Fig. 6) and its center is aligned exactly with respect to the original *X*, *Y* coordinates saved in the first part of the alignment. This imaging of the ODT *X* marker with the MHA-inked tip also ensures that the final ODT dot pattern remains clean and free of MHA overwriting/smudges. After the nanoscale alignment is performed with the center of the *X* mark, the second part of the LLA is complete. The final MHA pattern in the third layer can now be drawn at the exact location around the ODT dot drawn in the first layer. The entire procedure is software automated through the InkFinder tab in InkCAD with some manual clicking input required at certain stages of the alignment.

Figure 7 shows the final dual-ink multi layer pattern created with MHA and ODT showing precise alignment with the center of the dot. This is

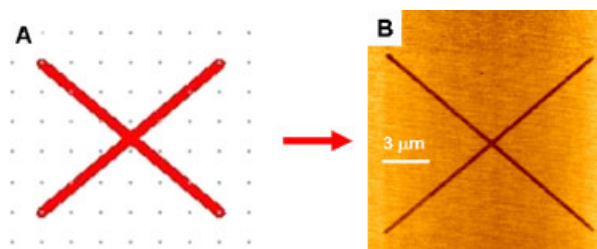


Fig 6. (A) An alignment *X* pattern designed in InkCAD. (B) LFM image of the actual *X* pattern made with ODT (dark contrast) and imaged with the MHA tip, which will write the second layer (the diamond). This is the second part of the LLA process wherein instead of imaging (smudging) the pattern made in the first layer (the ODT dot), the MHA-inked tip is made to image the layer alignment *X* marker.

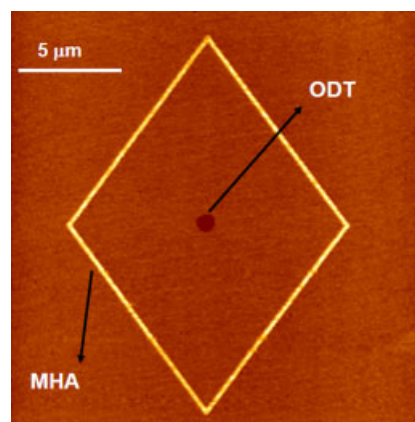


Fig 7. Final dual-ink multilayer diamond-dot pattern drawn with MHA (diamond) and ODT (central dot). The pattern shows the expected bright and dark LFM contrast of MHA and ODT inks, respectively.

the direct result of the nanoscale alignment performed to the center of the alignment *X* when it was imaged with the MHA-inked tip. The advantage of creating the pattern in the multiple layers is that each pattern (in each layer) now has independent pattern creation properties such as specification of ink diffusion rates, tip speed (tip dwell time), setpoint, tip lift after lithography (to avoid overwriting), specific pattern positioning and easy maneuverability within the overall design created. One can also specify the pattern to be drawn with a specific ink. Complicated patterns can then be precisely drawn with different inks with nanoscale alignment with respect to each other following the multi-layer pattern design approach outlined here.

Conclusions

In this work, we have demonstrated site-specific concentric patterns with two chemically diverse inks

on gold using our DPN platform. This multi-ink, multilayer patterning is very difficult to achieve on any other lithography platform besides the DPN 5000 system. To our knowledge, this is the first demonstration of precise multi-pattern alignment shown in DPN literature, which not only leverages advanced scanner positioning capabilities but also provides a way to perform multilayer lithography in nanoscale registry.

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