

Temperature controlled dip-pen nanolithography

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2010 Nanotechnology 21 115302

(<http://iopscience.iop.org/0957-4484/21/11/115302>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 160.80.2.8

The article was downloaded on 08/02/2012 at 17:23

Please note that [terms and conditions apply](#).

Temperature controlled dip-pen nanolithography

R G Sanedrin, N A Amro, J Rendlen and M Nelson

NanoInk Incorporation, 8025 Lamon Avenue, Skokie, IL 60077, USA

E-mail: namro@nanoink.net

Received 17 November 2009, in final form 2 February 2010

Published 22 February 2010

Online at stacks.iop.org/Nano/21/115302

Abstract

Dip-pen nanolithography (DPN) has emerged as a powerful tool for creating sophisticated micron- and nanoscale features of various molecules, such as small organic molecules, on a variety of substrates. Despite significant advances in recent years, the influence of temperature on molecular transport for nanostructure fabrication has not been fully explored. Herein, it is shown how the dimensions of patterned organic nanostructures can be controlled by using a cooling/heating module. This method allows nanometer-sized feature fabrication of a variety of small organic molecules, including ‘inks’ that have been deemed very difficult to write under ambient conditions. Features with dimensions as small as 30 nm have been successfully reproduced using the newly developed temperature control device in conjunction with DPN.

 Online supplementary data available from stacks.iop.org/Nano/21/115302/mmedia

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Many printing methods have been developed over the years, and have become essential tools in the field of nanoscience and nanotechnology. Lithographic tools that are able to create sub-100 nm to many micron-sized features over large areas are of great interest for various applications including electronics [1–3], biosensing [4, 5], and optics [6–8]. Examples of these methods that are frequently used and have significant impact in the academic, semiconductor, biological, and biomedical fields are photolithography [9, 10], electron (e)-beam lithography [11, 12], nanoimprint lithography [13–16], microcontact printing (μ -CP) [17, 18], and scanning probe microscopy (SPM) based lithographies [19–21]. Among the SPM based techniques, dip-pen nanolithography (DPN) [22] has emerged as a powerful tool for creating sophisticated micron- and nanoscale features with various molecules on a variety of substrates. Inks such as small organic molecules [23–27], polymers [28–33], polysaccharides [34], phospholipids [35], biomaterials [36–42], nanoparticles [23, 43–45], and metal ions [46] are just a few that have been successfully written or patterned onto a variety of surfaces ranging from metals to insulators. This versatile nanoscale writing methodology, which was initially a serial writing process, has been developed into a parallel lithographic tool that can generate nanometer-sized features over cm^2 areas [47]. Despite the significant

advances of DPN in recent years, however, important factors that influence nanoscale lithographic writing have not been fully explored. In particular, temperature effects on the use of low and high melting point alkanethiol molecules as inks for DPN writing are not well established, contrary to the well studied thiolated molecules such as 16-mercaptohexadecanoic acid (MHA) and 1-octadecanethiol (ODT). To date, these materials have been used as passivation molecules and not as direct-write DPN inks owing to the writing difficulties and uncontrollable patterning encountered when using such molecules [23]. One way to overcome the patterning difficulties associated with these molecules is to control the temperature of the tip–substrate system, since temperature can significantly influence the molecular transport of the ink material from a coated atomic force microscope (AFM) tip to a substrate surface [48, 49]. It was shown by Rozhok *et al* that while the diffusion of MHA from AFM tips to Au substrate surfaces was affected by temperatures above 30 °C, similar size features were generated at temperatures below 30 °C [49]. Their study was limited to the 23–33 °C temperature range. On the other hand, local temperature control was reported by Sheehan *et al* wherein octadecylphosphonic acid (OPA) molecules were deposited onto a substrate surface by heating an OPA coated AFM cantilever [50]. They reported that the widths of the line nanostructures that they generated using the

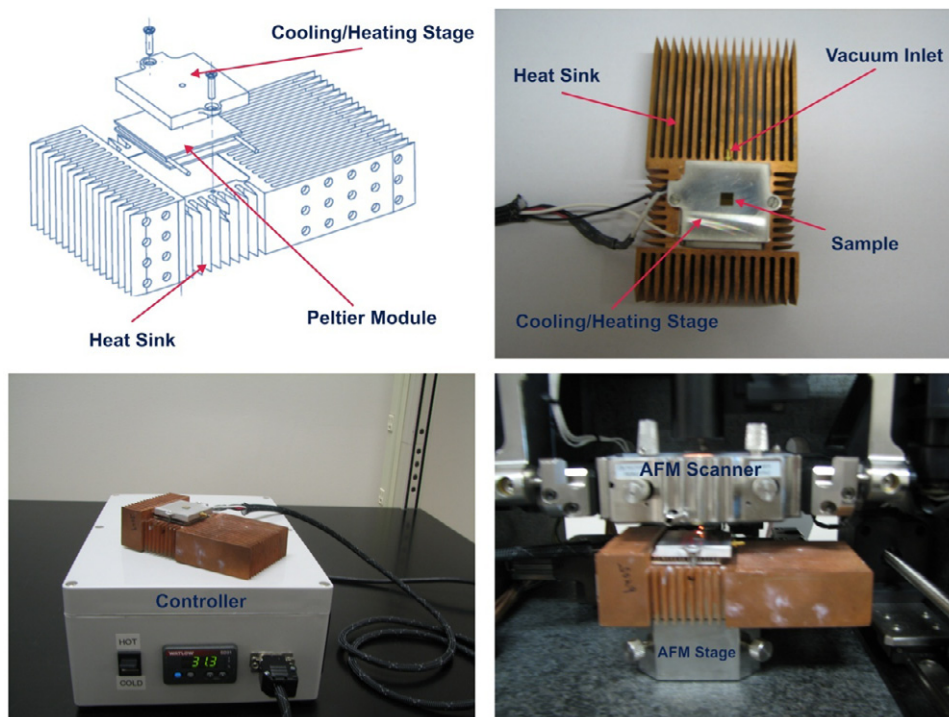


Figure 1. Cooling/heating device.

heated tips were independent of temperature and were mainly determined by the sharpness of the coated AFM tip. Herein, we report how temperature can be utilized in conjunction with DPN to control the diffusion of various molecules on a substrate surface for tailoring features from micron- to nanometer scale dimensions. Unlike previous work, wherein the temperature of the chamber housing a DPN system was controlled using heating fans to reach a maximum temperature of 33 °C [49], a cooling and heating apparatus (figure 1) derived from a Peltier module was developed to specifically control only the temperature of the substrate surface with increments of 1 °C in the temperature range from 4 to 80 °C. The temperature of the cooling/heating stage compared to that of the surface of a substrate situated on top of the stage has a variance of ± 0.5 °C. This approach, which is called temperature controlled DPN (TC-DPN), enables the deposition of a variety of molecules onto substrates that are deemed challenging to write under ambient conditions. Moreover, feature sizes of the generated nanostructures can be tailored by controlling the temperature of the substrate surface from as low as 4 °C to as high as 80 °C. Herein, we show that the newly developed apparatus in conjunction with DPN can efficiently and reproducibly generate structures of small organic molecules in the size range from many microns to sub-50 nm.

2. Experimental section

2.1. Materials

MHA, ODT, 11-mercapto-1-undecanoic acid (MUA), and Au nanoparticles were purchased from Sigma Aldrich

(Milwaukee, WI). 11-aminoundecane thiol (AUT) was purchased from ProChimia Co. (Gdansk, Poland). All chemicals were used as-received.

2.2. Preparation of substrates

Si(100) wafers (diameter 4 in) were cut into 5 mm $\times$ 5 mm squares. The cut substrates were then sonicated in ethanol for 1 h. They were then immersed in a solution of RCA2 containing ammonium hydroxide (NH₄OH), hydrogen peroxide (H₂O₂) and H₂O with a v:v:v ratio of 1:1:5, respectively, at 80 °C for 20 min, subsequently rinsed with copious amounts of Milli-Q deionized water, and dried with N₂ gas. The cleaned substrates were then placed in a thermal evaporator chamber (BOC Edwards, Canada). Substrates were coated with 5 nm titanium as an adhesion layer followed by 40 nm gold (Au). Au substrates were then immediately used for DPN experiments.

2.3. DPN procedure

AFM cantilever probes (NanoInk, Inc., Skokie IL) containing single or 52 tips, with a spring constant of 0.04 or 0.05 N m⁻¹, were either dipped or vapor coated into a MHA solution or with ODT, MUA, or AUT, respectively. The coated tips were then loaded into a NSCRIPTOR™ (NanoInk, Inc., Skokie, IL), and were used as pens to deliver molecular inks onto Au substrates. The stage was either cooled or heated by applying a continuously variable current to a Peltier module from a power amplifier. Changes in temperature were monitored using a resistor temperature device (RTD) coupled with a Watlo proportional integral differential (PID) controller. Before any

DPN experiment the substrate temperature was left for 15 min to equilibrate with the temperature of the cooling/heating stage. Written alkanethiol features were then either etched following published chemical etching procedures [28] or were imaged immediately after lithography using contact mode AFM.

2.4. Au nanoparticle assembly

DPN-generated AUT dots were initially passivated with MHA for 10 min. The substrates were then washed with ethanol and dried with N₂. The substrates were subsequently incubated in a 20 nm Au nanoparticle solution for 3 h, gently washed with DI water, and dried with N₂ gas.

3. Results and discussion

One of the major problems in DPN, especially for fast diffusing molecules, is non-specific deposition. Volatile molecules, for instance, can be easily transported from the non-tip portion of the cantilever to a substrate surface during a DPN experiment. In addition, writing extremely small features (less than 50 nm) is often challenging with these molecules owing to their fast diffusion rate, which often leads to the fabrication of large features. Although writing for a long period of time (>5 h) would substantially decrease the amount of ink on the tip and would eventually produce features with sub-100 nm dimensions, this process is time consuming. In such cases, lowering the environmental temperature of a DPN system would most certainly circumvent these problems because it can drastically slow down the diffusion rate of the ink molecule from the tip to the substrate surface as well as decrease the non-specific deposition of molecules. On the other hand, direct-write DPN of high melting alkanethiol molecules, such as AUT, has not been performed owing to the writing difficulties associated with these materials. Increasing the temperature of a DPN system would most certainly eliminate this problem because it can speed up the transport of molecules from the cantilever tip to the surface. The cooling/heating device (figure 1) was designed to increase or decrease the temperature of a substrate surface and maintain the desired temperature during array fabrication using DPN. For experiments requiring cold or high temperatures, a well designed cold/heat sink is needed to maintain the desired substrate surface temperature. The custom designed thermal sink has a surface area that promotes natural convection. Substrates mounted onto the newly designed cooling/heating device can sustain the desired temperature for at least 3 h.

In order to study the dependence of ink transport and nanostructure growth rate on temperature, MHA (melting point 65–69 °C) inks were deposited onto gold substrates at various substrate surface temperatures ranging from 28 to 10 °C. Alkanethiol dot features were written with tip–surface contact times of 4 and 0.4 s. Figure 2 shows lateral force microscopy (LFM) images of the fabricated MHA dot arrays. With the higher dwell time (4 s), average dot diameter sizes of 376 ± 22 , 284 ± 23 , 157 ± 16 , and 85 ± 11 nm were generated with substrate surface temperatures of 25, 20, 15, and 10 °C, respectively (figures 2(A)–(D)). A plot of dot diameter versus temperature shows that

with decreasing surface temperature the dimensions of the generated dots can be tailored down to the sub-100 nm size range (figure 2(I)). Furthermore, results suggest that with decreasing surface temperatures, the diffusion rate of the MHA molecules from the cantilever tip to the substrate also decreases. Using the area of the generated MHA dots, the diffusion coefficients at 25, 20, 15, and 10 °C are 0.0254, 0.017, 0.0076, and $0.0013 \mu\text{m}^2 \text{s}^{-1}$ (supplementary figure 1 available at stacks.iop.org/Nano/21/115302/mmedia). One of the key attributes of DPN is the ability to control and tailor feature size through variation of the tip–surface contact time. In order to investigate if the feature sizes of the generated dots can be further reduced, arrays of dots were generated with a surface contact time of 0.4 s at various surface temperatures (figures 2(E)–(H)). Similar to what was observed with higher dwell times, LFM images show that the generated dot diameter decreases with decreasing surface temperature. Temperatures of 27, 20, 15, and 13 °C gave average dot diameter size features of 193 ± 10 , 100 ± 7 , 71 ± 8 , and 42 ± 5 nm, respectively (figures 2(E)–(H)). Moreover, a plot of dot diameter versus temperature for a dwell time of 0.4 s shows that with the newly developed cooling/heating apparatus in conjunction with the DPN process, MHA dot feature sizes can be routinely tailored down to the sub-50 nm range by tuning the temperature of the substrate surface (figure 2(J)).

Other than dots, MHA lines were generated at various scan rates with surface temperatures of 25, 20, and 15 °C (figure 3). AFM images show that with the same scan rate, decreasing the temperature of the substrate surface decreases the widths of the written MHA lines. Similar to what has been observed with the MHA dot features, as the coated tip rasters through the surface, MHA molecules diffuse more slowly from the cantilever tip to the substrate surface generating lines with smaller feature dimensions. Line widths as small as 30 nm can be generated using TC-DPN.

In order to test the versatility of TC-DPN, other alkanethiols with low melting points were used as inks. ODT (melting point 30–33 °C) or MUA (melting point 46–50 °C) were vapor coated onto AFM tips and were used as pens for fabricating alkanethiol dots on gold substrates. ODT dots with average feature sizes of 164 ± 12 , 65 ± 7 , and 40 ± 5 nm were generated with a dwell time of 4 s and substrate surface temperatures of 20, 16, and 15 °C, respectively (figures 4(A)–(C)). Lowering the substrate surface temperature enabled the fabrication of dot features as small as 35 nm. On the other hand, with a dwell time of 10 s, 180–80 nm dot features of MUA were generated with surface temperatures of 30 and 20 °C, respectively (figure not shown).

High melting point alkanethiols diffuse to the surface less easily than the low melting point thiolated molecules. Writing these molecules at ambient conditions is often problematic and inconsistent. In fact, to the best of our knowledge, no direct-write DPN exists in the literature thus far that shows a successful and controllable fabrication of features using these molecules on Au substrates. While increasing tip–surface contact time would certainly produce features, fabricating nanostructures using these molecules over large areas would require extremely long writing times. In addition

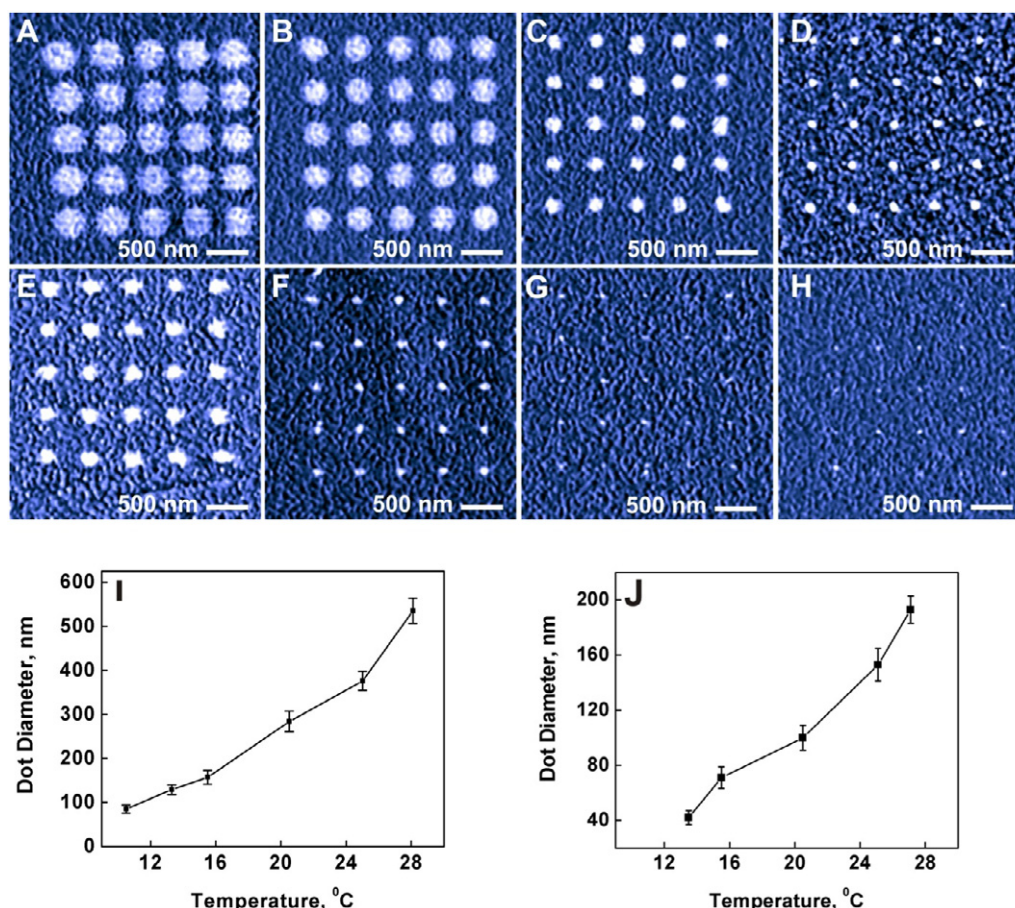


Figure 2. LFM images of MHA dots generated using a tip–surface contact time of 4 s ((A)–(D)) and 0.4 s ((E)–(H)) with surface temperatures of (A) 25, (B) 20, (C) 15, (D) 10, (E) 27, (F) 20, (G) 15, and (H) 13 °C. (I), (J) Plots of dot diameter sizes as a function of temperature for dwell times of 4 and 0.4 s, respectively.

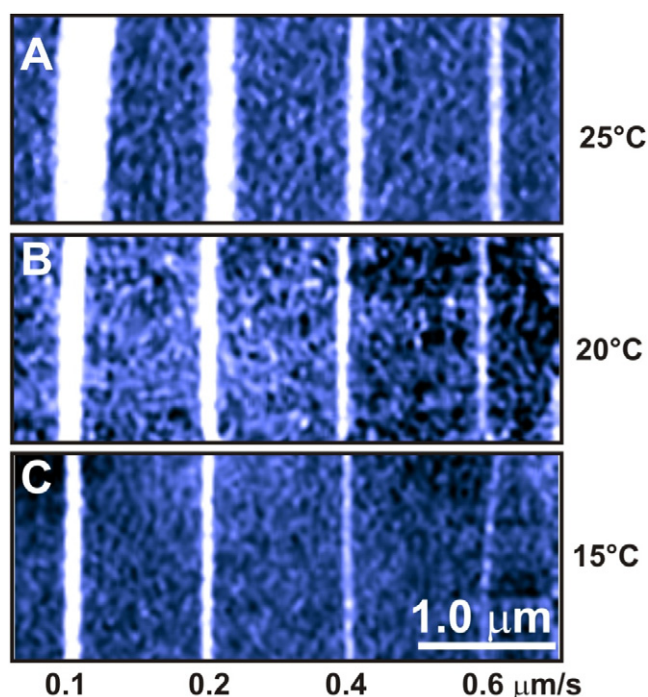


Figure 3. LFM images of MHA lines generated using scan rates of 0.1–0.6 μm s^{−1} at temperatures of (A) 25 °C, (B) 20 °C, and (C) 15 °C.

to using the newly designed thermal apparatus for cooling the substrate, it was reconfigured to operate as a heating element to increase the temperature of the substrate surface. Similar to the alkanethiol inks that have been used thus far, the diffusion rate of AUT (melting point 120–170 °C) also exhibits temperature dependence. Figure 5 shows that while dwell times of 5, 10, 30, and 60 s with a surface temperature of 23 °C produced dot features with average dot diameter sizes of 130, 190, 247, and 349 nm (figure 5(A)), the same tip–surface contact times at 80 °C gave 535, 821, 1302, and 1550 nm, respectively (figure 5(D)). Results showed that increasing the temperature of the substrate surface exhibited significant effects on the diffusion rate of AUT molecule from the AFM tip to the substrate surface and on the sizes of the generated structures. This is important when covering large areas with nanostructures because it can drastically decrease the total writing time. For instance, 190 nm dot features can be generated with surface–tip contact times of 10 s (figure 5(A)) and 1 s (figure 5(F)) for surface temperatures of 23 and 60 °C, respectively. Using the same DPN conditions (dwell times and temperatures), it will take 22.4 and 2.24 h to generate an array consisting of 8064 dots (190 nm dot diameter size, center-to-center dot distance of 500 nm, total writing area of 20 × 90 μm²) at 23 and 60 °C, respectively.

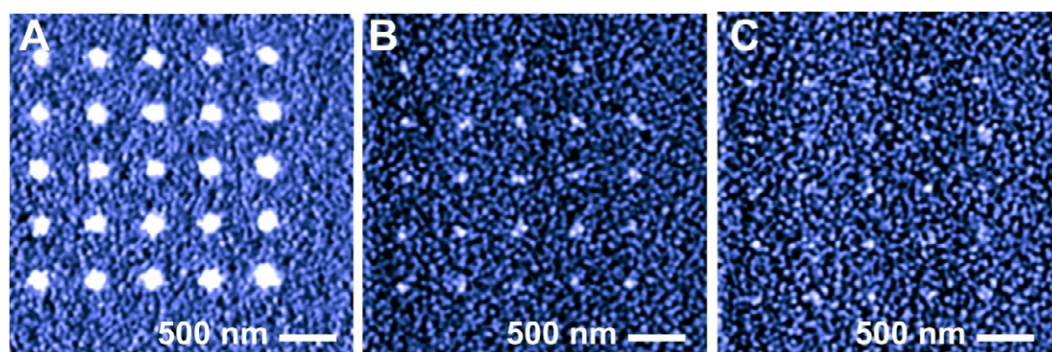


Figure 4. LFM images of ODT dots generated using a tip–surface contact time of 4 s and surface temperatures of (A) 20, (B) 16, and (C) 15 °C.

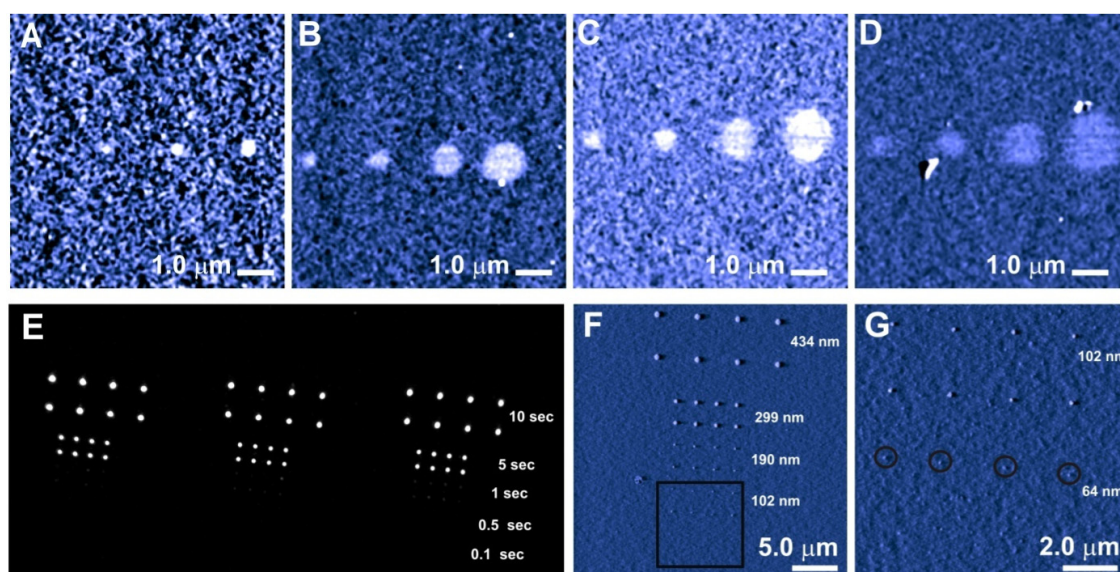


Figure 5. (A)–(D) LFM images of AUT dots generated using a tip–surface contact time of 5, 10, 30, and 60 s (left to right dot) with surface temperatures of (A) 23, (B) 60, (C) 70, and (D) 80 °C. (E) Dark field optical and ((F), (G)) AFM images of generated Au dots using AUT as the resist. Figures (E)–(G) are generated using 1D pen array tips consisting of 26 pens and (G) is a magnified image of inset in (F).

We have shown that the growth or reduction rates of DPN-generated patterns are directly affected by temperature. These are most likely due in part to the increase or decrease of the solubility of the alkylthiol molecules in the water meniscus as the substrate temperature was varied. In addition, the size and shape of the water meniscus formed between the cantilever tip and the substrate surface, which can change as a function of temperature and other DPN conditions (such as humidity [51]), can have important effects because it can significantly affect the feature size and shape of the generated nanostructures.

High-throughput feature fabrication using DPN can be easily accomplished with the use of parallel tips. In fact, recent works have shown that using these types of pens can cover mm² areas in short periods of time [47]. To assess the performance of TC-DPN using multiple tip arrays, a high melting point alkanethiol, AUT, was vapor coated onto 52 pen arrays at 90 °C (under a vacuum) for 2 h. The cantilever tips were left inside the vacuum chamber to slowly cool down overnight. The coated tips were then used as pens for writing AUT onto Au substrates with a surface temperature of 60 °C.

These substrates were then etched using previously reported protocols [28]. Figures 5(E)–(G) show Au dot nanostructures generated using a 52 pen array in conjunction with TC-DPN. AUT dots with diameter size features of 434 ± 9 , 299 ± 13 , 190 ± 6 , 102 ± 8 , and 64 ± 12 nm were generated with dwell times of 10, 5, 1, 0.5, and 0.1 s, respectively. LFM and dark field optical images show homogeneous dot diameter sizes within an array and between arrays using the same dwell time, respectively.

Direct writing of AUT molecules onto Au surfaces opens up many possible applications varying from biomolecule immobilization to particle assembly, using covalent or electrostatic immobilization onto nanometer-sized features. Various materials have been immobilized using electrostatic interactions and have been explored using various charged molecules [23, 30, 52]. While these molecules are used to prevent materials with similar charge from sticking to a surface, they have also been used to attract and adsorb oppositely charged molecules. To show the usefulness of the DPN-generated AUT dots as linker molecules, patterned and

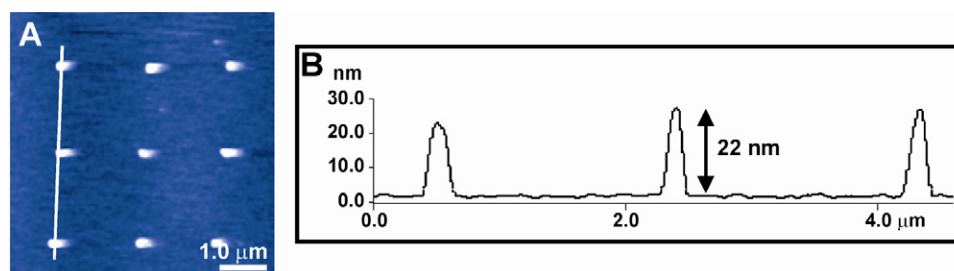


Figure 6. (A) AFM image and (B) height profile of Au nanoparticles attached to DPN-generated AUT dot features.

passivated substrates with 150 nm sized AUT dots and MHA, respectively, were incubated into a solution of citrate stabilized Au nanoparticles with diameter sizes of 20 nm. The negatively charged Au nanoparticles were electrostatically adsorbed onto the AUT dot patterns, while the MHA SAMs prevented them from sticking onto the surrounding areas (figure 6(A)). A contour plot (figure 6(B)), shows that the heights of the dot patterns were 22 nm, which corresponds to the diameter of the adsorbed Au nanoparticles.

4. Conclusion

Various alkanethiol inks were written onto gold substrates, and their feature sizes were controlled from the micron to sub-50 nm range using DPN in conjunction with the newly developed cooling/heating system. Substrates were cooled or heated using a Peltier module which can decrease or increase the temperature from 4 to 80 °C by increments of 1 °C. Using various temperatures in conjunction with DPN writing, dot diameter sizes as small as 80, 52, 37, and 35 nm were fabricated with MUA, AUT, MHA, and ODT inks, respectively. The DPN-generated organic molecules can be used to adsorb other materials, such as Au nanoparticles. Moreover, through the use of multi-pen cantilever AFM tips, structures with similar feature sizes that span macroscopic distances were generated routinely. It is conceivable that by combining TC-DPN with AFM pen arrays as large as 55 000, the newly developed methodology can be used to fabricate nanometer-sized features over large areas for possible applications in electronic devices and integrated optics.

References

- [1] Park S J, Taton T A and Mirkin C A 2002 Array-based electrical detection of DNA with nanoparticle probes *Science* **295** 1503–6
- [2] Kim E U, Baeg K J, Noh Y Y, Kim D Y, Lee T, Park I and Jung G Y 2009 Templated assembly of metal nanoparticles in nanoimprinted patterns for metal nanowire fabrication *Nanotechnology* **20** 355302
- [3] Niskala J R and You W 2009 Metal–molecule–metal junctions via PFPE assisted nanotransfer printing (nTP) onto self-assembled monolayers *J. Am. Chem. Soc.* **131** 13202–3
- [4] Bogunia-Kubik K and Sugisaka M 2002 From molecular biology to nanotechnology and nanomedicine *Biosystems* **65** 123–38
- [5] Park J U, Lee J H, Paik U, Lu Y and Rogers J A 2008 Nanoscale patterns of oligonucleotides formed by electrohydrodynamic jet printing with applications in biosensing and nanomaterials assembly *Nano Lett.* **8** 4210–6
- [6] Kawata S, Ono A and Verma P 2008 Subwavelength colour imaging with a metallic nanolens *Nat. Photon.* **2** 438–42
- [7] Xu Q B, Rioux R M, Dickey M D and Whitesides G M 2008 Nanoskiving: a new method to produce arrays of nanostructures *Acc. Chem. Res.* **41** 1566–77
- [8] Zheng Y B, Jensen L, Yan W, Walker T R, Juluri B K, Jensen L and Huang T J 2009 Chemically tuning the localized surface plasmon resonances of gold nanostructure arrays *J. Phys. Chem. C* **113** 7019–24
- [9] Odom T W, Love J C, Wolfe D B, Paul K E and Whitesides G M 2002 Improved pattern transfer in soft lithography using composite stamps *Langmuir* **18** 5314–20
- [10] Schanze K S, Bergstedt T S, Hauser B T and Cavaleiro C S P 2000 Photolithographically-patterned electroactive films and electrochemically modulated diffraction gratings *Langmuir* **16** 795–810
- [11] Kamp M, Emmerling M, Kuhn S and Forchel A 1999 Nanolithography using a 100 kV electron beam lithography system with a Schottky emitter *J. Vac. Sci. Technol. B* **17** 86–9
- [12] Wallraff G M and Hinsberg W D 1999 Lithographic imaging techniques for the formation of nanoscopic features *Chem. Rev.* **99** 1801–21
- [13] Guo L J 2007 Nanoimprint lithography: methods and material requirements *Adv. Mater.* **19** 495–513
- [14] Martini I, Dechow J, Kamp M, Forchel A and Koeth J 2002 GaAs field effect transistors fabricated by imprint lithography *Microelectron. Eng.* **60** 451–5
- [15] Martini I, Eisert D, Kamp M, Worschech L, Forchel A and Koeth J 2000 Quantum point contacts fabricated by nanoimprint lithography *Appl. Phys. Lett.* **77** 2237–9
- [16] Seekamp J *et al* 2002 Nanoimprinted passive optical devices *Nanotechnology* **13** 581–6
- [17] Xia Y N and Whitesides G M 1998 Soft lithography *Angew. Chem. Int. Edn* **37** 551–75
- [18] Zhou F, Zheng Z J, Yu B, Liu W M and Huck W T S 2006 Multicomponent polymer brushes *J. Am. Chem. Soc.* **128** 16253–8
- [19] Amro N A, Xu S and Liu G Y 2000 Patterning surfaces using tip-directed displacement and self-assembly *Langmuir* **16** 3006–9
- [20] Liu G Y and Amro N A 2002 Positioning protein molecules on surfaces: a nanoengineering approach to supramolecular chemistry *Proc. Natl Acad. Sci. USA* **99** 5165–70
- [21] Xu S and Liu G Y 1997 Nanometer-scale fabrication by simultaneous nanoshaving and molecular self-assembly *Langmuir* **13** 127–9
- [22] Piner R D, Zhu J, Xu F, Hong S H and Mirkin C A 1999 ‘Dip-pen’ nanolithography *Science* **283** 661–3
- [23] Li B, Lu G, Zhou X Z, Cao X H, Boey F and Zhang H 2009 Controlled assembly of gold nanoparticles and graphene oxide sheets on dip pen nanolithography-generated templates *Langmuir* **25** 10455–8

- [24] Giam L R, Wang Y H and Mirkin C A 2009 Nanoscale molecular transport: the case of dip-pen nanolithography *J. Phys. Chem. A* **113** 3779–82
- [25] Braunschweig A B, Senesi A J and Mirkin C A 2009 Redox-activating dip-pen nanolithography (RA-DPN) *J. Am. Chem. Soc.* **131** 922–3
- [26] Jang J W, Sanedrin R G, Maspoch D, Hwang S, Fujigaya T, Jeon Y M, Vega R A, Chen X D and Mirkin C A 2008 Electrically biased nanolithography with KOH-coated AFM tips *Nano Lett.* **8** 1451–5
- [27] Salaita K S, Lee S W, Ginger D S and Mirkin C A 2006 DPN-generated nanostructures as positive resists for preparing lithographic masters or hole arrays *Nano Lett.* **6** 2493–8
- [28] Sanedrin R G, Huang L, Jang J W, Kakkassery J and Mirkin C A 2008 Polyethylene glycol as a novel resist and sacrificial material for generating positive and negative nanostructures *Small* **4** 920–4
- [29] Huang L, Chang Y H, Kakkassery J J and Mirkin C A 2006 Dip-pen nanolithography of high-melting-temperature molecules *J. Phys. Chem. B* **110** 20756–8
- [30] Lee S W, Sanedrin R G, Oh B K and Mirkin C A 2005 Nanostructured polyelectrolyte multilayer organic thin films generated via parallel dip-pen nanolithography *Adv. Mater.* **17** 2749–53
- [31] Coffey D C and Ginger D S 2005 Patterning phase separation in polymer films with dip-pen nanolithography *J. Am. Chem. Soc.* **127** 4564–5
- [32] Nyamjav D and Ivanisevic A 2004 Properties of polyelectrolyte templates generated by dip-pen nanolithography and microcontact printing *Chem. Mater.* **16** 5216–9
- [33] Jang J W, Sanedrin R G, Senesi A J, Zheng Z J, Chen X D, Hwang S, Huang L and Mirkin C A 2009 Generation of metal photomasks by dip-pen nanolithography *Small* **5** 1850–3
- [34] Senesi A J, Rozkiewicz D I, Reinhoudt D N and Mirkin C A 2009 Agarose-assisted dip-pen nanolithography of oligonucleotides and proteins *ACS Nano* **3** 2394–402
- [35] Lenhert S, Sun P, Wang Y H, Fuchs H and Mirkin C A 2007 Massively parallel dip-pen nanolithography of heterogeneous supported phospholipid multilayer patterns *Small* **3** 71–5
- [36] Choi D S, Yun S H, An Y C, Lee M J, Kang D G, Chang S I, Kim H K, Kim K M and Lim J H 2007 Nanopatterning proteins with a stamp tip for dip-pen nanolithography *Biochip J.* **1** 200–3
- [37] Hsiao S C, Crow A K, Lam W A, Bertozzi C R, Fletcher D A and Francis M B 2008 DNA-coated AFM cantilevers for the investigation of cell adhesion and the patterning of live cells *Angew. Chem. Int. Edn* **47** 8473–7
- [38] Kim K H, Kim J D, Kim Y J, Kong S H, Jung S Y and Jung H 2008 Protein immobilization without purification via dip-pen nanolithography *Small* **4** 1089–94
- [39] Kim K H, Sanedrin R G, Ho A M, Lee S W, Moldovan N, Mirkin C A and Espinosa H D 2008 Direct delivery and submicrometer patterning of DNA by a nanofountain probe *Adv. Mater.* **20** 330–4
- [40] Lee S W, Oh B K, Sanedrin R G, Salaita K, Fujigaya T and Mirkin C A 2006 Biologically active protein nanoarrays generated using parallel dip-pen nanolithography *Adv. Mater.* **18** 1133–6
- [41] Vega R A, Maspoch D, Salaita K and Mirkin C A 2005 Nanoarrays of single virus particles *Angew. Chem. Int. Edn* **44** 6013–5
- [42] Vega R A, Shen C K F, Maspoch D, Robach J G, Lamb R A and Mirkin C A 2007 Monitoring single-cell infectivity from virus-particle nanoarrays fabricated by parallel dip-pen nanolithography *Small* **3** 1482–5
- [43] Wang W C M, Stoltzenberg R M, Liu S H and Bao Z N 2008 Direct patterning of gold nanoparticles using dip-pen nanolithography *ACS Nano* **2** 2135–42
- [44] Wang H T, Nafday O A, Haaheim J R, Tevaarwerk E, Amro N A, Sanedrin R G, Chang C Y, Ren F and Pearton S J 2008 Toward conductive traces: dip pen nanolithography (R) of silver nanoparticle-based inks *Appl. Phys. Lett.* **93** 143105
- [45] Chu H B, Ding L, Wang J Y, Li X M, You L P and Li Y 2008 *In situ* epitaxial growth of triangular CdS nanoplates on mica by dip-pen nanolithography *J. Phys. Chem. C* **112** 18938–42
- [46] Maynor B W, Li Y and Liu J 2001 Au ‘ink’ for AFM ‘dip-pen’ nanolithography *Langmuir* **17** 2575–8
- [47] Salaita K, Wang Y, Fragala J, Vega R A, Liu C and Mirkin C A 2006 Massively parallel dip-pen nanolithography with 55,000-pen two-dimensional arrays *Angew. Chem. Int. Edn* **45** 7220–3
- [48] Ivanisevic A and Mirkin C A 2001 ‘Dip-pen’ nanolithography on semiconductor surfaces *J. Am. Chem. Soc.* **123** 7887–9
- [49] Rozhok S, Piner R and Mirkin C A 2003 Dip-pen nanolithography: what controls ink transport *J. Phys. Chem. B* **107** 751–7
- [50] Sheehan P E, Whitman L J, King W P and Nelson B A 2004 Nanoscale deposition of solid inks via thermal dip pen nanolithography *Appl. Phys. Lett.* **85** 1589–91
- [51] Weeks B L, Noy A, Miller A E and De Yoreo J J 2002 Effect of dissolution kinetics on feature size in dip-pen nanolithography *Phys. Rev. Lett.* **88** 255505
- [52] Lee K-B, Park S-J, Mirkin C A, Smith J C and Mrksich M 2002 Protein nanoarrays generated by dip-pen nanolithography *Science* **295** 1702–5