Sub-wavelength metal nanostructure fabrication by parallel dip-pen nanolithography

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ABSTRACT

Metal nanostructures at sub-wavelength scale have been used as plasmonic diffraction gratings and negative index metamaterials and have attracted interests in materials engineering and optics research. E-beam lithography is commonly used to fabricate these metal nanostructures; however, e-beam lithography has limitation in scale-up of nanostructure fabrication and is expensive. In this study, a low cost and convenient scale-up fabrication method for metal nanostructures using Dip Pen Nanolithography® (DPN®) is demonstrated. DPN was used to deposit alkanethiol patterns, which were then used as etch resists for top-down nanofabrication processes to generate Au nano-features. As a proof of concept, arrays of three different designed double-ring Split-Ring Resonators (SRRs) were fabricated by DPN printing.

Keywords: dip-pen nanolithography, metal nanostructure, alkanethiol, metamaterials

1 INTRODUCTION

Sub-micron features have been researched in material engineering and optics because of their strong correlation with electromagnetic wave. Control of electromagnetic wave based on the strong correlation with subwavelength structures brought about an expectation about artificial materials with tailored optical properties. An obstacle in implementation of the artificial materials is difficulty in fabricating sub-micron structures. In recent years, numerous fabrication methodologies have been developed for micro/nano scale materials engineering. Methodologies including photolithography, e-beam lithography, laser ablation, LIGA, FIB, micro stamping, and nanoimprint lithography makes it possible to realize tailored micro/nano structures. In spite of remarkable development in micro/nanofabrication methodologies, there are still limitations with each of these technologies such as difficulty in scale-up, high cost and complexity in fabrication process.

E-beam lithography is the most commonly used methodology for metal nanostructure fabrication. While e-beam lithography does enable high resolution metal nanostructure fabrication, practical applications of this platform are limited because of the high cost and scale-up difficulties involved with e-beam lithography. Here we demonstrate a scalable, tip-based method of fabricating sub-wavelength metal nanostructures that overcomes the difficulties encountered with e-beam lithography.

2 DIP-PEN NANOLITHOGRAPHY (DPN)

Dip Pen Nanolithography® (DPN®) is an established method of nanofabrication in which materials are deposited onto a surface using a sharp tip (Figure 1).[1] The sharp tips (pens) are coated with the materials to be deposited and brought in close proximity of the surface to be patterned. A water meniscus is inherently formed between the tip and surface by moisture condensing from environment. The molecules from the pens are transferred to the surface through the water meniscus by a diffusion process. Moving the pens with precise control enables the generation of patterns. Diameter and line-width of ink patterns are controlled by tip dwell time and tip speed respectively. In case of patterning alkanethiols on an Au surface, self-assembled monolayer (SAM) of alkanethiol will form on the Au surface by means of Au-S binding. DPN can be used to fabricate features with diameters as small as 50 nm. Generally, sub 100 nm to several μm sizes can be achieved by DPN.[1]

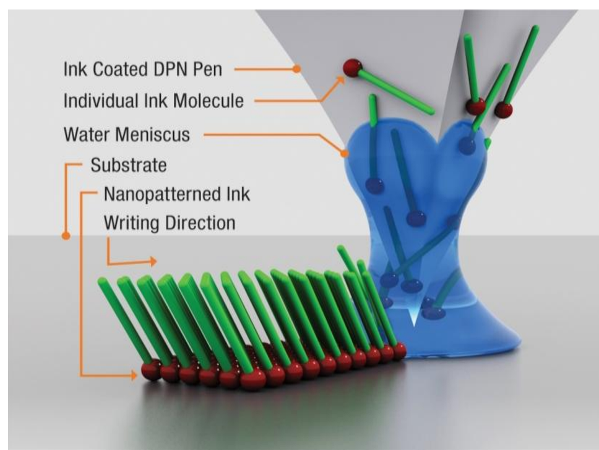

Figure 1: Illustration of Dip Pen Nanolithography (DPN).

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3 TOP-DOWN METAL NANOSTRUCTURE FABRICATION BY DPN

DPN-deposited alkanethiol patterns can be used as etch resists for top-down nanofabrication processes [2,3]. The top-down nanofabrication process is described in figure 2. 16-mercaptohexadecanoic acid (MHA) and 1-octadecanethiol (ODT) are commonly used as etch resists. Micro/nano scale MHA or ODT SAMs are patterned on an Au film deposited silicon substrate. To ensure Au film adhesion to the substrate, thin Ti or Cr layer deposited on silicon prior to the Au film deposition. The Au film is etched away by iron nitrate based Au etchant. At this step, MHA or ODT SAMs work as etch resists. Thin Ti or Cr buffer layer is also etched away by diluted HF solution or HCl based chromium etchant, respectively. After removal of alkanethiol SAMs by a gentle oxygen plasma treatment, Au micro/nano structures on silicon substrate are obtained.

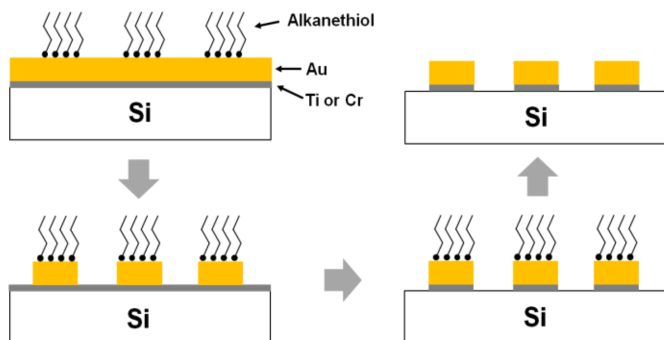


Figure 2: Scheme of top-down metal nanostructures fabrication process.

4 FABRICATION TOOLS

Alkanethiol DPN patterning on Au film deposited silicon substrate was carried out by the desk top scanning probe lithography system (DPN 5000™, NanoInk Inc., Skokie, USA) (Figure 3). DPN 5000 is a piezo scanner based system which allows for precise nanolithography and AFM imaging. In addition to generating small feature sizes, DPN 5000 system enables rapid and flexible design of feature geometry. The CAD based pattern designing software in DPN 5000 system (InkCAD™, NanoInk Inc., Skokie, USA) is available to conveniently design and align patterns.

Just as importantly, the fabrication process using the DPN 5000 system can be scaled up to pattern several hundred to over several thousand features in relatively short periods of time by using a NanoInk custom designed 1D or 2D multiple-tip cantilever "pen" array (Figure 4).[1] These features make DPN an efficient and cost effective method for fabricating a large number of nanostructures.

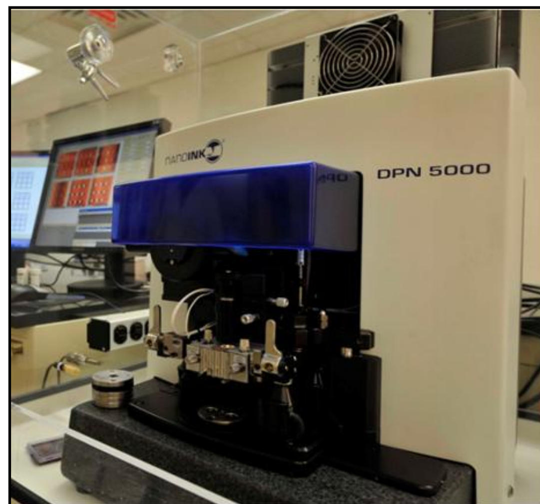
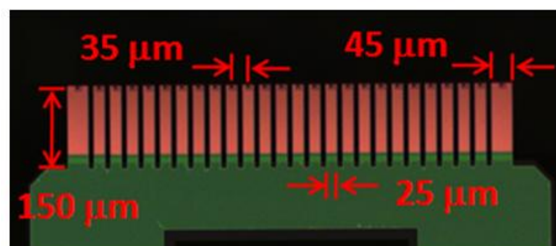


Figure 3: Snapshot picture of DPN5000 system



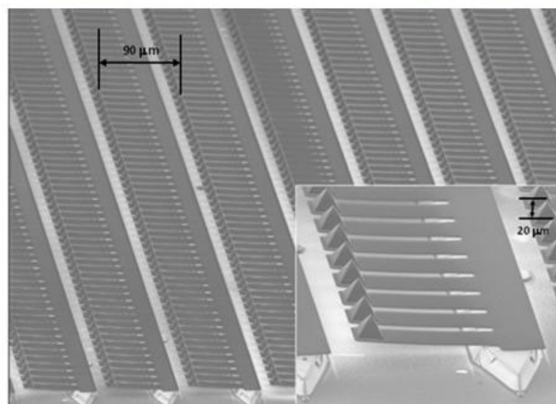


Figure 4: (Top) Optical microscope image of 1D probe array. The 26-pen array has 35 um tip-to-tip distance. The broad tips at the both end are used for feedback control during lithography. (Bottom) SEM image of 2D probe arrays (55,000 pens). The SEM image of 2D prove arrays showing multiple rows of cantilevers attached to the silicon ridges. The inset image shows the individual cantilevers, while also highlighting the 7.5 µm tall tips and inherent cantilever curvature (~6°).

5 SPLIT-RING RESONATORS (SRR) FABRICATION

Metamaterials are artificially engineered structures that have unusual properties that may not be found in naturally occurring materials.[4] The engineered structure, rather than the material composition is the basis for these unusual properties. The primary research topic in metamaterials is the negative refractive index behavior of metamaterials. The negative refractive index can be obtained by correlation between sub-wavelength structures in metamaterials and electromagnetic waves. Using this negative refractive index behavior, several research applications have been tried, including photonic metamaterials, superlens, cloaking devices, acoustic metamaterials, and metamaterial antennas.[5]

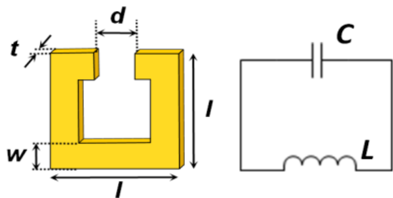


Figure 5: Illustrations comparing split-ring resonators (left) and conventional LC oscillators (right).

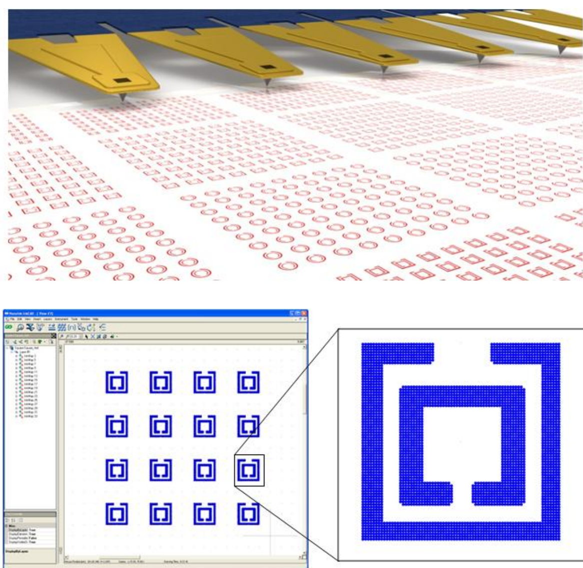


Figure 6: Illustration of molecular ink DPN patterning for SRR array fabrication (top) and DPN pattern for SRR array design (bottom). An array of 3057 dots was used for individual SRR design. Ring widths and distances between outer and inner rings are 400 nm. Gaps in outer and inner rings are 1.2 μm and 400 nm, respectively.

Split-ring resonator (SRR) structures comprise the most common examples of negative index metamaterials (NIMs). SRR structures have been studied for potential use in Terahertz (THz) and acoustic metamaterials, as well as in metamaterial antennas.[4,5] Figure 5 compares a SRR to a conventional LC oscillator. The resonance frequency of an LC oscillator (ω_{LC}) is determined by the inductance (L) and capacitance (C) of the circuit in the relationship $\omega_{LC} = (LC)^{-1/2}$. In SRRs, L and C are dependent on SRR dimension, so SRR resonance frequency can be controlled by manipulating its geometrical parameters. SRR structures fabricated to sub-micron dimensions generate electromagnetic responses in the THz range, which is close to the spectrum of visible light.

DPN is suitable for fabrication of nanoscale SRR. From sub 100 nm to several microns metal features can be straightforwardly fabricated by DPN printing of small molecule, typically alkanethiol, and sequential metal etching process.[2,3] Moreover, DPN has capability of precise pattern control and SRR array can be scaled-up by parallel DPN methods [5] (Figure 6). Example of SRR pattern for DPN fabrication is shown in figure 6 (bottom).

An array of DPN-fabricated SRR structures was

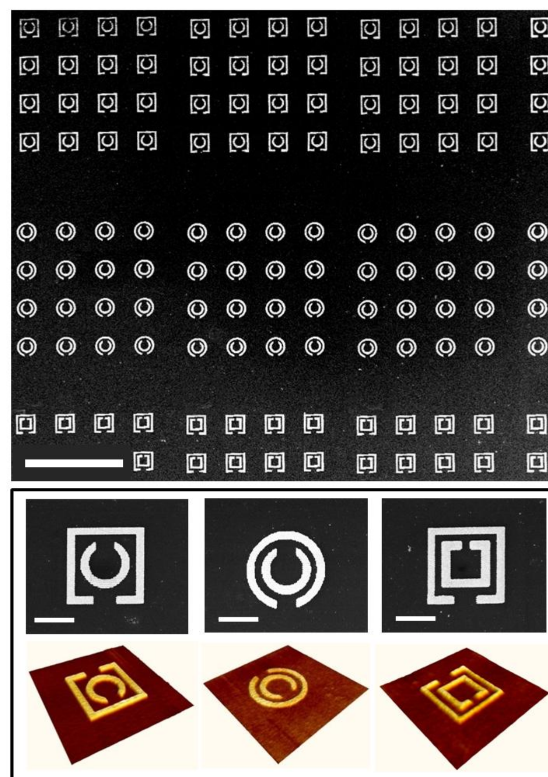


Figure 7: SEM image of DPN-fabricated SRR array (top), with scale bar of 20 μm. Highly magnified SEM images (middle) and 3-D AFM topographic images (bottom) of individual SRR circle-square, circle-circle, and square-square structures (left to right) fabricated without defect, with scale bars of 2 μm.

constructed by incorporating three different double-ring SRR designs (circle-square, circle-circle, and square-square). This nanoarray was created using a NanoInk 1D 26-“pen” array (DPN Pen Array: Type F) to pattern MHA ink on a 10 nm thick gold film with a 2 nm of Titanium adhesion layer, on a silicon oxide substrate. The MHA patterns were utilized as a resist to etch the gold surface.

Figure 7 shows an SEM image of the resulting SRR array structures, as well as high resolution SEM images and AFM images of the three different types of nanoscale SRRs. In total, this experiment generated 1248 SRRs, 416 each of the three different double-ring SRR designs, using a top-down DPN fabrication approach.

6 CONCLUSION

We have successfully fabricated nanoscale SRR arrays using the desk top scanning probe lithography system. Results demonstrate that parallel DPN methodologies are capable of quickly and easily fabrication of metal nanostructures, making DPN an enabling technology for future studies of applications in materials and optics research.

REFERENCES

[1] C. A. Mirkin, "The power of the pen: Development of massively parallel dip-pen nanolithography", *Acs Nano* **1**, 79-83, 2007.

[2] H. Zhang, S. W. Chung, and C. A. Mirkin, "Fabrication of sub-50-nm solid-state nanostructures on the basis of dip-pen nanolithography", *Nano Letters* **3**, 43-45, 2003.

[3] H. Zhang and C. A. Mirkin, "DPN-generated nanostructures made of gold, silver, and palladium", *Chemistry of Materials* **16**, 1480-1484, 2004.

[4] W. J. Padilla, D. N. Basov, and D. R. Smith, "Negative refractive index metamaterials", *Materials Today* **9**, 28-35, 2006.

[5] T. J. Yen, *et al.* "Terahertz magnetic response from artificial materials", *Science* **303**, 1494-1496, 2004.