NANO-PATTERNING OF 16-MHA OVER PALLADIUM SUBSTRATE USING DIP-PEN NANO-LITHOGRAPHY (DPN)*

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Abstract: *In this paper, the nanowriting process over palladium substrate with 16-MHA ink has been established using Dip-Pen Nanolithography. For nanowriting, the substrate was fabricated with very low rms roughness (~0.64nm) using e-beam deposition technique. After ink calibration, the lines and dots were fabricated with 5mM ink of 16-MHA. The width/diameter estimation of patterns was done in NanoRule image analysis software. The effect of humidity along with varying speed/dwell time is also demonstrated and results are explained in detail. The measured minimum line width ~269nm and dot diameter ~602 nm was successfully achieved. These SAM patterns could be very useful for positioning of carbon nanotubes (CNTs). The low contact resistance of Pd with CNTs would also be an additional advantage.*

Keywords: *Dip-Pen Nanolithography (DPN), Self-Assembled Monolayer (SAM), 16-MHA, Nano-Patterning, Nano-Writing.*

1. INTRODUCTION

Self-Assembled Monolayer (SAM) is an organized structure of amiphilic molecules, which can be patterned either by micro-contact printing [1], e-beam lithography or ion beam lithography [2] but none of them is as perfect as Dip Pen Nano-lithography (DPN) [3-6] because it allows direct patterning of SAM on compatible substrate with resolution in tens of nanometers [7]. DPN is a direct writing technique, in which ink molecules are transferred over desired substrate as shown in Fig. 1.

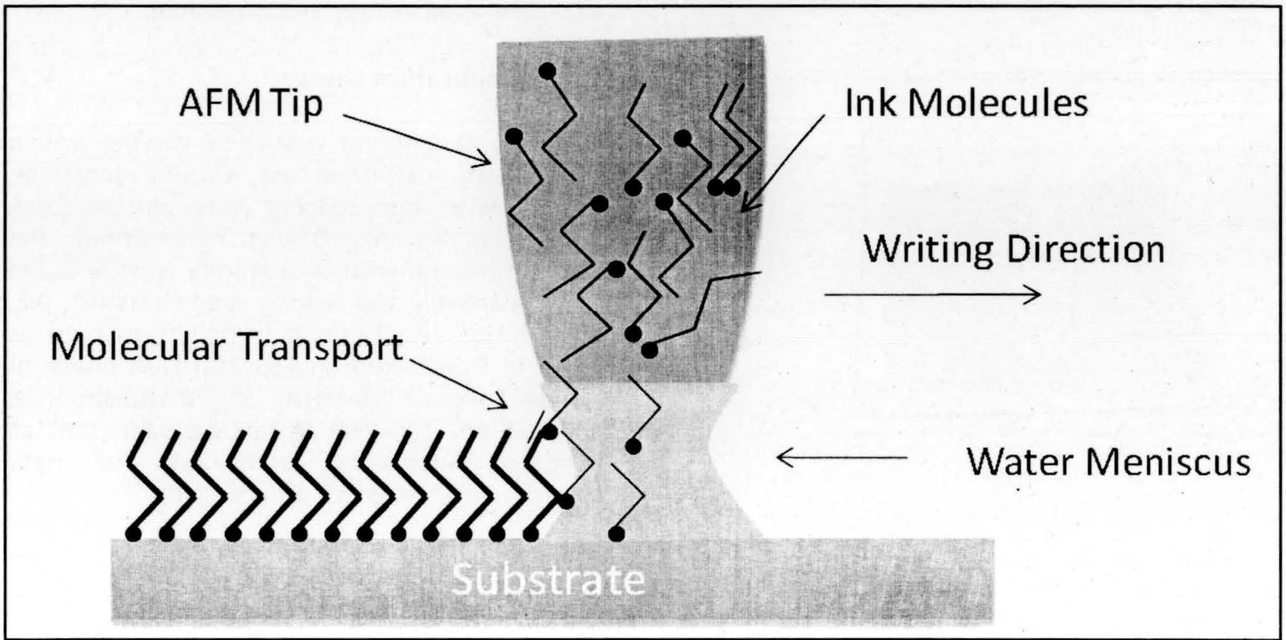


Fig 1. Schematic Diagram of Dip Pen Nano-Lithography (DPN) Concept

In this paper, nano-patterns of self-assembled monolayer of 16-Mercaptohexadecnoic acid (16-MHA) ink were written on fabricated palladium substrate [8]. The effect of humidity, writing speed and dwell time on written nano-patterns was studied in detail. The minimum line width of 269 nm and dot diameter of 602 nm was achieved.

2. EXPERIMENTAL DETAILS

Chemicals: All the chemicals including 16-MHA (Purity: 90%) and 1- Octanol (Purity: 99%), purchased from Sigma Aldrich were used as received. Palladium (Alfa Aesar, purity 99.95% was used for substrate fabrication for DPN. For all aqueous experiments, DI water (~18MΩ cm) was used.

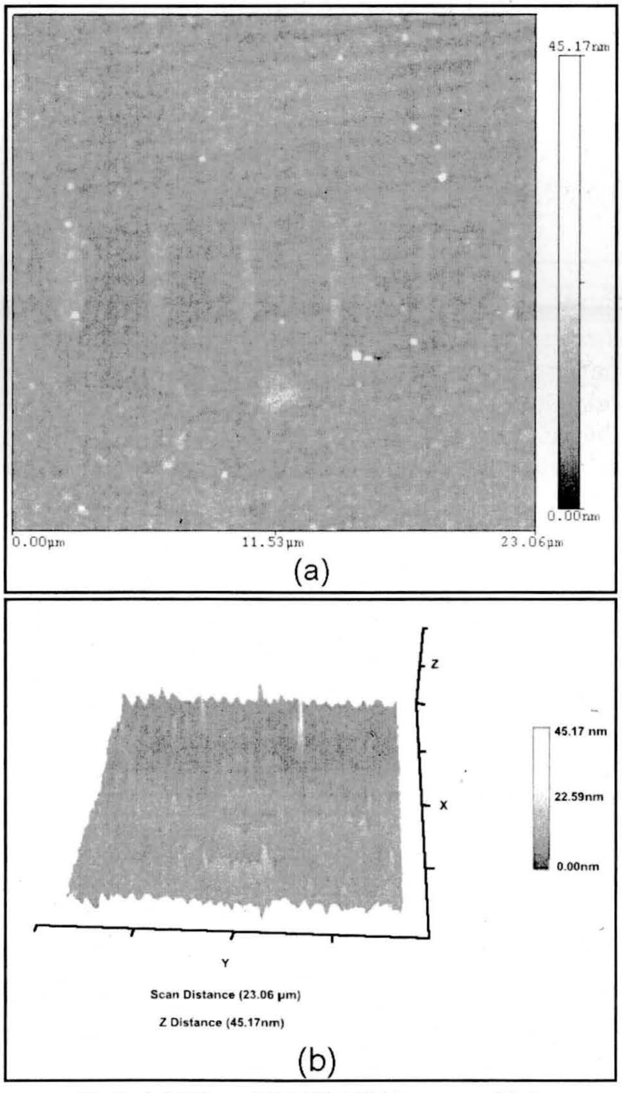


Fig 2. (a) 2D and (b) 3D LFM Images of ink Calibration Lines with Writing Speed from 0.1 µm/s -1.6 µm/s at RH 45% and Temperature 26°C

Substrate Preparation: N-type <111> 2"silicon wafers of resistivity 20-25 Ω cm were thoroughly cleaned by piranha solution followed by diluted HF dipping. After cleaning, a layerof silicon dioxide (thickness ~ 270nm) was thermally grown. The thickness was verified by Ellipsometer. Under vacuum condition (~ 6.7×10-7 mbar), the substrates were coated with a 5nm Titanium (worked as adhesion layer) followed by 30nm of Palladium using e-beam evaporation. These substrates were used further for DPN experiments [9].

Dip Pen Nano-lithography: 16-MHA ink was used for all nanowriting experiments. 5mM solution of 16-MHA ink was prepared in 1-octanol solvent. The tips were coated using double dipping method: For that first tips were dipped into saturated solution of 16-MHA in 1-octanol for ~10-20 sec and then dried in air for some time and then again dipped into solution of 16-MHA in 1-octanol.

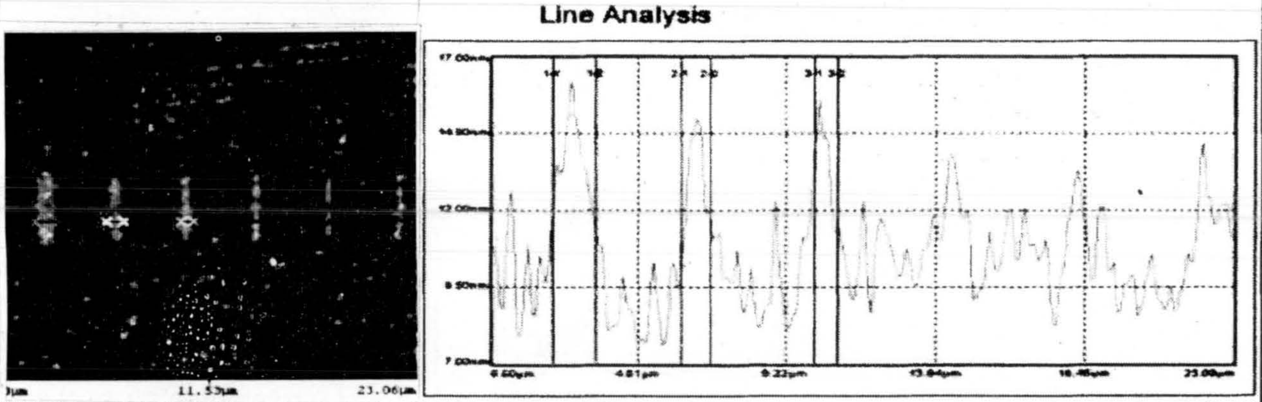
3. RESULTS AND DISCUSSIONS

Before performing nano-patterning of 16-MHA ink on to Palladium (Pd) substrate, ink testing and ink calibration has to be performed. Ink testing was done to check the diffusivity of ink, that whether it was diffusing or not. For it 1×1 µm2 area of substrate was scanned with slow scan rate ~1Hz, and then bigger area of 5×5 µm2 at higher scan rate ~5 Hz. For Ink calibration, different types of structures like parallel lines and dots were patterned onto substrate and then corresponding diffusion coefficient was calculated using in-built InkCal module.

3.1 Ink Calibration Lines

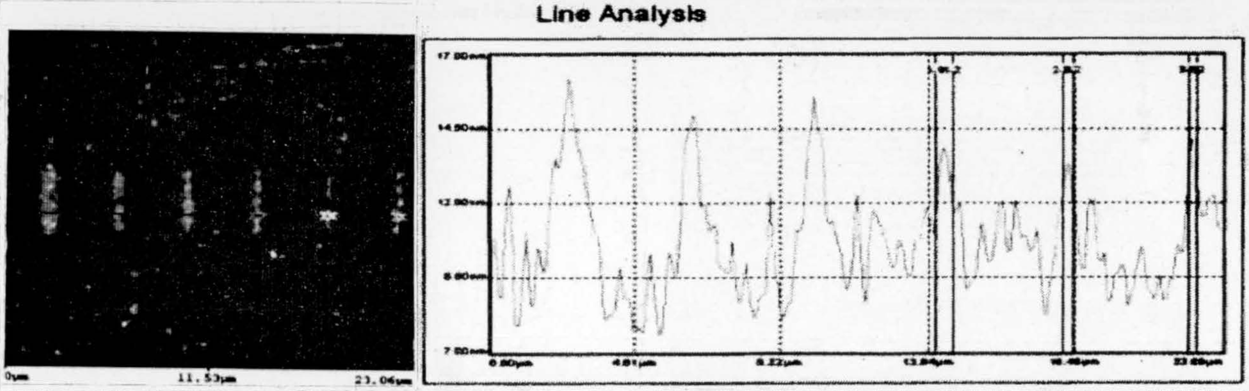
Here lines of different widths by varying writing speed were patterned on to Pd substrate. Six lines with 4µm spacing were written using 16-MHA as an ink. During nano-writing the temperature and relative humidity was 26°C and 45% respectively and writing speed was 0.1, 0.2, 0.4, 0.8, 1.2 and 1.6µm/s from left to right as shown in Fig. 2. Here in Fig. 2(a) LFM image of written lines of 16-MHA on Pd substrate is shown. From Fig. 2(a) it can be seen that as speed is increasing from left to right corresponding line width is decreasing.

Width analysis of lines (left to right), written on Pd substrate are shown in Fig. 3. As writing speed of left most three lines of Fig. 3(a) (0.1µm/sec, 0.2µm/sec, 0.4µm/sec) and right most



		Pair 1		Pair 2		Pair 3	
		X (µm)	Z (nm)	X (µm)	Z (nm)	X (µm)	Z (nm)
Line 1	1	1.845	11.887	5.880	9.546	10.031	13.880
	2	3.190	11.292	6.803	11.951	10.762	11.367
	distance	1.345	-0.596	0.922	2.405	0.730	-2.512
	pt angle	-0.03°		0.15°		-0.20°	

(a)



		Pair 1		Pair 2		Pair 3	
		X (µm)	Z (nm)	X (µm)	Z (nm)	X (µm)	Z (nm)
Line 1	1	13.990	11.038	17.987	12.205	21.984	12.858
	2	14.528	11.876	18.333	12.070	22.253	12.439
	distance	0.538	0.838	0.346	-0.135	0.269	-0.419
	pt angle	0.09°		-0.02°		-0.09°	

(b)

Fig 3. LFM Image Analysis in NanoRule Software for Width Measurements of (a) First Three Lines and (b) Next Three Lines (L-R)

three lines of Fig. 3(b) (0.8μm/sec, 1.2μm/sec, 1.6μm/sec) from left to right is increasing, the corresponding line width 1.345 μm, 0.922μm, 0.730 μm, 0.538 μm, 0.346 μm and 0.269 μm from left to right decreases.

3.2 Ink Calibration Dots

Here six dots with dwell time of 1, 2, 4, 8, 12 and 20 seconds, starting from left to right respectively were patterned on to Pd substrate at temperature~27^{0}C and humidity of 32%. The pattern is shown in Fig. 4.

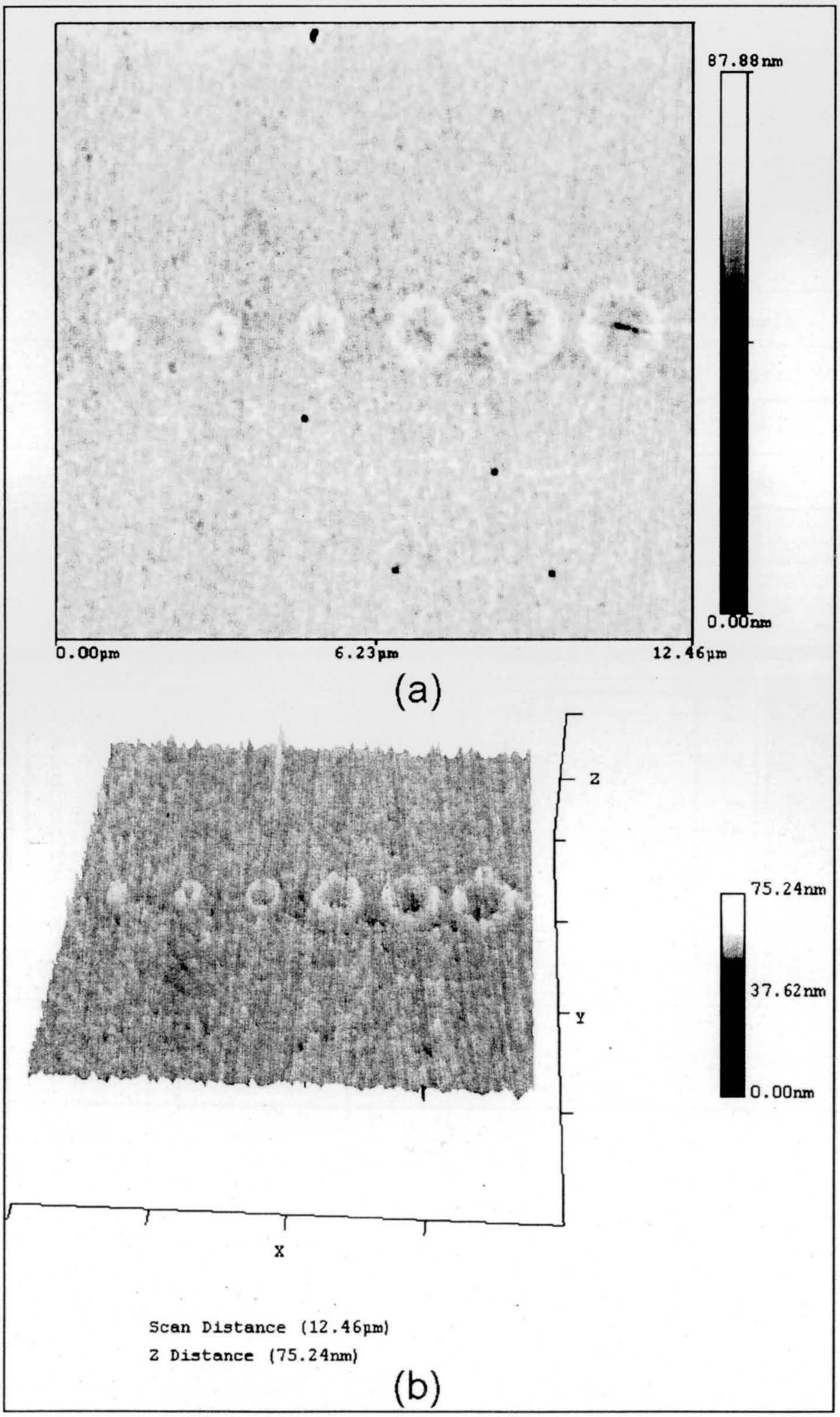


Fig 4. (a) 2D and (b) 3D LFM Images of Ink Calibration Dot Pattern on Pd Substrate using 16-MHA as Ink at RH 32% and Temp. 27^{0}C

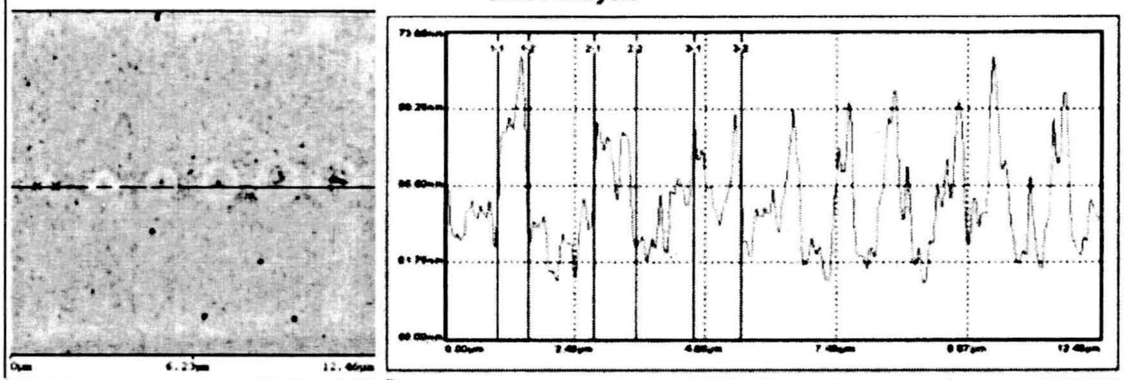
Here in Fig. 4(a) LFM image of nano-patterned dots on Pd substrate is shown. The effect of dwell time on to the dot area can be seen from Fig. 4(a). As dwell time is increasing from left to right corresponding dot area is also increasing. The corresponding 3D view is shown in Fig. 4(b). The analysis of these dot patterned images was also done in NanoRule software which is shown in Fig. 5. From Fig. 5 it is clear that as dwell time is increasing 1, 2, 4, 8, 12 and 20 seconds, starting from left to right respectively, correspondingly dot diameter is increasing.

In Fig. 5(a) analysis of three left most dots and in Fig. 5(b) analysis of three right most dots is described. From here it can be seen that dot diameter is increasing from left to right (0.602μm, 0.810 μm, 0.914 μm, 1.287μm,1.454 μm, and 1.557μm) with increase in dwell time from 1 to 20s.

3.3 Effect of Humidity over Patterned Substrate

As it is known that DPN process is strongly affected by environmental conditions i.e. relative humidity and temperature [10]. So to test the effect

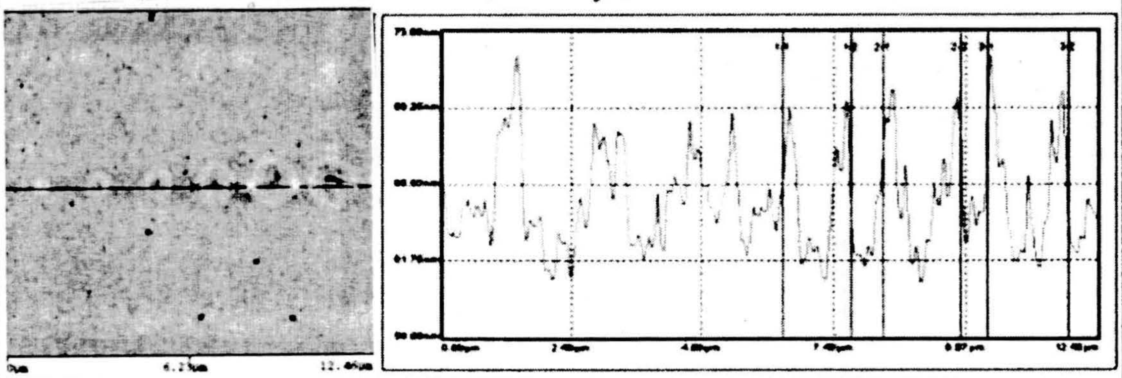
Line Analysis



		Pair 1		Pair 2		Pair 3	
		X (µm)	Z (nm)	X (µm)	Z (nm)	X (µm)	Z (nm)
Line 1	1	0.955	62.992	2.824	65.951	4.735	68.657
	2	1.557	63.078	3.634	62.534	5.648	65.209
	distance	0.602	0.086	0.810	-3.417	0.914	-3.448
	pt angle	0.01 °		-0.24 °		-0.22 °	

(a)

Line Analysis



		Pair 1		Pair 2		Pair 3	
		X (µm)	Z (nm)	X (µm)	Z (nm)	X (µm)	Z (nm)
Line 1	1	6.479	65.458	8.369	66.438	10.341	68.455
	2	7.766	64.862	9.822	68.658	11.899	64.416
	distance	1.287	-0.596	1.454	2.219	1.557	-4.038
	pt angle	-0.03 °		0.09 °		-0.15 °	

(b)

Fig 5. LFM Image Analysis in NanoRule Software for Diameter Measurement of (a) first three dots and (b) next three dots (L-R)