

# Nanodots Array Rapidly Fabricated By Dip-Pen Nanolithography with Temperature and Humidity Control\*

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**Abstract**— This study demonstrates the advantage of Dip-Pen Nanolithography (DPN) as a research and design tool for metal nano-structure fabrications. We design two different gold nano-structures, which are fabricated by DPN etching method with temperature and humidity control. The plasmon resonance frequencies of both structures are measured with dark field scattering spectroscopy. Our results show that with temperature and humidity control, DPN is highly potential in developing photonic circuit, solar cell and biomedical devices due to the rapid fabrication and cost effectiveness.

## I. INTRODUCTION

Dip-Pen Nanolithography (DPN) is a scanning probe lithography technique which transfer inks to the substrate surface by an atomic force microscope (AFM) tip. The working process of DPN, similar to the human writing, enables direct deposition of ink materials onto a substrate in a flexible manner [1-3]. DPN can rapidly fabricate a dots nano-array; in our research, only fifteen minutes was needed from mask design to final product for a 60X60  $\mu\text{m}$  dot array. Being a highly competitive method comparing to the E-beam nanolithography, DPN is now broadly using in nanostructure manufacture. However, the unstable ink transport rate has been a serious problem in DPN for real industrial applications. In our previous work, we found that with proper control of pen sharpness, dwelling time and substrates, this direct writing technique allows the pattern scale decreasing to sub-hundred nanometers at a very stable ink consuming rate [2]. In this manuscript, we demonstrate how to fast fabricate a large scale nano-array with DPN under well temperature and humidity control.

## II. MATERIALS AND METHODS

### A. Nano gold array chip

Glass (BK7) cover slide was used as a substrate of the array chip and two different materials were deposited on the glass as adhesive layers by E-beam evaporator. The first is chromium (Cr) with 7 nm thickness, and the second is

titanium (Ti) with 7 nm thickness. A 40 nm thick gold film was then formed on the cover glass by e-gun evaporation, and the chip was preserved in vacuum for later use. Then, written arrays on the gold films by DPN with the Nscriptor system (NanoInk) with type-A probes (spring constant = 0.041 N/m). Probes were previously immersed in piranha solution (valum ratio of 98%  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$  is 3:1) for thirty minutes, rinsed by DI water and blow dry with nitrogen before use. The transport rate of the tips was calibrated by using the built-in Ink-Cal function of the NanoInk software. The writing ink in this study was supersaturation carboxylic acid of 16-alkylthio solution dissolved in acetonitrile (MHA). The probes were immersed into MHA solution and dry with nitrogen. After installed the probe in the DPN machine, the ambient was controlled at 30 °C and 60% humidity.

### B. Array etching

The etchant for the Cr adhered Au film is with 0.076 g thiourea, 0.2686 g ferric nitrate and 18  $\mu\text{l}$  1-octanol in 50 ml DI water. For the chip with Ti as adhesion layer, 0.0304 g thiourea, 0.24 g ferric nitrate, and 70  $\mu\text{l}$  1-octanol dissolved in 20 ml DI water was used as etching solution. HCl solution was then added to reduce the pH to 1.85.

### C. Analysis

We used atomic force microscopy (AFM) and scanning electron microscopy (SEM) to measure and confirm nanogold arrays' geometric structure. The resonance scattering spectra was measured by dark field microscope with 100 X objective in 400 nm to 850 nm wavelength [10].

## III. RESULTS

MHA ink as the dot-array etching mask is written on gold film prepared beforehand. Due to dot size is concerned with environmental temperature, humidity, ink diffusion rate, probe size and contact time [11, 12], as shown in Fig. 1, our experiment is controlled at ambient temperature of 30 °C, and 60% humidity. Two types of dot array samples are produced by altering the contacting time. Fig. 2 shows the three-dimensional AFM image of a MHA etching mask with 150 nm dot diameter and 1  $\mu\text{m}$  pitch size. This MHA mask is made with one second probe contacting time for each dot. For 400 nm dot size, five second contacting time is needed. (The individual differences between probes should be considered.)

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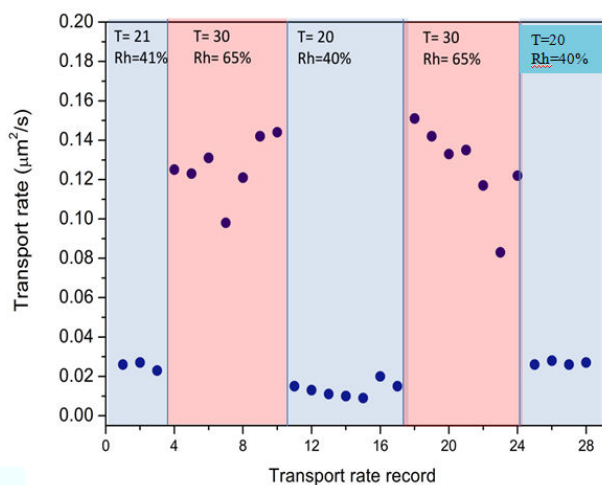


Figure 1. Probe transport rate with temperature and humidity control.

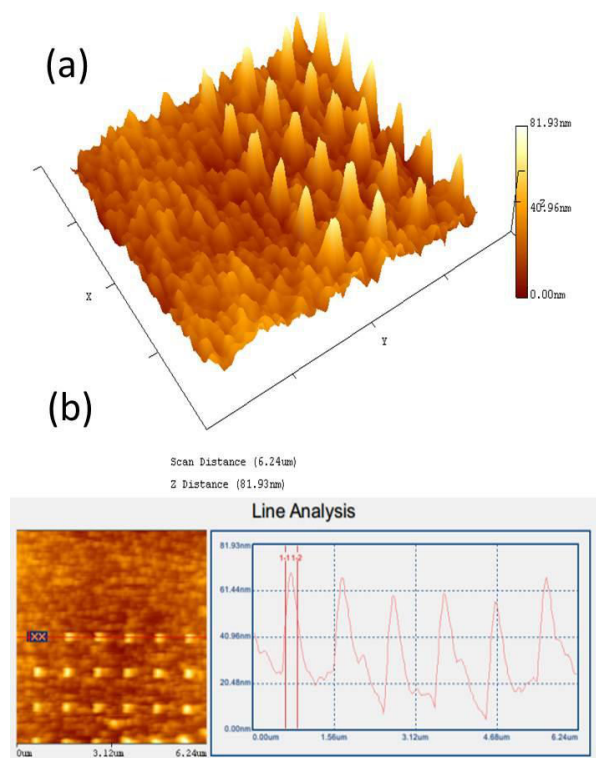


Figure 2. For the AFM scanning results (a) is represented by three-dimensional grayscale height map, the shape of array mask was apparent MHA for one second contract time. (b) analyzing of the dot diameter is 150 nm.

After 20 minute etching, two different nanoarray structures with 100 to 150 nm and 400 nm dot size, as the SEM image shown in Fig. 3, can be realized. The values of dot full width at half maximum after etching in Fig. 3 (b) are consistent with design dots size in Fig.2 (b). By using DPN etching technique with temperature and humidity control, we can easily use a single probe to produce 3600 dots with 100 nm diameters or 400 dots with 400 nm diameters in an hour. Besides, according to the experimental results, the gap size of the structures can be achieved between 50 to 100 nm. It can be seen that this method provide the real advantages in structure design.

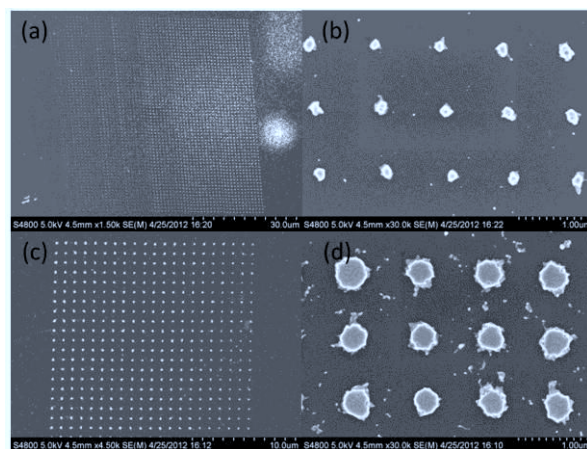


Figure 3. Nanogold array structure under the SEM. (a) 60x60 nanogold array with (b) 100 nm dot diameter. (c) 20x20 nanogold array with (d) 400 nm dot diameter.

To understand the optical resonance frequencies of two nanogold arrays with different materials as adhesive layers, we use the dark field microscope to collect the scattering spectra in visible spectrum window. Dark field image of nanogold array adhered by Cr is shown in Fig. 4. The resonant scattering center wavelength of 400 nm diameter nanogold dots is 665 nm (Fig. 4 (a)), which would shift to 622.8 nm when the dots diameter decrease to 150 nm (Fig.4 (b)).

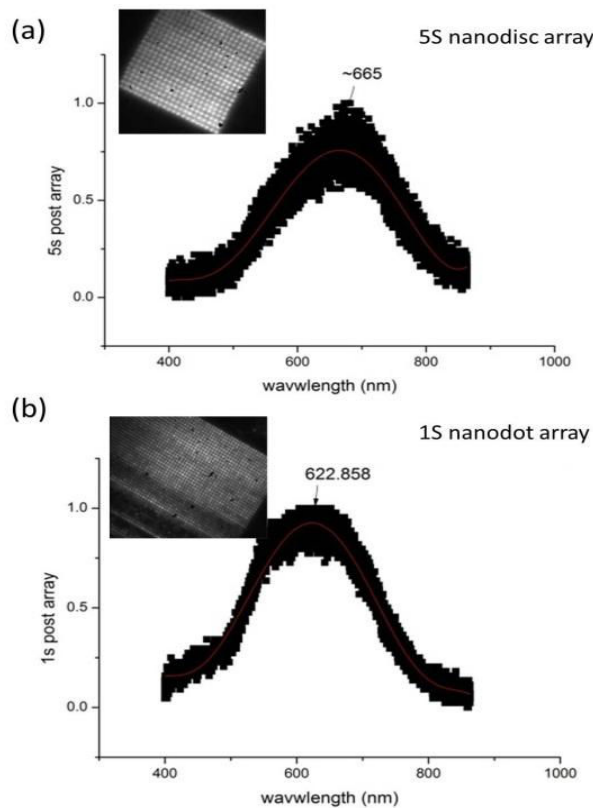


Figure 4. (a) The resonant scattering center wavelength of 400 nm diameter nanogold array is 665 nm. (b) The resonant scattering center wavelength of 150 nm diameter nanogold array is 622.8 nm

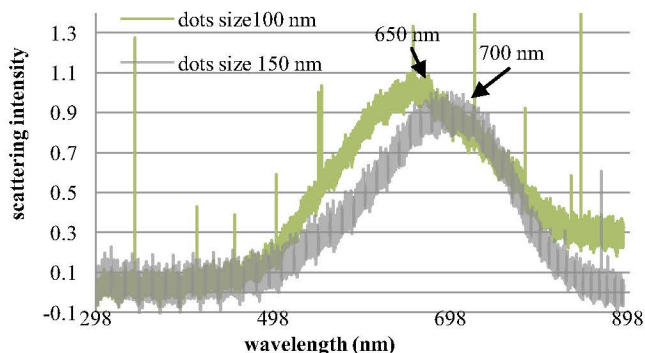


Figure 5. The resonant scattering center wavelength of 100 nm diameter nanogold array is 650 nm. The resonant scattering center wavelength of 150 nm diameter nanogold array is 700 nm.

The dark field image of nanogold array adhered by Ti is shown in Fig. 5. The resonant scattering center wavelength of 100 nm diameter nanogold dot is 650 nm, and which would shift to 700 nm when the dots diameter increasing to 150 nm.

#### IV. DISCUSSION AND CONCLUSIONS

We successfully take advantage of DPN etching technique base on temperature and humidity control to produce different nanogold arrays. The preliminary data shows that gold film which adhered by Ti has more obvious resonant scattering spectra differences, which infer to a better sensitivity for sensing.

Localized plasmon resonance of nano metal structure has been used in quite a few areas. In biomedical research and applications, biocompatible gold structures have been applied to cell cultures, bacteria detection, real-time optical detection and Raman spectrum enhancement [13-15]. Nanostructures are also used to break the optical diffraction limit, like nano optics components, near field microscopy and optical waveguide technology [16]. Beside, localized surface plasmon resonance, as a new and effective way to improve the existing solar panel conversion efficiency, provides a new possibility in rapidly developed green energy industries [17, 18].

Due to the convenience operation process, low environmental constraints, and impressive performance in detail resolving power, DPN has been a very high potential method for industrial application in rapid nanostructure manufacturing. We are trying to use DPN technology to do more immediate and cost-effective testing and validation of our structural designed by simulation software.

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