

**DEVELOPMENT OF NANOSTENCIL
LITHOGRAPHY AND ITS APPLICATIONS FOR
PLASMONICS AND VIBRATIONAL
BIOSPECTROSCOPY**

SERAP AKSU

Dissertation submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy



BOSTON UNIVERSITY
COLLEGE OF ENGINEERING

Dissertation

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by

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B.S., Sabanci University, 2008

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Iqra!

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ABSTRACT

Development of low cost nanolithography tools for precisely creating a variety of nanostructure shapes and arrangements in a high-throughput fashion is crucial for next generation biophotonic technologies. Although existing lithography techniques offer tremendous design flexibility, they have major drawbacks such as low-throughput and fabrication complexity. In addition the demand for the systematic fabrication of sub-100 nm structures on flexible, stretchable, non-planar nanoelectronic/photonic systems and multi-functional materials has fueled the research for innovative fabrication methods in recent years.

This thesis research investigates a novel lithography approach for fabrication of engineered plasmonic nanostructures and metamaterials operating at visible and infrared wavelengths. The technique is called Nanostencil Lithography (NSL) and relies on direct deposition of materials through nanoapertures on a stencil. NSL enables high throughput fabrication of engineered antenna arrays with optical qualities similar to the ones fabricated by standard electron beam lithography. Moreover, nanosten-

cils can be reused multiple times to fabricate series of plasmonic nanoantenna arrays with identical optical responses enabling high throughput manufacturing. Using nanostencils, very precise nanostructures could be fabricated with 10 nm accuracy. Furthermore, this technique has flexibility and resolution to create complex plasmonic nanostructure arrays on the substrates that are difficult to work with e-beam and ion beam lithography tools. Combining plasmonics with polymeric materials, biocompatible surfaces or curvilinear and non-planar objects enable unique optical applications since they can preserve normal device operation under large strain. In this work, mechanically tunable flexible optical materials and spectroscopy probes integrated on fiber surfaces that could be used for a wide range of applications are demonstrated. Finally, the first application of NSL fabricated low cost infrared nanoantenna arrays for plasmonically enhanced vibrational biospectroscopy is presented. Detection of immunologically important protein monolayers with thickness as small as 3 nm, and antibody assays are demonstrated using nanoantenna arrays fabricated with reusable nanostencils.

The results presented indicate that nanostencil lithography is a promising method for reducing the nano manufacturing cost while enhancing the performance of biospectroscopy tools for biology and medicine. As a single step and low cost nanofabrication technique, NSL could facilitate the manufacturing of biophotonic technologies for real-world applications.

Contents

1	Introduction	1
1.1	Motivation	1
1.2	What is Nanostencil Lithography?	5
1.3	Objectives	8
1.4	Thesis Content and Organization	9
2	Plasmonics: Fundamental Science and Novel Device Technologies	11
2.1	Introduction	11
2.2	Theoretical Background on Localized Surface Plasmon Resonances . .	12
2.3	Applications	19
2.3.1	Surface Enhanced Vibrational Biospectroscopy	19
2.3.2	Biosensing	20
2.3.3	Energy Harvesting	22
3	Nanofabrication Technologies and Nanostencil Lithography	24
3.1	Introduction	24
3.2	Conventional Nanofabrication Methods	25
3.2.1	Top down Approach	25
3.2.2	Bottom up Approach	30
3.3	Emerging Nanofabrication Methods	31
3.4	Nanofabrication and Patterning with Nanostencil Lithography	37
3.4.1	Historical Background	37

4	High-throughput Nanofabrication of Infrared Plasmonic Nanoantenna Arrays for Vibrational Nanospectroscopy	41
4.1	Nanostencil Lithography for Plasmonic Nanostructure Fabrication . .	43
4.2	Nanorod Fabrication: Nanostencil vs E-beam Lithography	45
4.3	Reusability of Stencil for High-throughput Nanofabrication	48
4.4	Collective Plasmonics and Engineered Plasmonic Nanoantennas by Nanostencil Lithography	53
4.5	Conclusion	57
5	Nanostencils: Versatility for Fabrication and Patterning	59
5.1	Deposited Material Flexibility of Nanostencil Lithography	59
5.1.1	Multiple Biofunctional Molecular Nanopatterns on Polymer Substrate	63
5.2	Design Flexibility of Nanostencil Lithography	74
5.3	Substrate Flexibility of Nanostencil Lithography	76
5.4	Conclusion	81
6	Flexible Plasmonics on Unconventional and Non-Planar Substrates	82
6.1	High Resolution Nanostencil Lithography with Elastomeric Interfaces	82
6.1.1	Analysis of Blurring in NSL and Improving Stenciling Precision	88
6.2	Flexible Plasmonic Dimers with Sub-50 nm Inter-particle Distances .	94
6.3	Flexible Plasmonic Nanoantennas at Mid-IR Wavelengths	98
6.4	Stretchable Plasmonics for Active Optical Tuning	101
6.5	Flexible Plasmonics on Non-Planar Surfaces	104
6.6	Conclusion	105
7	Plasmonically Enhanced Vibrational Biospectroscopy using Low-cost Infrared Antenna Arrays by Nanostencil Lithography	107

7.1	Post-processing Method to Eliminate Blurring Effect	110
7.2	Theoretical Examination of NSL Fabricated Nanorod Antenna Arrays	113
7.3	Vibrational Biospectroscopy on Low Cost Infrared Antenna Arrays .	116
7.4	Conclusion	120
8	Summary, Conclusions and Outlook	121
8.1	Summary of the Results	121
8.2	Conclusions	123
8.3	Outlook	125
	References	127
	Curriculum Vitae	139

List of Tables

3.1	Brief timeline of stencils in microfabrication. Modified from (Mena, 2010).	38
3.2	Brief timeline of stencils in nanofabrication. Modified from (Mena, 2010).	40
5.1	Deposition of different materials using nanostencils. Modified from (Mena, 2010).	60
5.2	Nanostencil Lithography demonstrated on unconventional substrates. Modified from (Mena, 2010).	77

List of Figures

1.1	Metallic nanostructures used for probing the protein interactions through vibrational spectroscopy	3
1.2	On the left, Ancient Hands Stencil Paintings, Rio Pinturas Canyon, Cave of the Hands, Patagonia, Province of Santa Cruz, Argentina. The art in the cave dates from 13,000 to 9,000 years ago. In the middle regular alphabet stencil used in arts is shown. On the right SEM image of sub-micron stencil for nanofabrication is shown.	7
1.3	Illustration of Nanostencil Lithography.	8
2.1	On the top propagation geometry is shown. Wave propagate along the x-direction. Bottom shows the dispersion relation of SPPs at the interface between a Drude metal with negligible collision frequency and air (gray curve) and silica (black curves) (Maier, 2007)	15
2.2	a spherical nanoparticle with (a)negative and (b) positive permittivity (ϵ) subject to uniform external field	17
2.3	Plasmonic nanorods are shown to enhance the vibrational signals of biomolecules (Adato et al., 2009).	20
2.4	Plasmonic nanoholes are shown to detect live viruses from biological media using LSPR shifts (Yanik et al., 2010).	21

2.5	New plasmonic solar cell designs (Atwater and Polman, 2010). (a) Semiconductors with different bandgaps are stacked on top of each other. (b) Plasmonic quantum dot solar cell designed for enhanced photo absorption. (c) Optical antenna array made from an axial heterostructure. (d) Array of coaxial holes in a metal film.	23
3.1	A typical optical lithography system. Adapted from Barrett Group at McGill University, Canada. (http://barrett-group.mcgill.ca/tutorials/nanotechnology/nano04.htm)	26
3.2	The Cymer™ LPP EUV Source System (http://www.cymer.com/euvl/)	27
3.3	Typical e-beam lithography configuration for nanoparticle fabrication. Adapted from (Guillot and de la Chapelle, 2012)	28
3.4	The structures fabricated by FIB. Adapted from Cabrini et. al. 2005	29
3.5	A wide variety of metallic nano particles could be synthesized with tight control of size and shape. Adapter from (Adams et al., 2012) . .	31
3.6	Schematic illustration of the fabrication of the topographically patterned elastomeric pattern-transfer agent (a mold or stamp depending on the application of soft lithography) by casting and curing an elastomer against a patterned relief structure, usually in photoresist (a master).A replica of the master is generated by molding against the patterned elastomer. PDMS is poly(dimethylsiloxane). Adapted from (Gates et al., 2004)	32
3.7	Schematic diagrams of four approaches to replica molding: (a) step-and- flash lithography, (b) replica molding (RM), (c) microtransfer molding (μ TM), and (d) micromolding in capillaries (MIMIC). Adapted from (Gates et al., 2004)	33

3·8	Schematic illustration of embossing procedures for (a) nanoimprint lithography and (b) SAMIM. Adapted from (Gates et al., 2004)	34
3·9	SEM images of structures patterned by nanoimprint: 10 nm diameter metal dots with a periodicity of 40 nm and Fresnel zone plates with a 125 nm minimum line width. SEM image of features patterned by SAMIM. Adapted from (Gates et al., 2004)	35
3·10	On the left SEM images of self assembled polystyrene spheres are shown. After oxygen plasma etching, sphere diameter could shrink to a desired value (middle image). After deposition and polystyrene lift off, gold thin film perforated with nano holes is obtained (Aksu and Altug, 2009)	36
3·11	Cu wires created by nanostencils as (a) line (b) loop. SEM image on the left shows the SiN_x cantilever used for dynamic stenciling featuring several holes milled by FIB. (Luthi et al., 1999)	39
4·1	Nanoapertures patterned on stencil and corresponding nanoantennas are shown on the left. Illustration of NSL in the middle. Reflectance of nanorod antenna arrays with a variety of periodicity.	42
4·2	Nanostencil lithography, a shadow-mask patterning technique, is used for high-throughput fabrication of plasmonic antenna arrays. a) Fabrication of free standing membrane and nanostencil is illustrated from 1 to 4. Dry and wet etching processes and EBL are used for achieving precisely defined pattern of nanoapertures/slits on the membrane. b) (i) Top and angled SEM images of the gold nanorod with 1100 nm length, 230 nm width and 100 nm height are shown. (ii) Gold deposition scheme with reusable mask is illustrated. (iii) Top view and cross sectional images of the stencil are shown.	44

4.3	Nanostencil lithography is used to fabricate plasmonic nanorod antenna arrays. a) SEM images of nanorods with 1100 nm length, 230 nm width and 100 nm height fabricated using EBL (left) and NSL (right) are shown for comparison. White scale bars represent $1\mu\text{m}$. NSL technique for large area patterning of nanorod arrays provides comparable quality with arrays fabricated using EBL. b) Nanorods fabricated using two different techniques give identical reflection spectrum with resonances at 1700 cm^{-1} . Reflectance intensities are calculated dividing measured particle reflectance spectrum by bare silicon substrate reflectance spectrum (R_s/R_o).	46
4.4	On the left SEM shows the condition of the circular nanoapertures after 1^{st} gold deposition. Middle SEM image shows the same stencil after 3^{rd} deposition. The nanostencils are clogging if no cleaning is applied. The SEM image on left shows the aperture used for nanowire fabrication. Accumulation of gold on stencil is observed.	48
4.5	The clogging of apertures after multiple depositions is illustrated. This problem could be overcome by recycling the stencil. The stencil returns to initial condition after cleaning procedures.	49
4.6	Mask can be reused multiple times. a) SEM images of the same mask are shown before its first usage and after the fourth usage. Apertures have dimensions of 1050 nm length, 200 nm width and 100 nm height. No sign of degradation and deformation is observed on the mask after fourth usage. b) Reflectance spectra are shown for different nanorod arrays obtained from four consecutive depositions using the same mask. The resulting spectra show negligible deviations on resonances 3.5 % around 1700 cm^{-1}	51

4.7	SEM images of the nanoapertures on the stencils after 5 th and 10 th depositions and cleaning. The SEM images of corresponding nanoparticles are shown in lower row. The nanorods have 1 μm length, 200 nm width and 1.6 μm periodicity.	52
4.8	Plasmonic gold nanorod arrays fabricated using nanostencil lithography displays antenna like behavior in Mid-IR frequencies. a) Reflectance spectra of randomly arranged nanorods with lengths indicated in the legend, 230 nm widths and 100 nm heights. b) Fundamental ($m = 1$) resonance wavelengths (blue squares) are linearly dependent on the rod length (dashed red line is linear fit). Effective refractive index (n_{eff}) and constant fitting parameter (C) are calculated as 2.52 and 1.89 μm , respectively.	55
4.9	Spectral characteristics of periodic nanorod arrays, fabricated using nanostencil lithography are shown. a) Reflectance spectra of the periodic nanorod antenna arrays with 1100 nm length, 230 nm width, 100 nm height and periodicities changing from 1.5 to 2 μm (indicated in the legend) are displayed. Spectrum of 1100 nm long individual nanorod antenna (black curve) is also presented for reference. b) Resonance wavelengths (blue square, left y-axis) and the line widths (red triangles, right y-axis) are shown for varying periodicities. The dashed line separates the evanescent (shaded) and the radiative spectral regions for the first grating order on the silicon/air interface.	56
5.1	Nanopatterning different metals on silicon substrate using similar stencil design. Ge, Au and Cr gives high surface quality structures due to their diffusive properties on silicon.	61

5.2	AFM scans of different depositions. Adapted from (RÁCZ and Seabaugh, 2007)	62
5.3	NSL technique is used to generate biomolecule patterns. (a) Schematic view of a stencil. The stencil has arrays of reservoirs and a SiN_x mask with nanoapertures under each reservoir. The volume of the reservoir is calculated to be around 0.12 mL. (b) Schematic diagrams of the NSL bionanopatterning technique. Oxygen plasma is applied to make the PDMS surface hydrophilic. Biomaterials are incubated in the reservoir and patterned through the apertures on the mask. Well defined biopatterns are left on the substrate after the stencil removal. (c) SEM images of three different stencil masks are shown. From left to right: a hole-array with 900 nm diameter and 1.5 μ m pitch, parallel lines with 800 nm width and 2 μ m spacing, and a cross shaped array with 1 μ m line width. (d) TRITC labeled anti-mouse IgG is incubated in the stencils. Fluorescence images of patterned antibody are shown. Each array is generated using the corresponding stencil mask shown above.	66
5.4	Anti-mouse IgG nanoarray with features down to 100 nm is demonstrated. (a) SEM image shows the nanohole mask fabricated on a SiN_x membrane. Hole size is measured to be 105 nm. (b) AFM image of patterned anti-mouse IgG nanoarray is shown. (c) Cross-sectional profile of a patterned row is shown. Data is taken along the red dash line in (b). The widths of the patterns are measured to be around 110 nm	68

5.5	The stencil can be used to generate different types of biomolecule patterns simultaneously. (a) Schematic diagram of different biomolecule patterning is shown. First we attach the stencil onto PDMS substrate. Then we load each reservoir with different biomolecule solutions. After the removal of stencil, biomolecules patterns with well defined shapes are achieved. (b) Fluorescence image shows that two different IgG nanoarrays are generated on the PDMS surface. Reds ones are anti-mouse IgG labeled with TRITC and green ones are anti-monkey IgG labeled with FITC. Pseudo color is applied for better illustration. Image in the yellow blanket shows the enlarged feature of the right-bottom array.	69
5.6	Stencils can be reused multiple times. (a) Left: SEM image of a newly made stencil. Right: fluorescence image of the patterned anti-Mouse IgG (TRITC labeled) arrays using this stencil. (b) Left: SEM image of the stencil before the 4 th usage. Right: fluorescence image of the patterned anti-monkey IgG (FITC labeled) array.	71

5.7	Proteins can be covalently patterned by functionalizing the PDMS surface, and the immobilized proteins retain their functionalities for further biointeractions. (a) Schematic diagram for the modification of PDMS surface and the following specific binding test. (b) Cross-section profiles show the thickness changes of the patterns after each interaction. The blue line shows the profile of anti-mouse IgG pattern generated by the stencil. The heights are measure to be 8 nm on average. After BSA occupies the unpatterned PDMS surface, the background rises about 3 nm as shown by the red line. The green line indicates that the mouse IgG is specifically captured only by the anti-mouse IgG patterned area, and the heights are increased by 6 nm on average. (c) AFM image of the nanopatterns after the interaction between the anti-mouse IgG and mouse IgG is shown. Mouse IgG is specifically captured by the anti-mouse IgG patterned areas, showing that the biofunctionalities are well retained after the bionanopatterning process.	72
5.8	Nanostencil lithography allows us to fabricate structures composed of various shapes, dimensions and materials. SEM images of a) circular gold nano-antenna arrays with 200 nm diameter and 600 nm period in triangular lattice, b) gold nanowires with uniform 350 nm width and 50 μ m length, c) gold nanorod arrays are shown. All structures are fabricated on silicon using NSL.	75
5.9	Dimers such as sharp edged bow-ties and asymmetric oligomers with inter particle spacings as small as 25 nm could be fabricated using NSL.	76

5·10	(a) SEM image of 300 nm circular gold nano dots with 500 nm periodicity on ITO covered glass. (b) Optical response of the structures in dark field shows strong resonances with narrow linewidths which is suitable for biosensing and photovoltaics	79
5·11	Reflectance spectra of randomly distributed nanorods a) on calcium fluoride and b) on glass substrate are shown. Legends indicate the rod lengths. CaF_2 substrate supports plasmonic resonances at shorter wavelengths and shows stronger resonances with narrower linewidths compared to the glass. c) Fundamental ($m = 1$) resonance wavelength on glass (red squares) and on CaF_2 (blue circles) substrates are linearly dependent on the rod length (dashed lines are linear fit). Effective refractive index calculated to be 1.64 for glass and 1.42 for CaF_2 are close to the actual values.	80
6·1	Flexible plasmonics and metamaterials on polymeric and non-planar substrates are demonstrated using nanostencil lithography. For the first time, high-resolution fabrication with 10 nm accuracy is achieved at high-throughput and low-cost in a single fabrication step. Remarkable precision is illustrated by fabricating sub-100 nm plasmonic particles with sub-50 nm interparticle distances. We showed optical tuning with mechanical stretching of the polymer substrate. We also showed patterning of nanostructures on curved surfaces, including optical fibers.	83
6·2	Comparison of PEEL (Henzie et al., 2007) with NSL.	85

6.3	Illustration and representative SEM images of functional plasmonic structures. Gap between substrate and stencil plays an important role for fabrication of high quality structures using Nanostencil Lithography (b). Using bowtie shaped stencil (SEM image seen at (a)), bowtie particles with sharp edge profiles and sub-50 nm gap distance could be obtained (AFM image seen at (c)) on flexible, stretchable, biocompatible, non-planar substrates. These substrates could be used to tune optical properties of plasmonic structures by applying mechanical strain (d). Also flexible films can be directly transferred (e) and wrapped around non-planar surfaces (f).	87
6.4	Blurring description. B_G occurs due to the shadowing effect and B_H (halo) occurs due to the materials diffusion on the substrate. The material halo surrounding the central structure is difficult to observe because it is an evanescent and very thin layer. Concerning the halo-blurring, currently there exists no model to estimate B_H due to the lack of analysis and understanding of the halo. Adapted from (Mena, 2010)	89

6.5	(a) SEM image of the stencil mask. (b) The gap between the stencil and the substrate will sacrifice the resolution. Evaporated gold goes under the stencil due to the gap, forming shadow parts. In addition, diffusion occurs on substrate beyond the shadows, resulting in a halo around the structure. (c)-(d) SEM images of the structures deposited on a Si substrate and on the PDMS substrate. Tapered structures and halo can be seen from the inset in (c) for Si substrate. Structures on PDMS, on the other hand, well replicate the apertures on stencil and have sharp edges due to the elimination of the gap effect. (e)-(f) 3D AFM images of the structures deposited on the Si substrate and on the PDMS substrate. (g)-(h) Line profiles obtained from AFM for the structure deposited on Si substrate and on PDMS substrate. Compared to the particles on PDMS, structures on Si have tapered wall profile with less height than evaporated due to the non-directional evaporation and the stencil-substrate gap.	91
6.6	(a) SEM image of a bowtie stencil mask. The triangles have side lengths of 645 nm and the dimer separation is about 55 nm. (b) SEM image of bowtie structures fabricated on PDMS substrate. Structures well replicate the stencils down to 10 nm accuracy. (c) AFM images of bow-tie particles shown in (b). The interparticle distance is measured to be 40 nm on average. Sharp edges and small bowtie gaps are confirmed.	95

- 6.7 (a) SEM image of the nanostencil used (top) and AFM images of the resultant bowtie antennas on PDMS, resonant at visible wavelengths (bottom). Scale bar represents 200 nm. For the nanostencil, the separation distance within the dimer is 25 nm and the side length of a triangle is 100 nm. Bowtie antennas have 35 nm interparticle distance and 85 nm side lengths. (b) Experimentally measured optical spectrum of the bowtie antenna arrays with 85 nm side lengths and interparticle distance changing from 25 nm to 45 nm. Clear red shift of resonance is observed with decreasing the bowtie gap by 10 nm. (c) Numerical calculations of bowtie antennas with the same dimensions as that of the fabricated ones. These calculations confirmed the experimentally obtained resonance locations and the shifts due to the interparticle distance changes. Inset shows charge distribution on bow-tie particles at resonance 97
- 6.8 (a) Transmission spectra of plasmonic antennas with $1.6\ \mu\text{m}$ periodicity and lengths varying from $1\ \mu\text{m}$ to $1.2\ \mu\text{m}$ on $5\ \mu\text{m}$ thick parylene-C film. With increasing antenna length, red shift of resonance is observed. (b) Transmission spectra of plasmonic antennas on $5\ \mu\text{m}$ thick parylene-C with $1\ \mu\text{m}$ length and periodicities indicated in legend. (c) Transmission spectra of materials used in Mid-IR regime. Polymeric substrates show characteristic absorption bands around $3000\ \text{cm}^{-1}$ due to $C-H$ bond stretch. For all spectra, Fourier decomposition technique is utilized in order to remove the interference fringes resulting from thin films. 99

6-9	(a) SEM image of nanorod antenna arrays on PDMS. Rods are 945 nm in length, 240 nm in width and separated by P, 1.51 μm (b) SEM image of the antenna arrays when mechanical force is applied on PDMS. The substrate is stretched, resulting in a homogeneous periodicity change along the direction of the applied force. The period is enlarged by 21.3 % to $P'=1.83 \mu\text{m}$. (c) SEM images of the antenna arrays when the force is removed. Nanorods return to their initial position without being damaged.	102
6-10	Measured and calculated (dashed) transmission spectra of nanorod arrays with 1.5 μm periodicity, 1200 nm length on a 13 μm thick LDPE film before (blue curve) and after stretching (red curve) are shown. Once the film is stretched (red curve) due to the increase in periodicity only along the direction of the applied force, resonance red shifts by 160 nm. Inset shows a resonance shift for 16 % strain on LDPE with 900 nm long gold nanorod arrays (with 1.8 μm periodicity).	103
6-11	Optical microscope images of a fiber optic cable covered with a flexible 10 μm thick parylene-C film patterned with circular gold particles of 2 μm diameter and 10 μm periodicity. Inset shows the same fiber under a lower magnification. The patterned flexible film can be easily wrapped on a curved surface without damaging the plasmonic area.	105
7-1	Engineered and precisely arrayed nanoantennas manufactured by low cost nanostencil lithography enable plasmonically enhanced vibrational biospectroscopy. These nanoantennas fabricated by reusable stencils lead to strong near field enhancements over large area. Antibody assays and detection of immunologically important small sized proteins with high absorption signals are demonstrated.	109

7.2	Nanostencil lithography is used for low cost nanofabrication of plasmonic antenna arrays. a) Gold deposition scheme is illustrated. Stencil shadows the deposited material. Due to finite gap between stencil and substrate nanoparticle clusters surrounds the nanoantennas. b) SEM images of the nanoapertures on the reusable 100 nm thick SiN stencil. Apertures have 1100 nm length and 250 nm width c) SEM image of gold nanoantennas fabricated on silicon substrate using the nanoapertures shown in b). Gold nanoparticle clusters are scattered around the nanorods.	111
7.3	SEM images of a) NSL fabricated nanorod antenna arrays. b) and c) show SEM images of nanorod arrays after post-processing with dry etch and wet etch, respectively. Dry etch post-processing is reliable for obtaining well-defined nanostructures with uniform surface. Wet etch post-processing heavily damages the nanorod antenna	113
7.4	Finite-difference time-domain calculations on a) NSL fabricated b) post-processed nanorod antenna arrays. NSL fabricated nanorods are simulated by incorporating nanorods with tiny nanoparticles (10 and 20 nm diameter) at the gold-silicon interface ($z = 0$). On the left column, field intensity distributions are shown at $z=0$, at 6 μm wavelength for both antenna arrays. NSL fabricated nanorods show an order of magnitude higher field enhancement. The total field-enhanced area calculated around the three-dimensional structures is three times larger for NSL fabricated nanorods. The right column shows the cross sections ($y = 0$) of the simulated designs.	114

7.5	Plasmonically enhanced biospectroscopy of protein A/G monolayer and antibody (IgG) is shown. a) Reflectance spectra of NSL fabricated nanorods before protein binding (black dotted curve), after protein A/G (blue solid) and after antibody (red solid) are shown. Inset show SEM image of NSL fabricated nanorod. b) Reflectance spectra of post-processed nanorod antenna arrays before and after proteins are shown. After antibody immobilization stronger dip is observed for both NSL fabricated and post-processed nanorods. Inset shows the SEM image of the post-processed nanorod. c) Reflectance difference between the spectra of nanorod antennas before and after protein A/G binding is shown for both nanorods. Peaks here correspond to the dips in a) and b). Signal due to amide I is almost three times higher for NSL fabricated nanorods. d) Reflectance difference after antibody binding (IgG) on protein A/G is shown for both nanorods. Similarly, signal due to amide I is almost three times higher for NSL fabricated nanorods.	118
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List of Abbreviations

AFM		Atomic Force Microscopy
DNA		Deoxyribonucleic Acid
E-Beam		Electron Beam
EBL		Electron Beam Lithography
FDTD		Finite Difference Time Domain
FIB		Focused Ion Beam
FTIR		Fourier Transform Infrared
IR		Infrared
LDPE		Low-Density Polyethylene
LSPR		Localized Surface Plasmon Resonances
MCT		Mercury Cadmium Telluride
NSL		Nanostencil Lithography
PBS		Phosphate Buffer Solution
PDMS		Polydimethylsiloxane
PMMA		Polymethylmethacrylate
RIE		Reactive Ion Etching
SEIRA		Surface Enhanced Infrared Absorption
SPP		Surface Plasmon Polariton
SPR		Surface Plasmon Resonance

Chapter 1

Introduction

1.1 Motivation

Nanotechnology is the natural continuation of the miniaturization revolution that has been witnessed over the last decades enabling the construction of elegant devices for human needs (Ramsden, 1990). It can be defined as engineering at a very small scale, and this term can be applied to all areas of research and development from medicine to manufacturing to computing. Nanotechnology keeps on pushing the limits of miniaturization, and many electronic devices we see today have nano features that can do more and cleverer things, use less raw materials and consume less energy (Bhushan, 2004). There are many examples of the application of nanotechnology from the simple to the complex; enabling nanotechnology to become one of the research area that is truly multidisciplinary (Schummer, 2004). Bio nanotechnology, similarly a highly interdisciplinary approach involving scientists from physics, chemistry, biology and engineering, is a new and rapidly advancing field of research lies at the interface between biology and nanotechnology (Taton, 2003). The goal of bionanotechnology is to study nanoscale phenomena associated with biological molecules and to develop new technologies based on these materials. For example, proteins have an impressive range of physical and functional properties depending upon their structure such as molecular recognition (Bosshard, 2001). Bionanotechnology aims to exploit these attributes to create new materials, sensors for medical and security applications (Spichiger-Keller, 2008), hybrid bio-electronic devices (Angione et al., 2011) and even

biologically inspired nanomachines (Nakano, 2011). Bionanotechnology has enabled novel developments and possibilities for biology and biomedical applications (Langer and Peppas, 2004; Prasad, 2004). In particular, the use of photonic techniques has recently contributed for innovation of incredible biomedical applications (Zia et al., 2006). Photonics is one of the fastest growing high-tech industries in the world today. It includes optical communications, optical imaging, optical data storage and optical computing, optical detectors, lasers and quantum optics (Yariv and Yeh, 2006). Among those, spectroscopy (e.g., chemical and biological detection, anti-terror detection) and biosensing has generated significant attraction in photonics community due to remarkable sensitivities obtained with simple, very miniaturized devices that are comparable to other state of the art methods (Kabashin et al., 2009). As a sub branch of photonics, plasmonics has become particularly promising for obtaining highly efficient optical biosensors (Zhao et al., 2006). Nanostructured metals can interact with light through the excitation of surface plasmons and offer much versatile and powerful detection methodologies by localizing the light below the diffraction limit and dramatically enhancing the local fields (Ebbesen et al., 1998; Liu et al., 2011). Plasmonic nanostructures can act as very efficient optical antennas and serve as optical transmitters and receivers (Novotny and van Hulst, 2011). By producing dramatically enhanced near field intensities confined to sub diffraction volumes, they can enable light bio-molecule interactions at extreme (Adato et al., 2009).

Given that plasmonics has been extensively used in photonics and nanotechnology community, new fabrication technologies for high resolution patterning at large scale and low costs, with single fabrication step and compatible with a wide range of materials has become crucial for the progress of the field. Especially the need of nanofabrication on flexible substrates for future device configurations in/on human body brings up questions about existing nanofabrication choices. Within the last

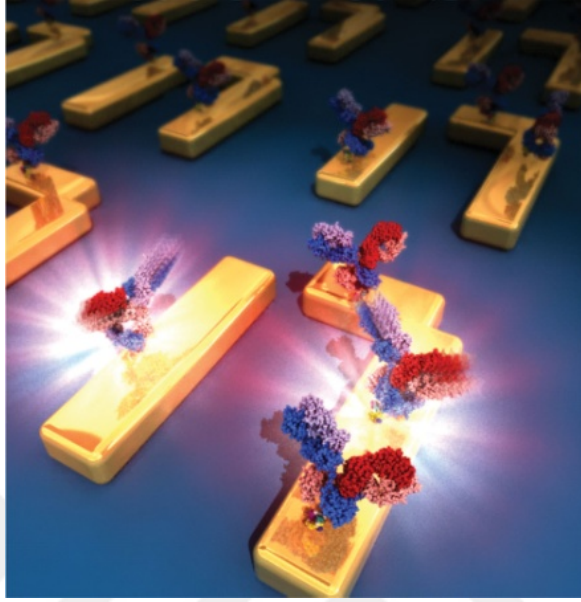


Figure 1.1: Metallic nanostructures used for probing the protein interactions through vibrational spectroscopy

decade, significant progress has been achieved in flexible electronics (Sun and Rogers, 2007). Broad range of novel systems including electronic paper-like display devices (Gelinck et al., 2004), artificial skin applications (Someya et al., 2004), conformal electronics for in-vivo brain monitoring (Kim et al., 2010a), electronic eye-type imagers (Ko et al., 2008) have been demonstrated. Contrary, there is very limited progress with photonics, particularly at dimensions relevant to nanoplasmonics operating in visible and infrared frequencies. This is mainly because we can not utilize traditional nanofabrication techniques for fabricating nanophotonic structures on flexible, non-planar and mechanically compliant surfaces. Soft lithography techniques that are used in flexible electronics is also limited by resolution and do not offer precise and high throughput fabrication at dimensions that are relevant to nanophotonics. All these drawbacks and the others that will be explained later have fueled the research on flexible nanofabrication methods.

In order to extend the capabilities of nanotechnologies to elegant materials and

facilitate their integration for device fabrication, current techniques need to be complemented with new technologies for nanofabrication. State of the art nanofabrication techniques based on top down or bottom up methods could fabricate nanostructures at high resolutions below 10 nm (Gates et al., 2004). Both approaches have been providing crucial contributions to potential applications of nanoscale structures. However, these techniques are mostly limited to certain materials and environments. In order to extend the capabilities of nanofabrication and integrate these capabilities for existing device fabrication schemes, bottom up and top down techniques need to be combined for developing new fabrication technologies. Among such new technologies, nanostencil lithography offers important advantages for nanopatterning with its single step processing and large compatibility with different materials that can overcome the limitations of existing nanofabrication methods. This thesis research investigates Nanostencil Lithography for systematic nanofabrication of plasmonic/photonic technologies as well as metamaterials at sub-100 nm resolution for bio detection and vibrational spectroscopy (Aksu et al., 2010; Aksu et al., 2011; Huang et al., 2012; Aksu, 2013). Nanostencil lithography is a parallel and versatile technique based on the simple principle of shadow masking that has demonstrated its capability for nanopatterning. The method relies on direct deposition of materials through a pre-patterned mask (Rácz and Seabaugh, 2007). The deposited material could be metallic, dielectric and organic. The mask, which acts as a stencil, is fabricated on suspended silicon nitride membrane. The stencils containing large numbers of nanoapertures/nanoslits with variety of shapes, sizes and arrangements can be fabricated on wafer scale for high throughput nanofabrication applications. When placed in contact on a desired substrate, direct deposition of materials (such as noble metal) enables lift-off free production of nanoparticles and nanowires with high reliability and uniformity. Since NSL does not require any resists, it has the advantage

of reducing the fabrication steps and allowing the patterning on different types of substrates. Another advantage of NSL is that the masks can be reused to pattern the same nanostructures multiple times with minimal effort. It is shown that NSL fabricated nanostructures have identical responses when compared to that of EBL fabricated ones (Aksu et al., 2010). As many other techniques, NSL offers important advantages. However, there are issues we have to consider for higher resolutions. Stencil lithography still faces the issue of the blurring, nanoparticle scattering around the deposited nanostructure, related to the inherent gap between the stencil and the substrate (Vazquez-Mena et al., 2008). The blurring is the main limiting factor for the resolution in stencil lithography at the nanoscale. In order to fully exploit the capabilities of stencil lithography for nanopatterning, it is required a further development of the technique and the demonstration of the functionality and applications of nanostructures deposited through stencils. In this thesis work, we demonstrate a way to solve the blurring problem by eliminating the inherent gap problem using polymeric substrates. Moreover, we present a post processing method to removed blurring on conventional rigid substrates and obtain well-defined nanostructures. Finally, we demonstrate the first application of NSL fabricated infrared antenna arrays for plasmonically enhanced vibrational biospectroscopy. Using NSL fabricated arrays we present detection of immunologically important proteins as small as 3nm and perform antibody assays with high sensitivity. The presented results introduce nanostencil lithography as low cost manufacturing method used as spectroscopy toolkit for biology, medicine pharmacology.

1.2 What is Nanostencil Lithography?

Stencil technique is well known in macro-world for arts and crafts, and decorative painting. Stencils are made to transfer a single pattern, like alphabet stencils. The

first use of stenciling technique dates from 13,000 to 9,000 years ago on the walls of Cave of the Hands located in the province of Santa Cruz, Argentina (Gansser, 1995). The age of the paintings was calculated from the remains of bone-made pipes used for spraying the paint on the wall of the cave to create silhouettes of hands. Stencil paintings of hands were common throughout the prehistoric period. Stencils may have been used to color cloth for a very long time. In Europe, from about 1450 they were commonly used to color old master prints printed in black and white, usually woodcuts. This was especially the case with playing-cards, which continued to be colored by stencil long after most other subjects for prints were left in black and white. Stencils were used for mass publications, as the type didn't have to be hand-written (Kafka, 1973). In positive stencils, first apertures complementary to the shape of the desired pattern are cut out and then paint, ink, or another agent is applied through the apertures. Here, the stencil behaves like a mask and shadows the applied agent around the pattern, at the end giving the shape complementary to the apertures. Nanostencil lithography is basically exploiting the same notion at nano-scales. For example, to create gold nanorod antenna arrays, we fabricate a nanostencil with rectangular shaped nanoaperture arrays, place on a substrate and then deposit gold through the nanoapertures. When the nanostencil is removed, we get gold nanorod particles on our substrate with shapes complementary to the nanoapertures used in the stencil.

The nanostenciling process could be divided in two parts: preparation of nanostencils and deposition of gold through the nanoapertures of the stencils. We generate our stencils on mechanically robust thin suspended silicon nitride membranes using photolithography and consecutive dry and wet etching techniques. The suspended membranes are then patterned by nanoapertures using EBL. Once we get the nanoapertures, stencil is directly placed on the substrate and secured tightly with



Figure 1.2: On the left, Ancient Hands Stencil Paintings, Rio Pinturas Canyon, Cave of the Hands, Patagonia, Province of Santa Cruz, Argentina. The art in the cave dates from 13,000 to 9,000 years ago. In the middle regular alphabet stencil used in arts is shown. On the right SEM image of sub-micron stencil for nanofabrication is shown.

clips. Directional gold deposition is performed over the stencil. When the mask is removed from the substrate, it leaves plasmonic nanostructures on the substrate with the shapes complimentary to the nanoapertures. Distinct feature of this technique is that any pattern will be transferred positively to any surface in a single-step process. Existing nanolithography techniques use resist base patterning, which means extra chemical lift-off process is needed. The deposited structures can either be used directly, transferred into a sub-layer, combined by lift-off processes, or refined by self assembly or other growth processes. More importantly, like stencils in macro-world, nanostencils used for deposition are mechanically robust and can be cleaned and reused multiple times for fabrication of the same antenna arrays. This capability is particularly useful when high-throughput replication of the optimized nanoparticle arrays is desired. Series of plasmonic nanoantenna arrays created from a single nanostencil gives nearly identical optical responses. These specifics make the stencil method applicable to surfaces that are either mechanically unstable, such as cantilevers and membranes, and/or functionalized for e.g. bio-sensor applications (Aksu et al., 2010).

Another important advantage of NSL, some substrates are so sensitive that their deposition has to be the very last process step. For example the application of pho-

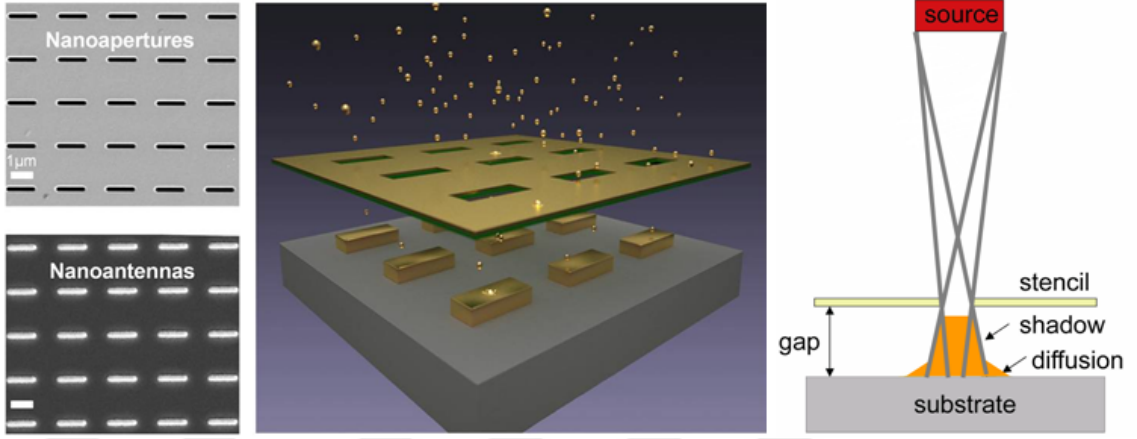


Figure 1-3: Illustration of Nanostencil Lithography.

toresist on some polymeric substrates and thin films is not possible since the organic solvents used for lift off process have detrimental effects on substrates. This makes the usage of conventional lithography techniques impossible on this kind of substrates. Another reason for using stencil masks is that wafer topology may not allow photoresist spinning on pre-patterned surfaces such as wafer holes or free standing cantilevers, graphene sheets. And the shadow mask saves a lot of process steps including resist spinning, baking, exposure, development, rinsing and drying. In theory any hole larger than atomic size can be used as shadow masks but minimum dimension possible with shadow mask are in the 10 nm range. One special limitation of the shadow masks is the impossibility of donut shaped structures. There are tricks around this by using very narrow bridges and relying on deposition diffusion under the mask donut shapes can be patterned. The general solution is to perform shadow mask deposition twice with half masks (Mena, 2010).

1.3 Objectives

This thesis research investigates Nanostencil Lithography for systematic nanofabrication of plasmonic/ photonic technologies as well as metamaterials at sub-100 nm

resolution. The aim is to use NSL fabricated low cost plasmonic infrared sensors for bio detection and vibrational spectroscopy. The important aspects of this thesis are:

- 1) Nanofabrication of metallic nanostructures using the nanostencils over conventional semiconductor substrates and investigating the pattern transfer phenomena.
- 2) Overcoming the resolution constraints of nanostencil lithography and nanofabrication at sub-100 nm with a resolution close to standard e-beam lithography over challenging substrates.
- 3) Investigating the versatility of the NSL with different deposition materials, different substrates and various design preferences.
- 4) Theoretical investigation and optical characterization of NSL fabricated plasmonic nanostructures and metamaterials over polymeric and non planar substrates. Investigating mechanically tunable optical materials.
- 5) Application of NSL fabricated antenna arrays for biosensing and plasmonically enhanced vibrational spectroscopy.

1.4 Thesis Content and Organization

This thesis is organized in eight chapters. This first chapter has presented the need of NSL with a brief overview and the objectives of this work. In chapter 2, physical origin of plasmons on metallic nanoparticles is analyzed. Chapter 3 presents an overview of the current nanopatterning methods and the details of nanostencil lithography. Chapter 4 presents a study on the high-throughput nanofabrication of infrared nanorod antenna arrays for vibrational nanospectroscopy applications. Chapter 5 presents the compatibility of the nanostencil lithography to a variety of environments (different deposited materials, substrates and designs, etc.). Chapter 6 presents flexible plasmonics and metamaterials on unconventional and non-planar substrates using nanostencil lithography, allowing mechanically tunable optical materials. Chapter 7

presents plasmonically enhanced vibrational biospectroscopy using low-cost infrared antenna arrays manufactured by nanostencil lithography. Finally, chapter 8 presents the summary, conclusions and outlook of this work.



Chapter 2

Plasmonics: Fundamental Science and Novel Device Technologies

2.1 Introduction

The second chapter of the thesis is presented to discuss the physical origin of plasmon resonances in metallic nanoparticles, to describe their basic properties and to outline the approach to the study of plasmon resonances adopted in this thesis.

Nanostructured metals show very complex and interesting optical properties. The most striking phenomenon encountered in these structures are electromagnetic resonances due to collective oscillations of the conduction electrons termed plasmons. Plasmon modes exist mostly in noble metals such as gold and silver. Under certain circumstances plasmons are excited by light, which leads to strong light scattering and absorption and an enhancement of the local electromagnetic field. The interest in plasmon modes dates back to the beginning of the 20th century (Mie, 1908), but recent advances in structuring, manipulating and observing on the nanometer scale have revitalized this field (Ebbesen et al., 1998). Even though these technological advances were at first driven by the increasing demand for semiconductor based integrated electronic components, optical applications are now receiving increasing attention. Guiding light in integrated optical systems interfacing with electronic components and enabling compact, low cost virus/cancer biodetection systems remain important challenges for research and development today. Nanostructured metals are believed

to be one of the key ingredients of such future optoelectronic devices. In the next part of this chapter, a theoretical background on plasmonics and localized surface plasmon resonances will be provided. The equations presented demonstrate the basic principles of nanoparticle antennas and the theory behind their use for bio and chemical sensing. In the last part, some examples of leading plasmonic applications related to this thesis such as surface enhanced spectroscopy, biosensing, energy harvesting will be presented.

2.2 Theoretical Background on Localized Surface Plasmon Resonances

Electromagnetics of Metals

The interaction of metals with electromagnetic fields can be understood in a classical framework based on Maxwell's equations (Maier, 2007). As is well known from everyday experience, for frequencies up to the visible part of the spectrum metals are highly reflective and do not allow electromagnetic waves to propagate through them. In this low-frequency regime, the perfect or good conductor approximation of infinite or fixed finite conductivity is valid for most purposes, since only a negligible fraction of the impinging electromagnetic waves penetrates into the metal. At higher frequencies towards the near-infrared and visible part of the spectrum, field penetration increases significantly, leading to increased dissipation, and prohibiting a simple size scaling of photonic devices that work well at low frequencies to this regime. Finally, at ultraviolet frequencies, metals acquire dielectric character and allow the propagation of electromagnetic waves depending on the details of the electronic band structure. Alkali metals such as sodium have an almost free-electron-like response and thus exhibit an ultraviolet transparency. For noble metals such as gold or silver on the other hand, transitions between electronic bands lead to strong absorption in

this regime. These dispersive properties can be described via a complex dielectric function $\epsilon(\omega)$.

Metals in optical frequencies are generally characterized by a Drude + Lorentz model but for simplicity we will assume a Drude model which characterizes the permittivity of the metal as

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (2.1)$$

where ω_p is defined as plasma frequency of metal and γ is the Drude damping parameter which is linked to the inherent ohmic loss in the metal. The real and imaginary components of this complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ are given by

$$\epsilon_1(\omega) = 1 - \frac{\omega_p^2\tau^2}{1 + \omega^2\tau^2} \quad (2.2)$$

$$\epsilon_2(\omega) = \frac{\omega_p^2\tau}{\omega(1 + \omega^2\tau^2)} \quad (2.3)$$

where $\gamma = 1/\tau$. It is insightful to study 2.1 for a variety of different frequency regimes with respect to the τ . We will omit ourselves here to frequencies $\omega < \omega_p$. For frequencies close to ω_p , the product $\omega\tau \gg 1$, leading to negligible damping. Here, $\epsilon(\omega)$ is predominantly real and

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad (2.4)$$

We consider next the regime of very low frequencies, where $\omega \ll \tau^{-1}$. Hence, $\epsilon_2 \gg \epsilon_1$, and the real and the imaginary part of the complex refractive index are of comparable magnitude with

$$n \approx \kappa = \sqrt{\frac{\epsilon_2}{2}} = \sqrt{\frac{\tau\omega_p^2}{2\omega}} \quad (2.5)$$

κ is called the extinction coefficient and determines the optical absorption of electromagnetic waves propagating through the medium. In this region metals are mainly

absorbing, with an absorption coefficient of

$$\alpha = \left(\frac{2\omega_p^2 \tau \omega}{c^2} \right)^{1/2} \quad (2.6)$$

At higher frequencies ($1 \leq \omega\tau \leq \omega_p\tau$), the complex refractive index is predominantly imaginary (leading to a reflection coefficient $R \approx 1$) (Jackson, 1999).

Metal-Insulator Interfaces

Surface plasmon polaritons are electromagnetic excitations propagating at the interface between a dielectric and a conductor, evanescently confined in the perpendicular direction (Maier, 2007). These electromagnetic surface waves arise via the coupling of the electromagnetic fields to oscillations of the conductor's electron plasma. We assume a harmonic time dependence $E(r, t) = E(r)e^{i\omega t}$ of the electric field that yields to *Helmholtz Equation* (Equation 2.7) where $k_o = \omega/c$ is the wave vector of the propagating wave in vacuum.

$$\nabla^2 E + k_o^2 \epsilon E = 0 \quad (2.7)$$

Specifically the waves propagate along the x-direction of a cartesian coordinate system, and show no spatial variation in the perpendicular, in-plane y-direction (Figure 2.1). The plane can now be described as $E(x, y, z) = E(z)e^{i\beta x}$ where parameter $\beta = k_x$ is called the propagation constant of the traveling waves and corresponds to the component of the wave vector in the direction of propagation. Inserting this into Helmholtz equation yields

$$\frac{\partial^2 E(z)}{\partial z^2} + (k_o^2 \epsilon - \beta^2) E = 0 \quad (2.8)$$

Solving Equation 2.8 in both half spaces ($z > 0, z < 0$) and utilizing the Drude model (Equation 2.1) for permittivity of the metal will result in the dispersion relation of

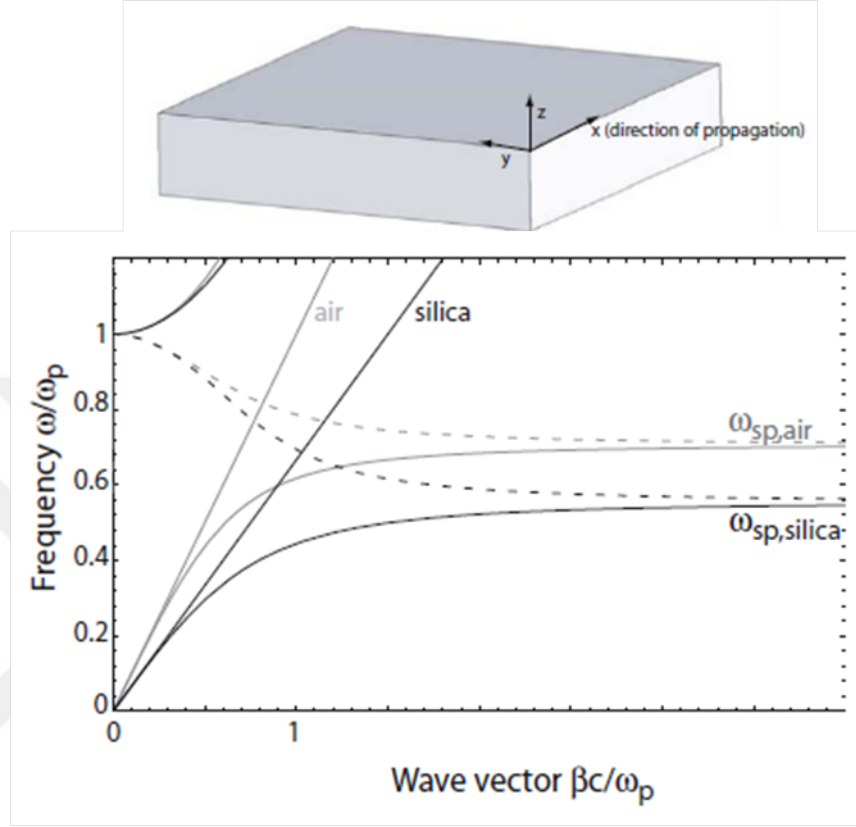


Figure 2.1: On the top propagation geometry is shown. Wave propagate along the x-direction. Bottom shows the dispersion relation of SPPs at the interface between a Drude metal with negligible collision frequency and air (gray curve) and silica (black curves) (Maier, 2007)

SPPs

$$\beta = k_o \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \quad (2.9)$$

where ϵ_1 and ϵ_2 are the permittivities of two materials. Continuity of the wave demands $\text{Re}[\epsilon_1] < 0$ if $\epsilon_2 > 0$ which means the surface waves exist only at interfaces between materials with opposite signs of the real part of their dielectric permittivities, i.e. between a conductor and an insulator.

SPPs propagating at the flat interface between a conductor and a dielectric are essentially two-dimensional electromagnetic waves. Confinement is achieved since the

propagation constant is greater than the wave vector k in the dielectric, leading to evanescent decay on both sides of the interface. The SPP dispersion curve (Figure 2.1) therefore lies to the right of the light line of the dielectric (given by $\omega = ck$), and excitation by three-dimensional light beams is not possible unless special techniques for phase-matching are employed. The mismatch in wavevectors can be overcome by several methods such as prism coupling (O'Hara et al., 2005), patterning the metal surface with a shallow grating of grooves or holes with lattice constant (Hooper and Sambles, 2002)

Localized Surface Plasmon Resonances

SPPs are propagating, dispersive electromagnetic waves coupled to the electron plasma of a conductor at a dielectric interface. Localized surface plasmons on the other hand are non-propagating excitations of the conduction electrons of metallic nanostructures coupled to the electromagnetic field (Maier, 2007). These modes arise naturally from the scattering problem of a small, sub-wavelength conductive nanoparticle in an oscillating electromagnetic field. The curved surface of the particle exerts an effective restoring force on the driven electrons, so that a resonance can arise, leading to field amplification both inside and in the near-field zone outside the particle. This resonance is called the localized surface plasmon or short localized plasmon resonance. Another consequence of the curved surface is that plasmon resonances can be excited by direct light illumination, in contrast to propagating SPPs.

The interaction of a particle of size d with the electromagnetic field can be analyzed using the simple *quasi-static approximation* provided that $d \ll \lambda$ meaning the particle is much smaller than the wavelength of light in the surrounding medium.

The electrostatic nature of plasmon resonances in nanoparticles and their negative dielectric permittivity suggest the enhancement of local electric fields inside nanoparticles and their vicinities as follows. Consider an example of a spherical nanoparticle

with negative permittivity ϵ subject to uniform external field E_0 (Figure 2.2(a)). Since $\epsilon < 0$, the polarization vector P has the direction opposite to E_0 and this results in surface electric charges which create the depolarizing field E' with the same direction as E_0 . This naturally leads to the enhancement of the total electric field $E = E_0 + E'$ inside the spherical nanoparticle. To better appreciate this fact, it is instructive to consider the case of a spherical nanoparticle with positive permittivity (Figure 2.2(b)) where the depolarizing field E' results in the attenuation of the external field E_0 .

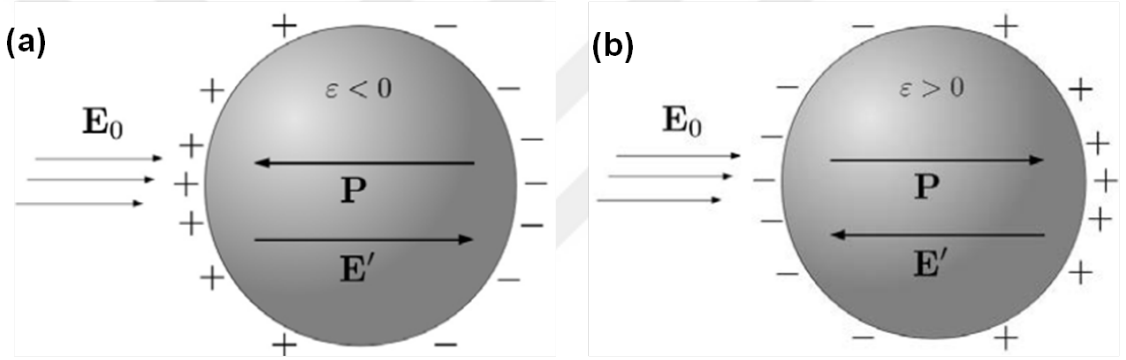


Figure 2.2: a spherical nanoparticle with (a) negative and (b) positive permittivity (ϵ) subject to uniform external field

In the electrostatic approach, the total field E_{tot} is found solving the equation for the potential, $\nabla^2 V = 0$, and then from its gradient, $E = -\nabla V$. For a spherical particle in the presence of a uniform field $E_o = E_o \hat{z}$, the solution in spherical coordinates to the potential equation involves the Legendre polynomials. The solutions for the field E inside and outside the sphere could be calculated and written as a function of dipole induced in the sphere (Jackson and Fox, 1999; Mena, 2010)

$$E_{out} = E_o + \frac{3\vec{n}(\vec{n} \cdot \vec{p}) - \vec{p}}{4\pi\epsilon_o\epsilon_{air}r^3} \quad (2.10)$$

where

$$\vec{p} = 4\pi\epsilon_o\epsilon_{air}R^3 \frac{\epsilon_{sph} - \epsilon_{air}}{\epsilon_{sph} + 2\epsilon_{air}} E_o \quad (2.11)$$

Here R is the radius of the sphere. The polarization expressed in Equation 2.11

shows resonance enhancement at the condition

$$Re[\epsilon_{sph}(w) + 2\epsilon_{air}] = 0 \quad (2.12)$$

The imaginary part for the dielectric function of a dielectric material is normally negligible.

$$Re[\epsilon_{sph}(w)] = -2\epsilon_{air} \quad (2.13)$$

The application of LSP in nanoparticles for sensing applications is based in Equation 2.13. The resonance condition depends on the dielectric constant of the surrounding media. Any change in the surrounding media ϵ_{air} would lead to a change in the required ϵ_{sph} for resonance and hence in the resonance wavelength λ_R . van Duyne et al. approximate the shift in λ_R with a linear relation on the refractive index (Willems and Van Duyne, 2007)

$$\Delta\lambda_R = m(\Delta n)(1 - e^{2d/l_d}) \quad (2.14)$$

where m is the sensitivity factor, n is the refractive index of the surrounding, d is the effective thickness of the adsorbed layer surrounding the particles and l_d the electromagnetic field decay length. Similarly, the binding of biomolecules to metallic nanoparticles produce a change in the dielectric environment, which produces a shift in the resonance wavelength of the LSPR (Mena, 2010).

Equation 2.13 is valid only for spherical particles much smaller than the wavelength. For a general shape it could be corrected as

$$Re[\epsilon_{particle}(w)] = -\chi\epsilon_{air} \quad (2.15)$$

where χ depends on the shape and aspect ratio of the particle (Mena, 2010).

So far, only the electrostatic case approximation has been treated. However, when

the light illuminates a particle, the oscillating motion of the electrons will produce a radiative field and a scattering of the incoming light plane wave (Jackson and Fox, 1999). The complete electrodynamic solution within an array can be calculated by using either the retarded potential of a dipole or using the vector potential of an oscillating dipole. Then Equation 2.10 gets transformed into an expression including the radiative and oscillatory behavior.

$$E_{out} = E_o + \frac{1}{4\pi\epsilon_o\epsilon_{air}} \left[k^2 (\vec{n} \times \vec{p}) \times \vec{n} \frac{e^{ikr}}{r} + [3\vec{n}(\vec{n} \cdot \vec{p}) - \vec{p}] \left(\frac{1}{r^3} - \frac{ik}{r^2} \right) e^{ikr} \right] \quad (2.16)$$

The first term from the induced field with the $1/r$ dependance corresponds to the far-radiative field, whereas the second term with $1/r^3$ dependance correspond to the strong near field. This expression is important for nanoparticle arrays, where the particle interactions also determine the behavior of the localized surface plasmons. The distance r can be associated with the particle array periodicity P .

2.3 Applications

2.3.1 Surface Enhanced Vibrational Biospectroscopy

Mid-infrared (IR) absorption spectroscopy, in contrasts with numerous other biosensing methods, can directly probe molecular structure via bond specific vibrational modes and monitor structural changes even in the absence of any mass transfer. The technique is therefore a valuable tool for a wide range of applications critical for understanding basic biological function and important aspects of e.g. disease progression and treatment. Despite these attractive features, IR absorption spectroscopy is limited as its acquired signal depends on a molecular bonds intrinsic absorption cross-section and path length (via Beers Law). Sensitivity issues therefore restrict applications to a limited set of strong bands and/or relatively thick samples. Additionally, due to the strong absorption of water in the IR, measurements in fluid are

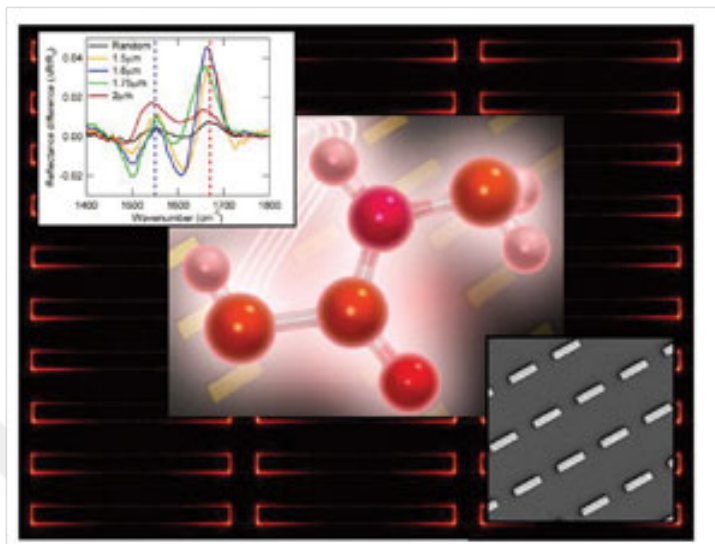


Figure 2.3: Plasmonic nanorods are shown to enhance the vibrational signals of biomolecules (Adato et al., 2009).

cumbersome, requiring specialized equipment and extremely high analyte concentrations. Plasmonic nanostructures supporting resonances at mid-IR wavelengths offer an attractive means with which to overcome many of these limitations. In particular, plasmonic resonances result in strongly enhanced near-field intensities confined to the surface of metallic particles, which allow one to dramatically increase the absorption signal of molecules (Figure 2.3)(Adato et al., 2009). This concept is termed SEIRA (Surface Enhanced Infrared Absorption Spectroscopy). In the chapter 7, we demonstrate surface enhanced vibrational biospectroscopy using NSL fabricated plasmonic infrared antenna arrays (Aksu, 2013).

2.3.2 Biosensing

Biosensors that take advantage of the plasmonic properties of noble metal films and nanostructures have emerged as an alternative by detecting changes in the reflectance intensity or angle of thin gold films (Riboh et al., 2003). They have been commercialized for nearly two decades and are commonly used to probe the kinetics and strength

of binding interactions (Sepúlveda et al., 2009). Localized SPR sensors, which employ noble metal nanoparticles, are increasingly used as an alternative to SPR sensors because the highly localized electromagnetic fields that occur at nanoparticle surfaces can enable improved detection of nanoscale biological analytes (Lesuffleur et al., 2007). LSPR sensors can sensitively monitor binding events in real time and have been used to detect a variety of processes, including self-assembled monolayer formation, protein-ligand and antibody-protein interactions, DNA hybridization, protein conformational changes, and gas detection (Haes et al., 2005). The spectral position of the nanoparticle extinction peak (λ_{max}) is highly dependent on the local refractive index at the nanoparticle surface. Biomolecule binding to specific surface-bound ligands changes the local refractive index, causing changes in the lambda max that are easily monitored using UV-visible spectroscopy. However, sensitivity losses arise when LSPR sensors utilize longer surface ligands and molecules, such as in the ELISA-style antibody sandwich binding, that place the detecting molecule far from the surface and outside the sensing volume (Wang et al., 2010).

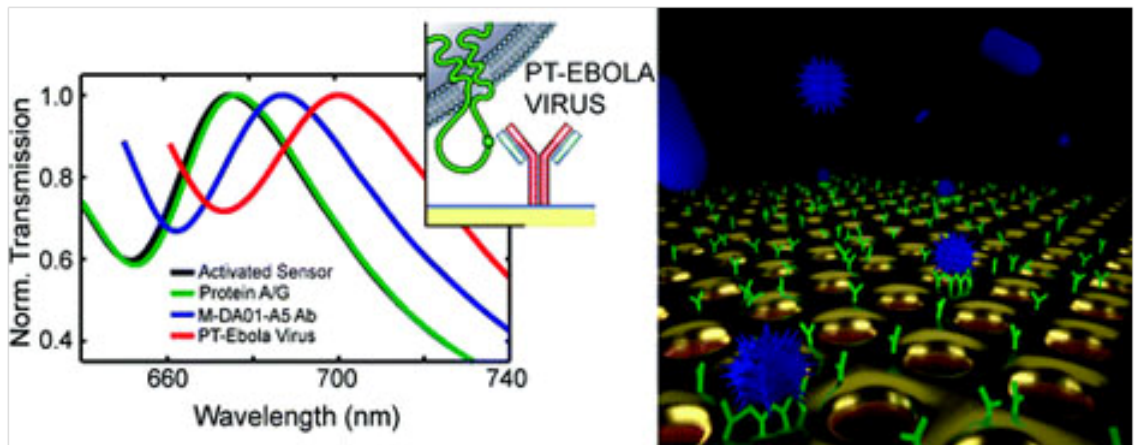


Figure 2-4: Plasmonic nanoholes are shown to detect live viruses from biological media using LSPR shifts (Yanik et al., 2010).

Several methods exist for enhancing the sensitivity of plasmonic sensors (Jain et al., 2008). Careful design of spectroscopic instrumentation can reduce noise levels

as low as 10^{-3} nm, enabling the detection of spectral shifts of only hundredths of nanometers (Nusz et al., 2009). Rational design of nanostructures can also lead to sensitivity improvements via narrowing of spectral linewidths and hence reduction of the standard deviation of resonance determinations (Liu et al., 2009).

2.3.3 Energy Harvesting

Photovoltaics, the conversion of sunlight to electricity, is a promising technology that may allow the generation of electrical power on a very large scale. Worldwide photovoltaic production was more than 5 GW in 2008, and is expected to rise above 20 GW by 2015 (Atwater and Polman, 2010). Photovoltaics could thus make a considerable contribution to solving the energy problem that our society faces in the next generation.

At present most of the solar-cell market is based on crystalline silicon wafers with thicknesses between 180-300 μm , and most of the price of solar cells is due to the costs of silicon materials and processing. Conventionally, photovoltaic absorbers must be optically thick to allow near-complete light absorption and photocarrier current collection. A large fraction of the solar spectrum, in particular in the intense 600-1100 nm spectral range, is poorly absorbed for 2 μm thick crystalline Si film. This is the reason that, for example, conventional wafer-based crystalline Si solar cells have a much larger thickness of typically 180-300 μm (Atwater and Polman, 2010). But high-efficiency solar cells must have minority carrier diffusion lengths several times the material thickness for all photocarriers to be collected, a requirement that is most easily met for thin cells. Solar-cell design and materials-synthesis considerations are strongly dictated by these opposing requirements for optical absorption thickness and carrier collection length.

Plasmonic structures can offer at least three ways of reducing the physical thickness of the photovoltaic absorber layers while keeping their optical thickness constant

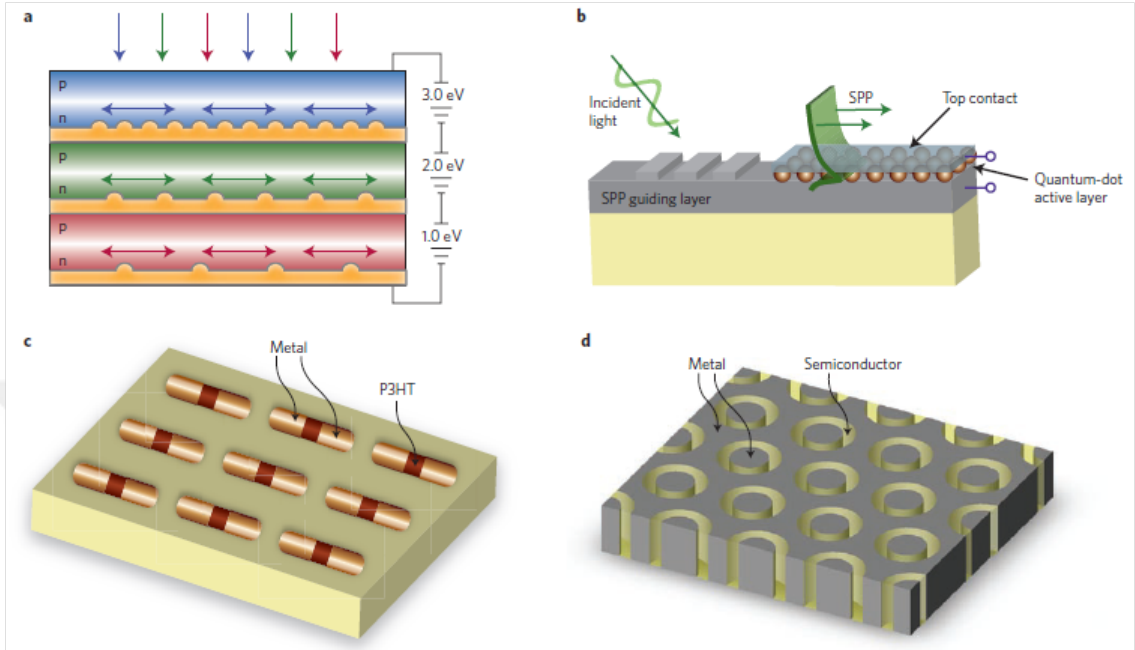


Figure 2.5: New plasmonic solar cell designs (Atwater and Polman, 2010). (a) Semiconductors with different bandgaps are stacked on top of each other. (b) Plasmonic quantum dot solar cell designed for enhanced photo absorption. (c) Optical antenna array made from an axial heterostructure. (d) Array of coaxial holes in a metal film.

(Figure 2.5) (Atwater and Polman, 2010). First, metallic nanoparticles can be used as subwavelength scattering elements to couple and trap freely propagating plane waves from the sun into an absorbing semiconductor thin film, by folding the light into a thin absorber layer. Second, metallic nanoparticles can be used as subwavelength antennas in which the plasmonic near-field is coupled to the semiconductor, increasing its effective absorption cross-section. Third, a corrugated metallic film on the back surface of a thin photovoltaic absorber layer can couple sunlight into SPP modes supported at the metal/semiconductor interface as well as guided modes in the semiconductor slab, whereupon the light is converted to photocarriers in the semiconductor. These three light-trapping techniques may allow considerable shrinkage (possibly 10 to 100 fold) of the photovoltaic layer thickness, while keeping the optical absorption (and thus efficiency) constant.

Chapter 3

Nanofabrication Technologies and Nanostencil Lithography

3.1 Introduction

Nanofabrication has been one the most important factor that leads the rapid pace of discoveries in photonics and plasmonics. Therefore the research on nanofabrication is substantial and has to cover critical aspects such as achieving high precision and resolution, applicability on wide range of materials, enabling minimum number of nanofabrication steps, reducing cost and efforts, and integration of nanostructures into current technologies. A number of techniques can pattern nanostructures. These techniques in general could be classified as either conventional or unconventional. Conventional techniques are highly developed, well optimized and widely used for fabricating microelectronic circuits and semiconductor fabrication. A number of unconventional methods developed for nanofabrication enable new types of alternative fabrication and overcome important technical and financial limitations of conventional methods. In this chapter an overview of nanofabrication methods is presented. In the first section, the conventional nanofabrication methods based on the top down and bottom up approaches are discussed. In the second section up to date nanofabrication approaches and their breakthrough contributions are presented, and in the third section the state of the art of nanofabrication by nanostencil lithography is presented.

3.2 Conventional Nanofabrication Methods

Fabricating structures at the nano level can be broken down into two main methods: top down and bottom up construction.

3.2.1 Top down Approach

Top down fabrication can be likened to sculpting from a block of stone as Miguel Angel got David out of a piece of marble. A piece of the base material is gradually eroded until the desired shape is achieved. The most top down fabrication technique is nanolithography. In this process, required material is protected by a mask and the exposed material is etched away. Depending upon the level of resolution required for features in the final product, etching of the base material is performed chemically using acids or mechanically using optical ultraviolet light, X-rays, electron beams or ion beams. Other top down approaches include methods such as scanning probe lithography, nanoimprint lithography and block co-polymer lithography, etc. (Whitesides and Love, 2001)

Optical lithography: The microelectronics industry frequently uses optical lithography for patterning nanoscale features. Optical lithography techniques were first introduced in the 1960's to fabricate integrated circuits. Conventional optical or photolithographic approaches use light that is collimated through a quartz plate supporting a chromium (or iron) coating to create patterns on a surface (Figure 3.1). The quartz plate which serves as a mask is placed in contact or close proximity to the resist-coated wafer. The photoresist is an organic, light sensitive material that can be coated on semiconductor wafers. There are two possible transformations that a photoresist polymer can undergo upon exposure to light. If a positive photoresist material is illuminated, the exposed regions will present a higher solubility in the developing solutions. The photoresist that was exposed can then be removed from the solution.

A negative photoresist material becomes cross-linked when exposed to light and will be characterized by a high solubility in the developing solution. After the interaction with the developing solution, the areas that were not exposed to light will be etched away. The remaining photoresist patterns will therefore protect the substrate from being removed and/or from the deposition of additional materials. The photoresist can be removed after the desired process is completed leaving behind the pattern design on the substrate. Conventional photolithography is a simple technique that

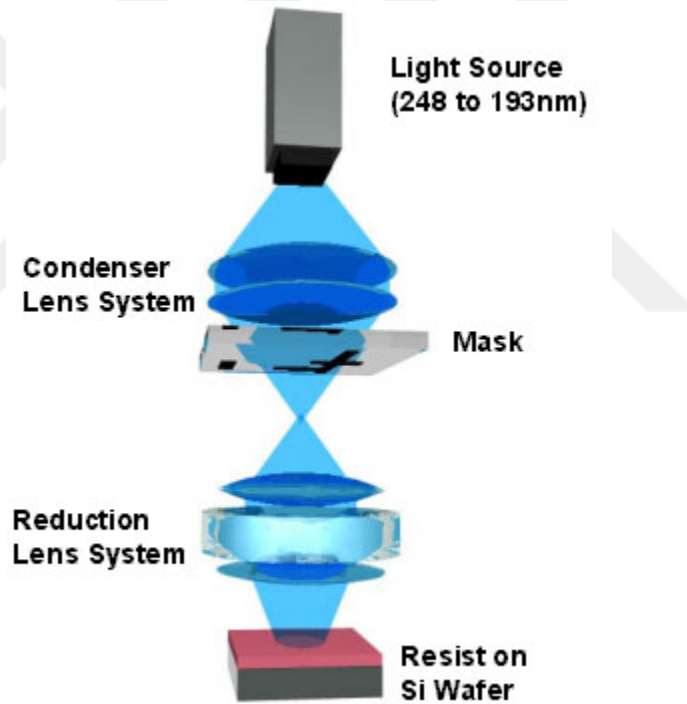


Figure 3.1: A typical optical lithography system. Adapted from Barrett Group at McGill University, Canada. (<http://barrett-group.mcgill.ca/tutorials/nanotechnology/nano04.htm>)

makes possible a resolution of about $1\text{ }\mu\text{m}$ using light of 400 nm (?). Naturally, the ultimate patterning density can be increased with decreasing illumination wavelength. The wavelength becomes the limiting factor in this fabrication scheme. As the wavelength is reduced, however, the situation becomes more and more complicated, and more expensive. The sources become more costly to produce, and lenses transparent

at the given wavelength become harder to find. In order to overcome wavelength limitations, current efforts are directed toward developing extreme ultraviolet lithography or EUV that uses long wavelength X-rays, where transmitted light reticles are replaced by reflected light masks, and Bragg scattering from multiple, nm-thick layers creates the desired pattern (Gwyn et al., 1998). EUV is under development by the semiconductor industry in the hopes of extending patterning resolution well beyond the current 32 nm node, but many problems are yet to be overcome, primarily related to production cost (Figure 3.2).



Figure 3.2: The Cymer™ LPP EUV Source System
(<http://www.cymer.com/euv1/>)

Electron Beam Lithography is the practice of emitting a beam of electrons in a patterned fashion across a surface covered with a resist and of selectively removing either exposed or non-exposed regions of the resist with a lift off process (Figure 3.3). Feature sizes of 30 nm are routinely obtained with this technique. The key limitation of electron beam lithography is throughput, i.e., the very long time it takes to expose an entire silicon wafer or glass substrate. A long exposure time leaves the user vulnerable to beam drift or instability which may occur during the exposure. Also, the turn-around time for reworking or re-design is lengthened unnecessarily if the pattern

is not being changed the second time (Brewer and Ballantyne, 1980). In addition, for EBL, the choice of substrates is also limited due to the dependence of the e-beam exposure on the substrate conductivity. For example, patterning on glass substrates could be done by adding a conductive film (such as ITO). But, this conductive layer could interfere with the optical responses of the fabricated nanostructures (Augu   and Barnes, 2008). Plasmonic nanoparticle and nanowire fabrication with EBL often involves a lift-off process, which can be restrictive in creating nanostructures with high aspect ratios. Although, multilayer lithographic processes are offered to be solutions for this limitation (Sun et al., 1998), they are cumbersome due to the involvement of multiple fabrication steps. Furthermore, the lift off step involves extensive use of chemicals (i.e. resists and solvents) which may not be compatible with polymer based, bio-compatible substrates.

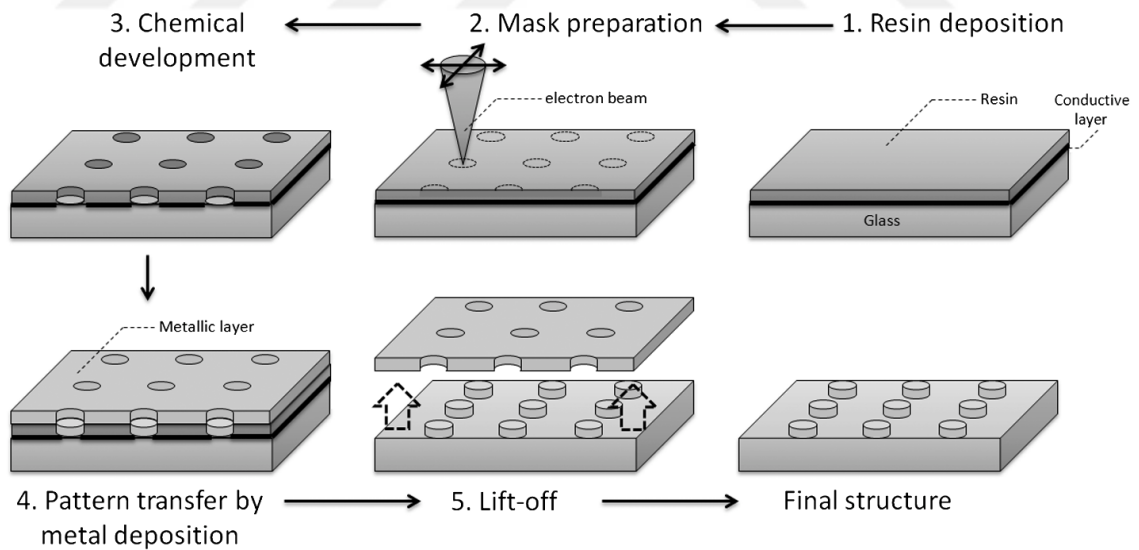


Figure 3.3: Typical e-beam lithography configuration for nanoparticle fabrication. Adapted from (Guillot and de la Chapelle, 2012)

Focused Ion Beam Lithography: Another aspect of nanofabrication is direct writing of nanostructures with Ga ions using the FIB technique. An FIB setup resembles a scanning electron microscope (SEM). However, while the SEM uses a focused beam

of electrons to image the sample in the chamber, an FIB setup uses a focused beam of ions. The smallest milled features are (10-15 nm) dependent on the total beam size and interactions with the sample being milled (Figure 3-4). One of the drawbacks of the FIB is the implantation of gallium atoms into the top few nanometers of the surface, and the surface will be made amorphous. In addition, FIB is also substrate selective: magnetic materials could not be used for FIB milling (Melngailis, 1987).

The top-down approach has allowed the drastic miniaturization of many devices. However they are serial techniques and their throughput is limited. Due to their serial nature, each nanostructure has to be created one at a time, which is both slow and expensive. These technologies were mainly developed for the silicon based processing, and unfortunately their implementation for other kind of materials or processes is not always feasible, like in non-planar substrates or biomaterials.

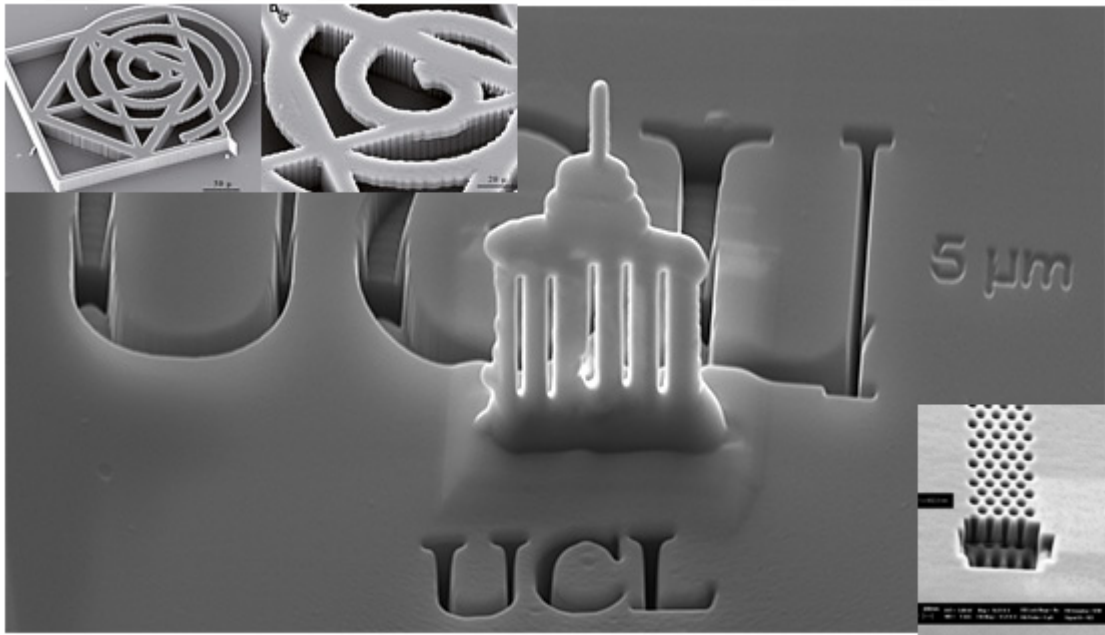


Figure 3-4: The structures fabricated by FIB. Adapted from Cabrini et. al. 2005

3.2.2 Bottom up Approach

The self-assembling processes of component molecules drive bottom up nanofabrication. It is based on chemical synthesis of structures using one by one gathering of atoms into almost single crystal nanostructures. Very small (1 to 20 nm) and nearly defect free nanostructures could be obtained (Link and El-Sayed, 1999). Various examples based on colloidal synthesis of nanoparticles have been intensively investigated. Gold nanoparticles have been synthesised for over 2000 years in a whole range of media including glasses, salt matrices, polymers have resulted in the formation of spheres (Stokey, 1949). It is only in the past decade that significant progress towards non-spherical nanoparticle synthesis has been achieved. Not only the nanoparticles but also nanowires or nanotubes can be chemically synthesized (Sun et al., 2002). This technique is generally used for fabrication of nanoparticles as SERS substrates or for cancer therapy (Kennedy et al., 2011) but most of the recent efforts in this area is focused on the explanation of nanoparticle growth mechanisms. Morphology control in the nanometer scale is hot topic because of the spectacular effects that small changes in the shape of the nanoparticles have on a variety of physical optical magnetic electronic properties of materials. As shown in Figure 3-5 colloidal synthesis has proven extremely useful to prepare a wide variety of nanoparticles with tight control of size and shape (Adams et al., 2012). However, still much of the knowledge in this area is empirical; there is no accepted mechanism to explain how shape control works. And also, no general rules can be applied similar to conventional nanofabrication technologies for a rational nanomaterial design, particularly in a material such as gold where the surface free energies and chemistry of the major facets are similar. In addition the positioning and localization of these structures is normally random in solution. The researchers are using many resources to drive the assembly of such structures into arrays or place of interest. There is still a major challenge of

organizing these nanostructures into well-defined patterns for integrated, functional devices.

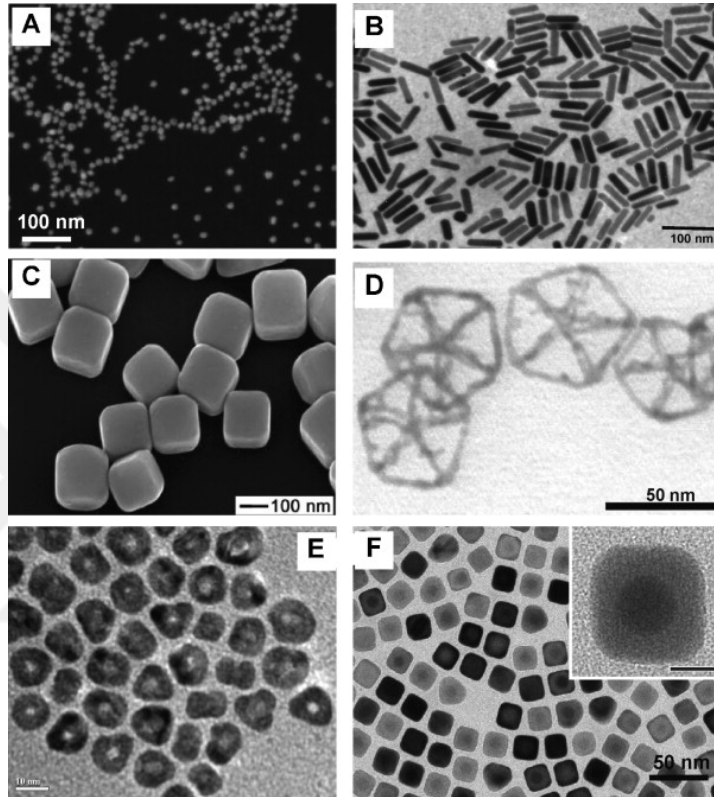


Figure 3-5: A wide variety of metallic nano particles could be synthesized with tight control of size and shape. Adapter from (Adams et al., 2012)

3.3 Emerging Nanofabrication Methods

Soft Lithography is based on self-assembly and replica molding for carrying out micro and nanofabrication. It provides a convenient, effective, and low-cost method for the formation and manufacturing of micro and nanostructures. In soft lithography, an elastomeric stamp with patterned structures on its surface is used to generate complementary patterns and structures with feature sizes ranging from 30 nm to 100 μm . The term soft refers to the stamp and/or to the substrate when they are

composed of soft matter (e.g., polymers or self-assembled monolayers). Fabrication of the master usually employs conventional tools (Gates et al., 2004). The pattern transfer consists of three steps: (a) fabricating a topographically patterned master, (b) molding this master to generate a patterned stamp, and (c) generating a replica of the original template in a functional material or a 1:1 projection of the pattern on a surface by applying the stamp (Figure 3·6).

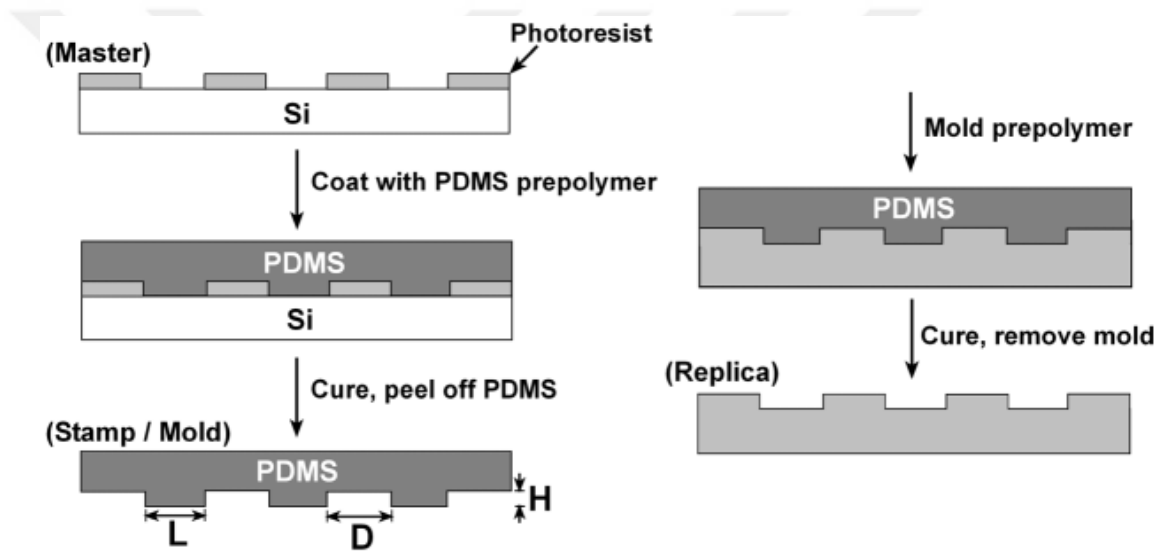


Figure 3·6: Schematic illustration of the fabrication of the topographically patterned elastomeric pattern-transfer agent (a mold or stamp depending on the application of soft lithography) by casting and curing an elastomer against a patterned relief structure, usually in photoresist (a master). A replica of the master is generated by molding against the patterned elastomer. PDMS is poly(dimethylsiloxane). Adapted from (Gates et al., 2004)

The area of soft lithography includes a wide variety of procedures. These procedures could be organized into three categories: replica molding, embossing, and microcontact printing (Figure 3·7).

Replica Molding is any process that transfers topographical features from a rigid or elastomeric mold into another material by solidifying a liquid in contact with the original pattern (Kloosterboer and Lippits, 1984). Molding techniques include mi-

crotransfer molding (μ TM) (Zhao et al., 2004), micromolding in capillaries (MIMIC) (Prebiotic, 1995), and step-and-flash lithography (Michaelson et al., 1999).

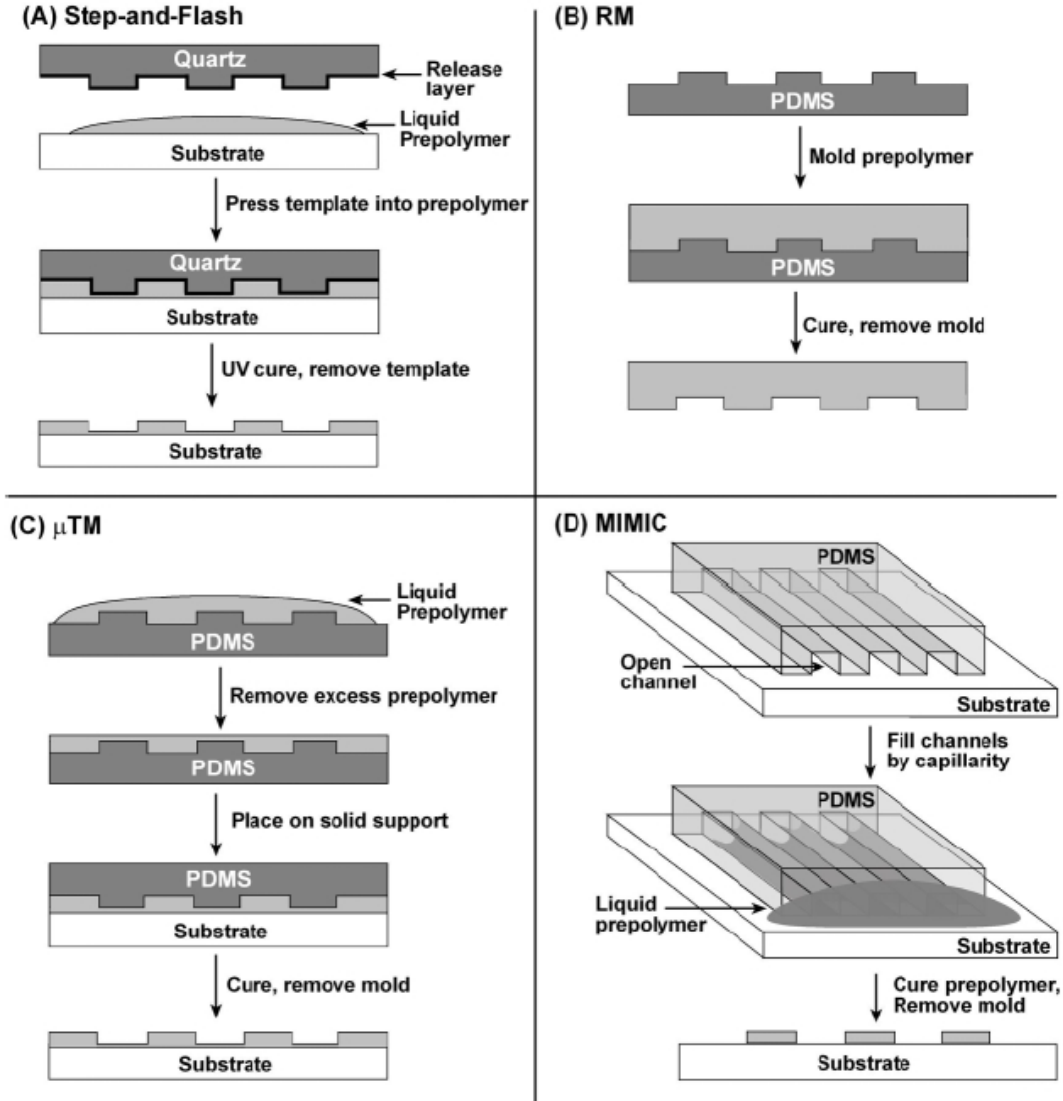


Figure 3-7: Schematic diagrams of four approaches to replica molding: (a) step-and- flash lithography, (b) replica molding (RM), (c) micro-transfer molding (μ TM), and (d) micromolding in capillaries (MIMIC). Adapted from (Gates et al., 2004)

Embossing is the process of imprinting a pattern into an initially flat substrate by pressing a mold into the surface; this term includes techniques such as nanoim-

printing (using either a rigid or soft mold) (Chou et al., 1995) and solvent assisted micromolding (SAMIM) (King et al., 1997) . These methods thermally imprint a polymer film with a rigid mold or use solvent assistance to imprint a polymer film with a soft polymeric mold (Figure 3.8).

The Nanoimprint Lithography is widely used in the microelectronics community. After the seminal paper of Chou (Chou et al., 1996), nanoimprint lithography received significant attention by enabling 20 nm resolution structures in low cost (Figure 3.9). There are many types of nanoimprint lithography but common ones are thermal and UV based one (Jung et al., 2004). Resist is heated or exposed to UV for a better pattern transfer. But wear of mold and multiple pattern transfers including reactive ion etching limits the resolution and applicability on polymeric materials.

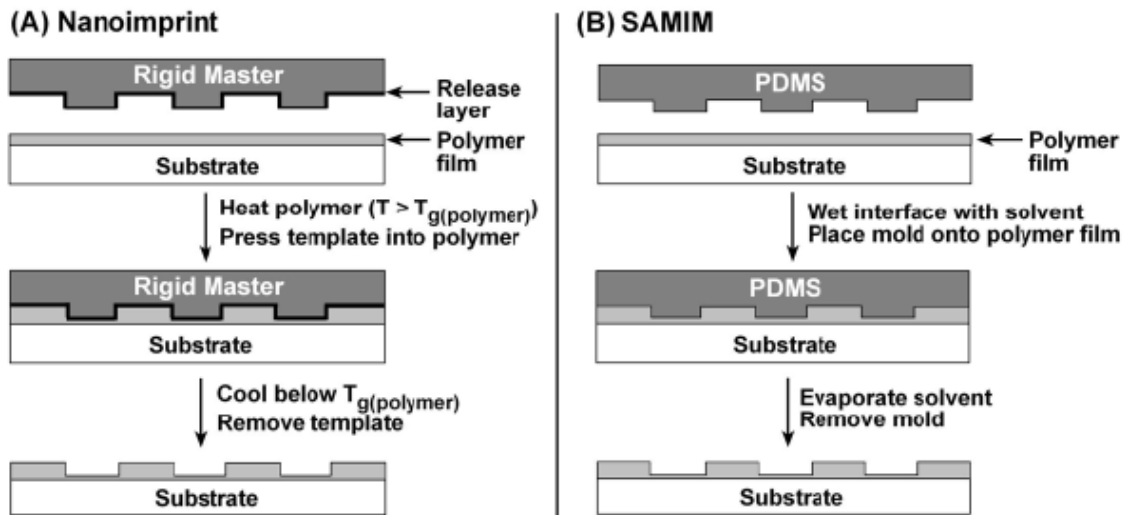


Figure 3.8: Schematic illustration of embossing procedures for (a) nanoimprint lithography and (b) SAMIM. Adapted from (Gates et al., 2004)

Soft lithography is well suited for fabricating microscale (10 to 100 μm) structures, but extension of these techniques to generate nanostructures is not straightforward. On a larger scale, flexible displays can be fabricated by patterning multiple layers of

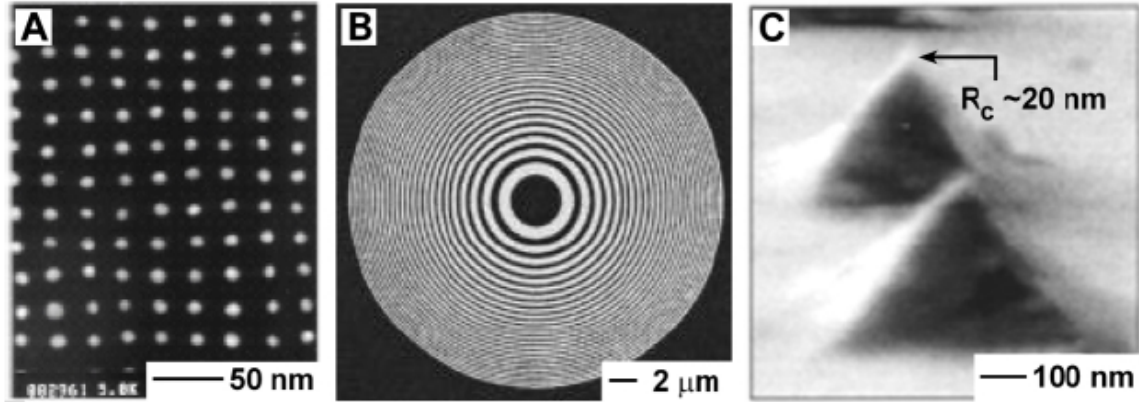


Figure 3-9: SEM images of structures patterned by nanoimprint: 10 nm diameter metal dots with a periodicity of 40 nm and Fresnel zone plates with a 125 nm minimum line width. SEM image of features patterned by SAMIM. Adapted from (Gates et al., 2004)

organic semiconductor using soft lithography (Rogers et al., 2001). The fabrication of complex functional nanostructures using soft lithography techniques will, however, require a further understanding and control of several issues. These issues include (a) distortion or deformation of polymer nanostructures, (b) optimization of conditions for pattern transfer and replication of nanoscale features, and (c) registration of nanoscale features in soft materials for patterning multilayered structures.

Nanosphere Lithography uses self-assembled monolayers of spheres (typically made of polystyrene) as evaporation masks (Figure 3-10). This method has been used to fabricate arrays of gold nanodots, triangles or circular apertures. Even though using tilted metal depositions a variety of nanostructure arrangements could be achieved, colloidal lithography lacks of fabricating many special structure designs. Due to the self arrangement of the nanospheres, fabricated structures could have boundary like defects and non uniform periodicities resulting in broad plasmonic resonances which are not suitable for refractive index change based sensing platforms (Aksu and Altug, 2009).

It is not hard to tell that conventional nanofabrication will continue to dominate

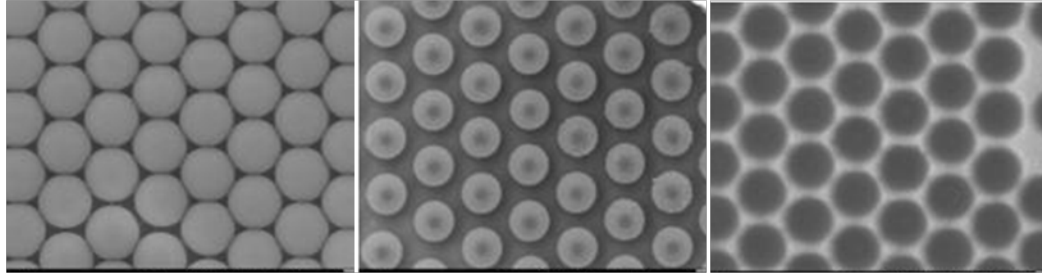


Figure 3.10: On the left SEM images of self assembled polystyrene spheres are shown. After oxygen plasma etching, sphere diameter could shrink to a desired value (middle image). After deposition and polystyrene lift off, gold thin film perforated with nano holes is obtained (Aksu and Altug, 2009)

nanoelectronics. There is little motivation for large companies to adopt new, unproven technologies unless the risk is low and the potential advantage large. The nature of the optical systems will bring new materials and light sources and extensive use of front-surface optics. Electron beam and X-ray methods will also continue to develop. Where then do unconventional nanofabrication techniques fit into this world of ever-shrinking components? A significant advantage of techniques for unconventional nanofabrication is the ability to prototype new structures rapidly, often using ordinary laboratory facilities, without specialized equipment. Unconventional methods could inexpensively reproduce patterns created by other lithographic means and can generate numerous molds and replicas from the same master. This process can replicate and pattern nanoscale features over large areas ($>cm^2$). Soft lithography can also pattern materials other than photoresist and nonplanar surfaces. On the other hand, one area where nanotechnology is beginning to have an impact is new materials. Nanoscale structures have a number of important properties such as superparamagnetism (Xiang-Cheng, 2002) on electronic structure and optical properties that differ from microscale structures. Fusing top-down and bottom-up approaches and creating hybrid method to produce more complex nanostructured materials may provide a means to control the placement of new materials as well as advancement of

conventional rigid substrates. Examples include the assembly of nanoparticles within templates as in the stenciling method.

3.4 Nanofabrication and Patterning with Nanostencil Lithography

3.4.1 Historical Background

The first micro machining process involves stencils goes back to 1969 with the title 'A convenient stencil for glass etching' in the Journal of Chemical Education (Alix, 1969). In 70's there are reports showing the use of stencils as shadow masks for deposition of millimeter scale sputtered films (Ingle, 1974). In 80's the advantages of stencil masks over photolithography has started to be realized. Nguyen et al. proposed using Si masks to avoid the photolithographic step and deposit metal contacts on top of solar cells (Nguyen, 1980). The first breakthrough in stencil fabrication is achieved in 1982. M. Sango and T. van Duzer reported the fabrication EBL defined stencils made of 200 μm thick silicon with apertures down to 10 μm width (Sango and Van Duzer, 1982). In 1996, K. Ono et al., reported the fabrication of arrays of Al/Al oxide/Al tunnel junctions based on silicon nitride stencils for the first time with 200 nm thickness patterned by e-beam lithography (Ono et al., 1996). They achieved structures in the 100-500 nm range, being one of the first works to achieve submicron structures by stenciling. At the end of the last century, couple of groups demonstrated the patterning of metallic nanostructures by stencil lithography in the 100 nm scale (Mena, 2010).

Year 1999 has been the milestone for nanostencil lithography. Two groups Luthi et al. in IBM Zurich and Deshmukh et al. at Cornell University could pattern structures below 100 nm (Luthi et al., 1999; Deshmukh et al., 1999). Luthi et al. prepared silicon nitride cantilevers with submicron nanoholes which are milled by

Table 3.1: Brief timeline of stencils in microfabrication. Modified from (Mena, 2010).

Description	Reference
Local glass etching in liquid solution	(Alix, 1969)
Sputtering through mm size apertures	(Ingle, 1974)
Stencils to deposit top contacts on solar cells	(Nguyen, 1980)
Stencils patterned with EBL	(Sango and Van Duzer, 1982)
Submicron nano structures through stencils	(Luthi et al., 1999)

FIB. They could perform metal deposition through the nanoholes and simultaneously move the cantilever. They showed the first demonstration of dynamic nano stenciling. They obtained structures down to 80 nm, demonstrating the capability of stencils for patterning sub 100 nm features even the ones that are not possible using static mask depositions, such as ring loops (Figure 3.11). Around same time, Deshmukh et al. worked in the limits of the technique with apertures holes down to 5 nm in diameter. They deposited 10 nm of erbium and obtained dots of 15 nm in width on an Al oxide substrate. In 2004, the nanofabrication has been extended to a full wafer scale (Van Den Boogaart et al., 2004). In 2005 Zahl et al. combined stencil mask with a scanning tunneling microscope, allowing a fine control to perform dynamic stencil depositions (Zahl et al., 2005). They reported the deposition of Cu structures 40 nm wide in static mode. Shin et al. used stencils to deposit PZT (ferroelectric material made of lead-zirconium-titanium) which is sensitive to contamination from resists or chemical solvents (Shin et al., 2005). In 2005, Yan et al. also reported the deposition of silicon oxide to clog the nanoperture holes to further reduce the size of the deposited structures (Yan et al., 2005). In 2007, Park et al. developed a

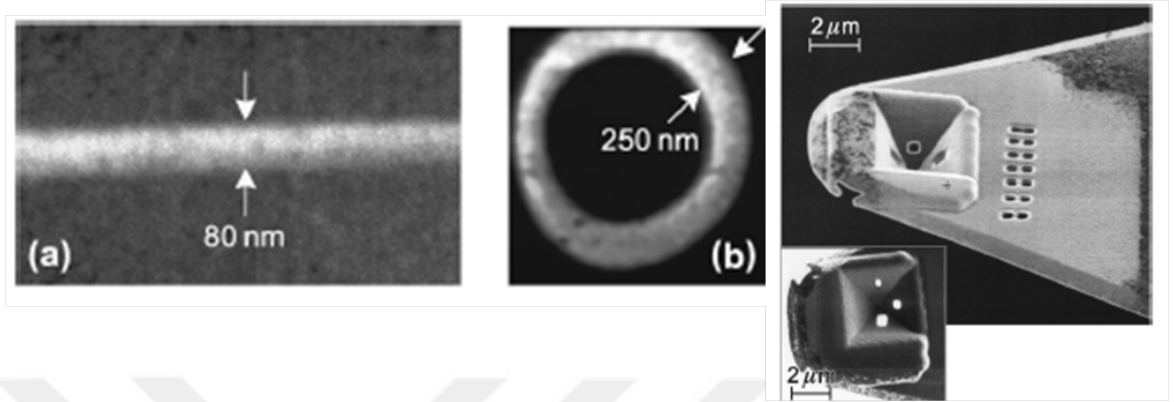


Figure 3.11: Cu wires created by nanostencils as (a) line (b) loop. SEM image on the left shows the SiN_x cantilever used for dynamic stenciling featuring several holes milled by FIB. (Luthi et al., 1999)

reverse patterning stencil processing (Park et al., 2007). In 2008, Vazquez-Mena et al. reported the fabrication of sub-100 nm wide Au and Al nanowires on a full wafer scale and aligned on predefined contacts on the substrate, allowing the electrical study of the nanowires (Vazquez-Mena et al., 2008). All of the breakthrough literature of nanostencil lithography is presented in Tables 3.1 and 3.2.

Table 3.2: Brief timeline of stencils in nanofabrication. Modified from (Mena, 2010).

Description	Size	Reference
Al junctions	100-500 nm	(Ono et al., 1996)
Cu lines	300-80 nm	(Luthi et al., 1999)
Er dots	10-20 nm	(Deshmukh et al., 1999)
Cr/Au dots	300 nm	(Brugger et al., 2000)
Er dots	10-20 nm	(Champagne et al., 2003)
Full wafer	200 nm	(Van Den Boogaart et al., 2004)
Cu lines	40 nm	(Zahl et al., 2005)
PZT dots	120 nm	(Shin et al., 2005)
Pt dots	50 nm	(Yan et al., 2005)
Cr lines	80 nm	(Park et al., 2007)
Cu lines	40 nm	(Zahl et al., 2005)
Au/Al nanowires	50-100 nm	(Vazquez-Mena et al., 2008)
Au bowties, nanorods	25 nm	(Aksu et al., 2011)

Chapter 4

High-throughput Nanofabrication of Infrared Plasmonic Nanoantenna Arrays for Vibrational Nanospectroscopy

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The introduction of high-throughput and high resolution nanofabrication techniques operating at low cost and low complexity is essential for the advancement of nanoplasmonic and nanophotonic fields. In this chapter, we demonstrate nanostencil lithography for high-throughput fabrication of engineered infrared plasmonic nanorod antenna arrays (Aksu et al., 2010). Our technique enables plasmonic substrates supporting spectrally sharp collective resonances (Figure 4.1). We show that reflectance spectra of these antenna arrays are comparable to that of arrays fabricated by electron beam lithography. We also show nanostencils can be reused multiple times to fabricate series of infrared nanoantenna arrays with identical optical responses. Finally we show that our nanostencil lithography technique offers the flexibility and the resolution to engineer nanoantenna arrays and can be effectively used to fabricate in a high-throughput fashion plasmonic substrates supporting spectrally sharp collective excitations at mid-infrared wavelengths. The extinction spectra of these antenna arrays are comparable to that of the arrays fabricated by EBL.

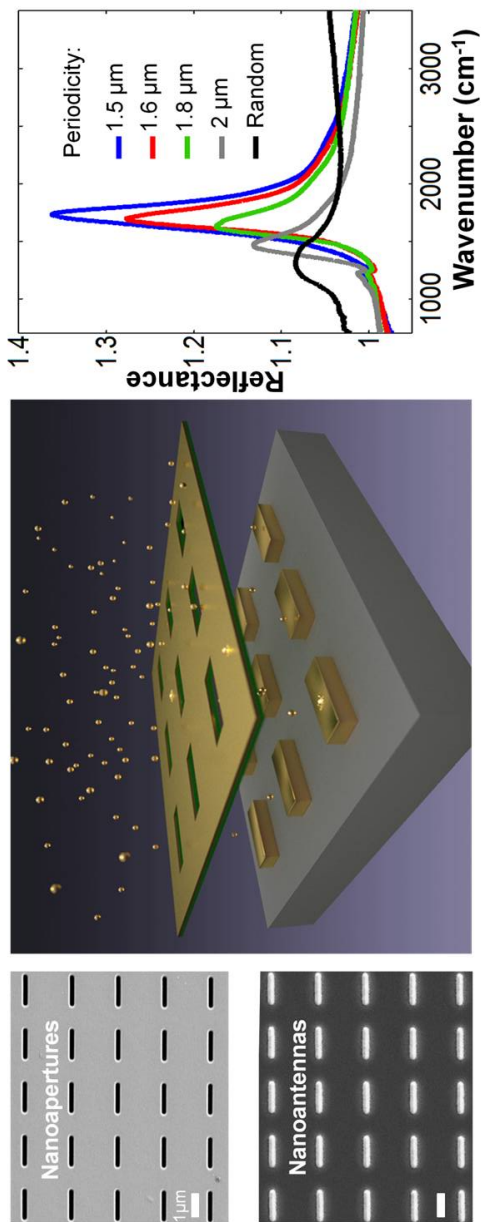


Figure 4-1: Nanoapertures patterned on stencil and corresponding nanoantennas are shown on the left. Illustration of NSL in the middle. Reflectance of nanorod antenna arrays with a variety of periodicity.

4.1 Nanostencil Lithography for Plasmonic Nanostructure Fabrication

Nanostencil technique, summarized in Figure 4-2, consists of three stages: (i) fabrication of the free standing membrane, (ii) patterning on the membrane and (iii) direct deposition of metallic plasmonic devices. Processing steps for free standing membrane fabrication is illustrated in Figure 4-2(a). An important consideration here is the mechanical strength of the membranes. Highly robust Low Pressure Chemical Vapor Deposition (LPCVD) SiN_x films are excellent choice. We start with 550 μm thick silicon wafer coated with 400 nm thick LPCVD SiN_x on double sides. After cleaning with organic solvents, 2 μm thick *MICROPOSITTM* S1818TM positive photoresist is spin coated. 800 μm x 800 μm apertures on the SiN_x layer are defined by photolithography with SUSS MicroTec MA/BA6 Mask Aligner and reactive ion etching (RIE) with Plasma Therm 790 RIE/PECVD System. Then, the chips are immersed in KOH solution to selectively etch Si layer. Finally, 200 μm x 200 μm and 400 nm thick free standing SiN_x membranes are obtained once the etching stops at the SiN_x layer. Si is etched with 54.7° angle side-wall profile, as shown at Figure 4-2(a).

The second stage is nanoaperture patterning on the membrane. This process involves spinning positive e-beam resist poly (methylmethacrylate) (PMMA) followed by e-beam exposure using Zeiss Supra 40VP with GEMINI electron-optics column. Here, the EBL process is needed only once for the creation of the mask, since the mask can be used multiple times. After development of PMMA resist, patterns are transferred to the SiN_x membrane by RIE using SF_6 and Ar gases. The resulting structure used as stencil. The top and the cross sectional views of a fabricated stencil masks are show in Figure 4-2(b).

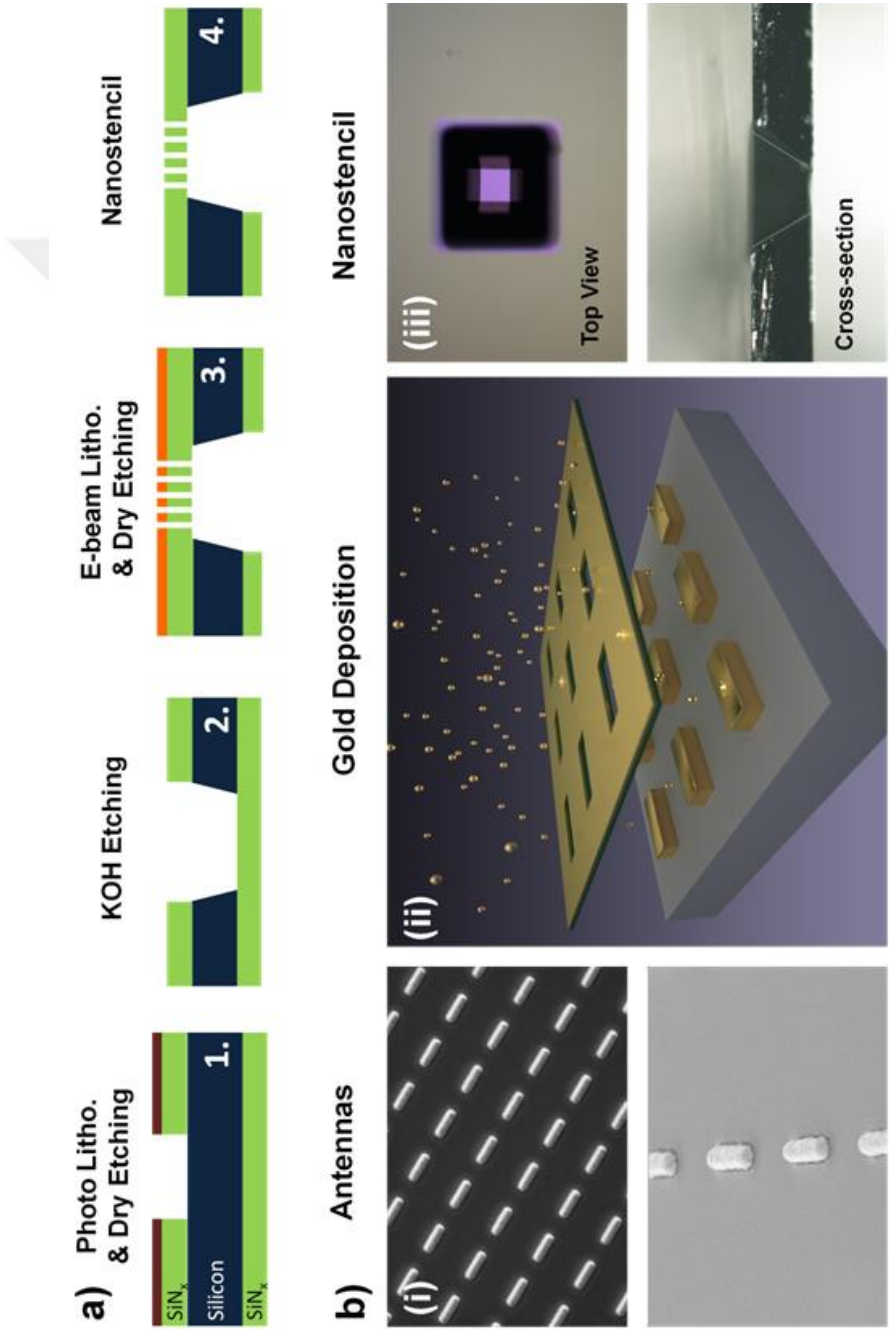


Figure 4-2: Nanostencil lithography, a shadow-mask patterning technique, is used for high-throughput fabrication of plasmonic antenna arrays. a) Fabrication of free standing membrane and nanostencil is illustrated from 1 to 4. Dry and wet etching processes and EBL are used for achieving precisely defined pattern of nanoapertures/slits on the membrane. b) (i) Top and angled SEM images of the gold nanorod with 1100 nm length, 230 nm width and 100 nm height are shown. (ii) Gold deposition scheme with reusable mask is illustrated. (iii) Top view and cross sectional images of the stencil are shown.

The final stage of our nanostencil method involves direct deposition of the plasmonic structures to the desired surface. To get high quality structures, the gap between substrate and the mask must be minimized (Vazquez-Mena et al., 2008). The stencil is directly placed on the substrate and secured tightly with clips so that the silicon side is facing up, while the patterned SiN_x layer is nominally kept in contact with the substrate. Here, the sturdiness of the LPCVD SiN_x layer plays important role for the durability of the mask. Directional gold deposition at 3×10^{-6} Torr is performed in CHA-600S e-beam evaporator for 100 nm gold film without depositing any prior adhesion layer (such as Ti or Cr) (Figure 4.2(b)). Unlike EBL, an adhesion layer is not necessary since NSL does not require metal lift-off processes. When the mask is removed from the substrate, it leaves plasmonic nanostructures on the substrate with the shapes complimentary to the nanoapertures.

4.2 Nanorod Fabrication: Nanostencil vs E-beam Lithography

In the previous part, we explained the fabrication scheme of plasmonic nanostructures. In the following, we will particularly focus on the fabrication details and the optical characterization of the gold nanorod arrays as they act very efficient infrared plasmonic antennas. Nanorod arrays, obtained by our NSL technique are investigated using SEM and compared against the nanorods with the same dimensions fabricated using EBL. Figure 4.3(a) displays nanorod arrays fabricated on silicon with periods $1.5 \mu\text{m}$, width 230 nm and height 100 nm using EBL and NSL. No irregularities on the periodicity or the physical dimensions are detected for the nanorod arrays fabricated using NSL. During the experiment, a 15 % enlargement is observed in the nanorod lengths and the widths compared to the dimensions of the corresponding apertures.

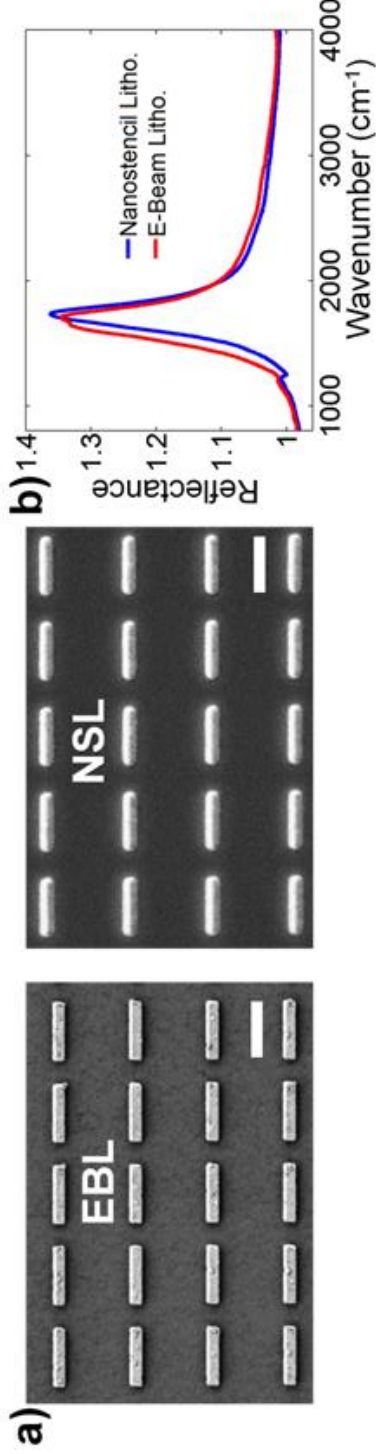


Figure 4-3: Nanostencil lithography is used to fabricate plasmonic nanorod antenna arrays. a) SEM images of nanorods with 1100 nm length, 230 nm width and 100 nm height fabricated using EBL (left) and NSL (right) are shown for comparison. White scale bars represent 1 μm. NSL technique for large area patterning of nanorod arrays provides comparable quality with arrays fabricated using EBL. b) Nanorods fabricated using two different techniques give identical reflection spectrum with resonances at 1700 cm^{-1} . Reflectance intensities are calculated dividing measured particle reflectance spectrum by bare silicon substrate reflectance spectrum (R_s/R_o).

To obtain nanorods with desired sizes, this enlargement is compensated by scaling the apertures on the stencils properly. Round edged nanoapertures on the mask caused particles to have rounded tips. Due to unavoidable gap between the mask and the substrate, scattering of gold particles at 20 nm vicinity of the nanorods has also been observed. As we demonstrate below, however, this scattering has negligible effect on the optical quality of the structures.

The optical responses of the antennas are the ultimate metrics for determination of the fabricated nanostructure qualities. The reflection spectra are obtained from the NSL fabricated arrays in the mid-IR frequency range and the results are compared with the spectra of the structures fabricated using EBL. Our experimental set-up consists of an IR microscope coupled to a *BrukerTM* Fourier Transform Infrared (FTIR) spectrometer with a KBr beam splitter. Light is normally incident on the nanopatterned surface. Reflected infrared signal is collected using a Cassagrian reflection optics (NA=0.4) and coupled into a mercury cadmium telluride (MCT) detector. Reflectance spectrum at Figure 4-3(b) shows a strong resonance at the designed wavelength of 5.77 μm . Absorption losses due to the naturally grown oxide layer on silicon substrates are corrected with baseline fitting. Intensities of the reflected light obtained from the same size arrays are comparable for both fabrication schemes. The spectral linewidth of the resonances of the antenna arrays fabricated by the nanostencil technique is comparable or narrower than that of the arrays fabricated using EBL. This observation indicates high optical quality. We associate this to the absence of an optically lossy adhesion layer (5 nm of Ti), which is normally required in lift-off based nanofabrication schemes for sticking the gold on the substrate. Our spectral and SEM measurements faithfully confirm the feasibility of NSL technique for large area patterning of nanorod antenna arrays with optical qualities achievable by EBL.

4.3 Reusability of Stencil for High-throughput Nanofabrication

One of the major problems associated with stenciling is the clogging of the stencils. Due to the accumulation of deposited material on the nanostencils, size reduction of the apertures is observed after depositions (Figure 4.4). In the case of micron sized

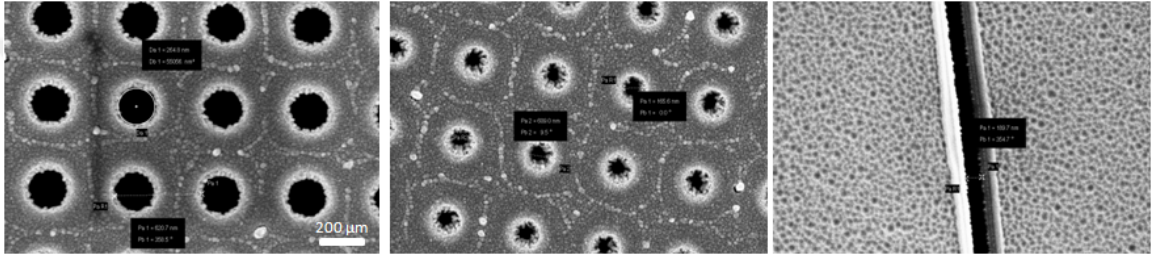


Figure 4.4: On the left SEM shows the condition of the circular nanoapertures after 1st gold deposition. Middle SEM image shows the same stencil after 3rd deposition. The nanostencils are clogging if no cleaning is applied. The SEM image on left shows the aperture used for nanowire fabrication. Accumulation of gold on stencil is observed.

apertures, the clogging is not a major problem since the size reduction is very small compared to the size of the apertures. However, in the case of nanostencils, this problem becomes relevant since the thickness of material deposited (10-200 nm) is in the same order of magnitude as the aperture size (50-200 nm). This limits the life time of stencils and effects reproducibility of the deposited structures because the size of the apertures is reduced after each deposition and eventually the apertures get completely closed (Figure 4.5). Since the fabrication of nanostencils implies the use of a high resolution technique (EBL) it is also highly convenient to extend the useful lifetime of the stencils and keep the size and quality of the apertures as long as possible. As a solution, self-assembled monolayers have been reported to reduce the clogging (Kölbel et al., 2002). It has been proven that for membranes coated with self-assembled monolayers the clogging is slowed down, but it is still present and eventually the stencil apertures get closed (Mena, 2010).

In the case of gold, the aperture reduction corresponds closely to the amount of material deposited through the stencils. However, the clogging rate can change with different materials. It has been proven that using wet etching solutions the remnants of the deposited material on the stencils can be removed and the clogging of the aperture could be prevented. This cleaning procedure allows the multiple-time reutilization of the stencils for reliable and repeatable depositions of metallic nanostructures.

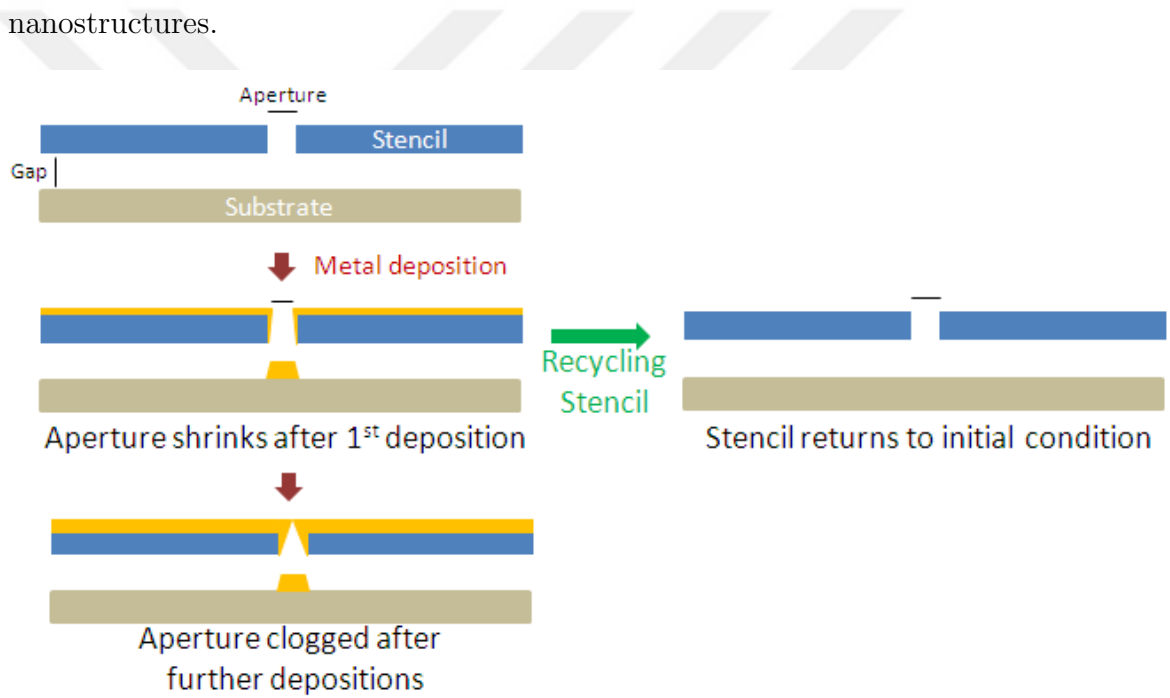


Figure 4.5: The clogging of apertures after multiple depositions is illustrated. This problem could be overcome by recycling the stencil. The stencil returns to initial condition after cleaning procedures.

The recycling ability of stencils has been one of the unique advantages of the nanostencil lithography over conventional lithography techniques since the same stencils can be reused for multiple usages. This capability is particularly useful when high-throughput replication of the optimized nanoparticle arrays is desired. We achieve recycling by first dipping the used stencil in wet metal etchant and then rinsing in DI-water. Here, we used gold etchant to clean the stencil including the remnants

inside the nanopertures after deposition. Once the deposited metal is stripped away, the stencil is ready to be used again. SEM images in Figure 4-6 show the condition of stencil mask right before it is used for the first time, and also after the fourth usage (and subsequently cleaned). The sizes of the apertures, 1050 nm and 200 nm in width and height, are almost same for both cases. There is no sign of degradation and deformation after the fourth usage, indicating that the stencil can be further reused many times. Figure 4-6(b) shows the reflection spectrum of the four different series of nanorod arrays fabricated on different silicon chips by using the same stencil. The resulting spectra for all the structures have very similar spectral profiles. They show strong resonances around 1700 cm^{-1} with deviations in the spectral peak position less than 3.5 %, which could be due to the slight variations in the deposited metal thicknesses and the gap between mask and the substrate. Our observations clearly indicate that with a single stencil, optimized designs can be replicated many times with high degree of plasmonic antenna uniformity and similar optical response. This high-throughput fabrication capability is in stark contrast to the serial nature of the e-beam lithography.

In order to prove NSL is a useful technology for highthroughput nanofabrication, we showed the use of same stencil 12 times for the patterning of plasmonic nanostructures (Figure 4-7). The cleaning of the stencils has allowed the use of the same stencil. With this result it is also demonstrated that stencil lithography can be a cost-effective, reliable and durable technique for nanopatterning. Even though this study is only applied to Au, there are various wet etching liquids for metals that are highly selective to silicon nitride and allow the cleaning of stencils for a variety of materials.

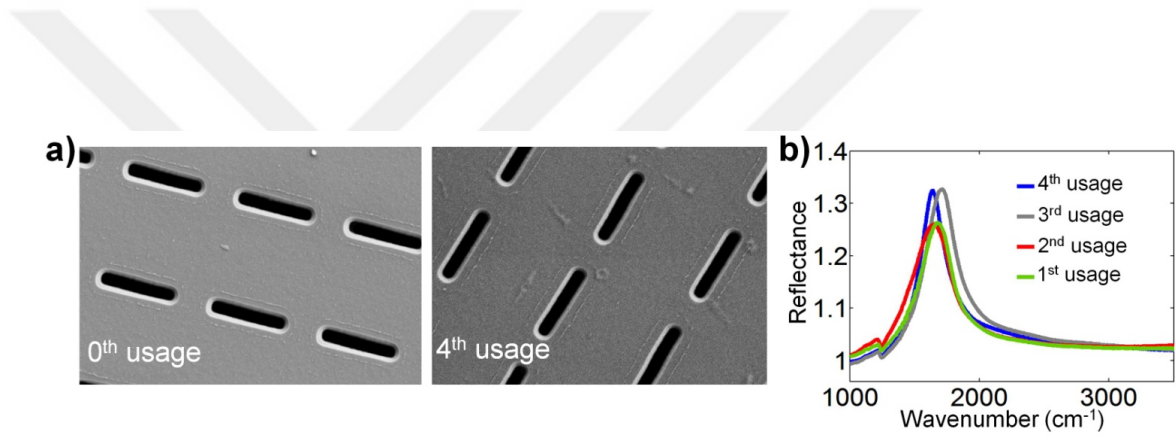


Figure 4-6: Mask can be reused multiple times. a) SEM images of the same mask are shown before its first usage and after the fourth usage. Apertures have dimensions of 1050 nm length, 200 nm width and 100 nm height. No sign of degradation and deformation is observed on the mask after fourth usage. b) Reflectance spectra are shown for different nanorod arrays obtained from four consecutive depositions using the same mask. The resulting spectra show negligible deviations on resonances 3.5 % around 1700 cm^{-1}

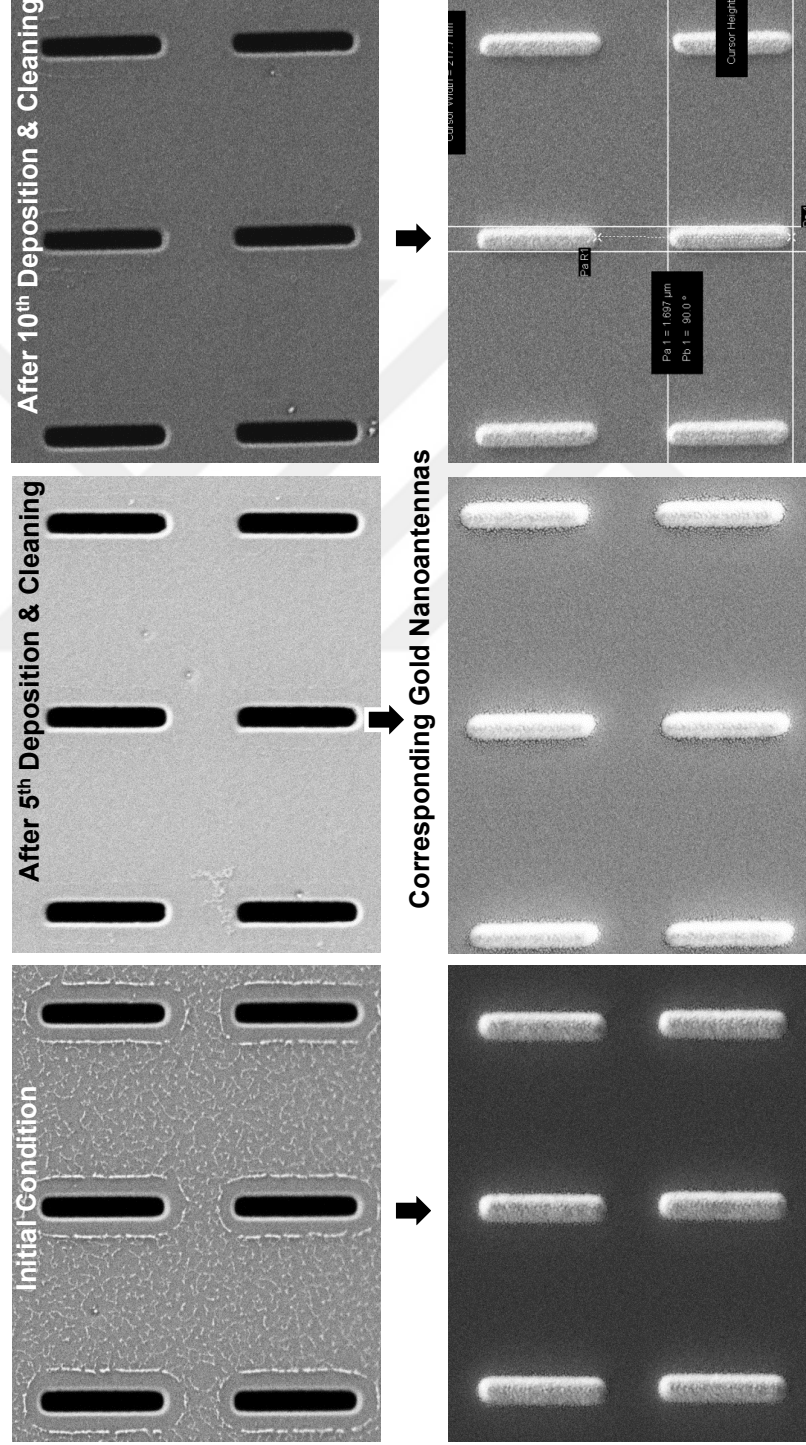


Figure 4.7: SEM images of the nanoapertures on the stencils after 5th and 10th deposition and cleaning. The SEM images of corresponding nanoparticles are shown in lower row. The nanorods have 1 μm length, 200 nm width and 1.6 μm periodicity.

4.4 Collective Plasmonics and Engineered Plasmonic Nanoantennas by Nanostencil Lithography

As the stencils are fabricated by EBL, NSL preserves the inherent flexibility of EBL in creating wide variety of nanoparticle shapes and composition at high resolution. This ability is especially useful for arrayed structures as interesting physics have been shown in repetitive patterns of dielectric and metallic nanostructures (Altug and Dirk Englund, 2006; Adato et al., 2009). In the following, we show that periodic arrays of plasmonic nanorods can be radiatively engineered to excite collective plasmons leading to spectrally sharp resonances with extremely strong local fields. Such collective behavior in arrays offers means to boost capabilities of the individual plasmonic nanorods. Collective excitations can be explained from the fundamental principles using coupled dipole approximation (Novotny, 2007; Adato et al., 2010). Plasmonic nanorods respond to an acting electric field on them with an induced dipole moment, which has maximum strength at the localized plasmon resonance. For an individual antenna, this acting field is simply the electric field of the incident light. Once arrayed, the acting field on an individual antenna includes both (i) the incident field, and (ii) the sum of the retarded dipolar fields due to the other nanorods in the array:

$$\vec{E}_{acting,i} = \vec{E}_{incident,i} + \sum_{i \neq j} \vec{E}_{retarded,ij} = \vec{E}_o e^{i\vec{k} \cdot \vec{r}_i} + \sum_{i \neq j} (\vec{c}_{ij} \cdot \vec{P}_j) e^{ikr_{ij}} \quad (4.1)$$

Here, E_o is the incident field, P_j is the induced polarization of j-th antenna in the array, and c_{ij} is the dipolar interaction matrix among nanorods without the phase term. Accordingly, the strength of total field acting on an individual nanorod strongly depends on the phase-delay experienced among the dipolar interactions. This acting field could be extremely large when the scattered fields are almost in-phase for a particular grating order ($\lambda_{incident} \approx n_{substrate} d_c / (i^2 + j^2)^{1/2}$). This happens when the

diffractive grating order is still evanescent such that the radiative damping of the plasmonic excitations is suppressed. Tuning of the individual antenna resonances (LSPs) to this incident wavelength (where the scattered fields are almost in-phase) strongly enhances the collective behavior and leads to extremely strong near-field excitations that are suitable for applications related to SEIRA, SERS and second harmonic generation.

For best performances, tailoring of the nanorod arrays requires optimization of the individual nanoantenna characteristics through the rod dimension as well as the phases of the retarded dipolar interactions through the periodicity (Adato et al., 2010). To obtain the individual antenna response, we fabricated randomized (but consistently oriented) arrays of nanorods. The random arrangement of nanorods cancels out any long-range dipolar interactions among the nanorods, while allowing us to measure the individual antenna behavior at high signal to noise ratios with an interferometer (Atwater and Polman, 2010). Figure 4-8 shows the resonance spectrum of the randomized nanorod arrays with varying lengths for a fixed width (230 nm) fabricated on silicon over an area of $100 \times 100 \mu m^2$. In analogy with half-wave dipole antenna from the microwave theory, nanorod resonances scale linearly with the rod length as $\lambda_{Res} = 2n_{eff}L + C$. Here, n_{eff} is the effective refractive index of the medium (silicon and air) surrounding the antenna and C accounts for the finite width and height. For a cylindrical antenna with hemispherical ends and its fundamental mode ($m = 1$), constant C is given by $4Rn_{eff}/m$ (Adato et al., 2010). As shown in Figure 4-8(b), nanorod resonances closely follow the linear scaling relation. Increasing the rod length results in red shifting of the resonance wavelength. Fitting of the experimentally observed resonance wavelengths to the dipolar antenna formula yields $n_{eff} = 2.52$. The constant fitting parameter C resulted in an effective cross-sectional radius of 188 nm, which is in close agreement with the average value of the width and

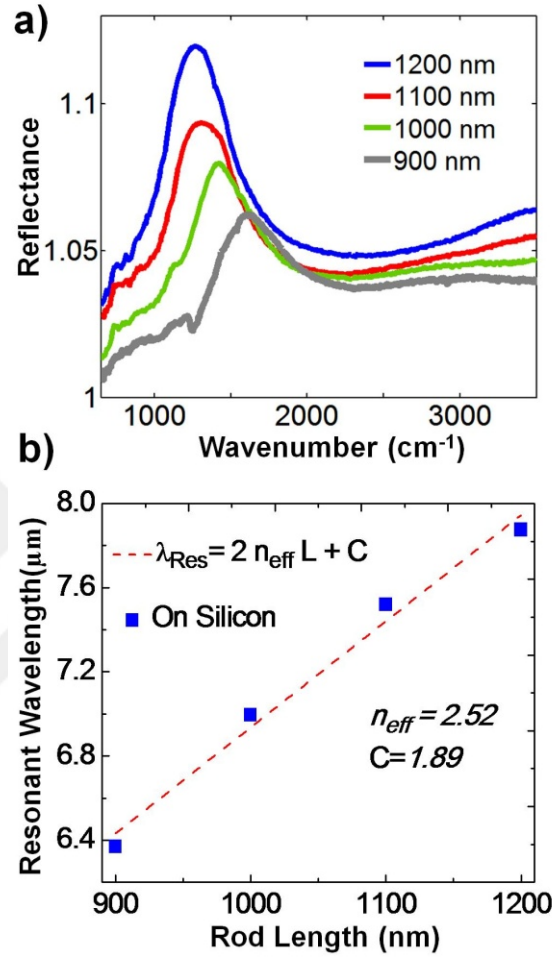


Figure 4.8: Plasmonic gold nanorod arrays fabricated using nanostencil lithography displays antenna like behavior in Mid-IR frequencies. a) Reflectance spectra of randomly arranged nanorods with lengths indicated in the legend, 230 nm widths and 100 nm heights. b) Fundamental ($m = 1$) resonance wavelengths (blue squares) are linearly dependent on the rod length (dashed red line is linear fit). Effective refractive index (n_{eff}) and constant fitting parameter (C) are calculated as 2.52 and 1.89 μm , respectively.

the height of the antennas, 170 nm. Figure 4.9(a) shows spectral narrowing of the far-field responses as a result of collective excitation of the plasmons. The data are shown for nanorod arrays ($L = 1100\text{nm}$) with changing periodicities ($d = 1.5, 1.6, 1.8, 2\mu\text{m}$). Spectrum of an 1100 nm long individual nanorod antenna indicating LSPR, (obtained

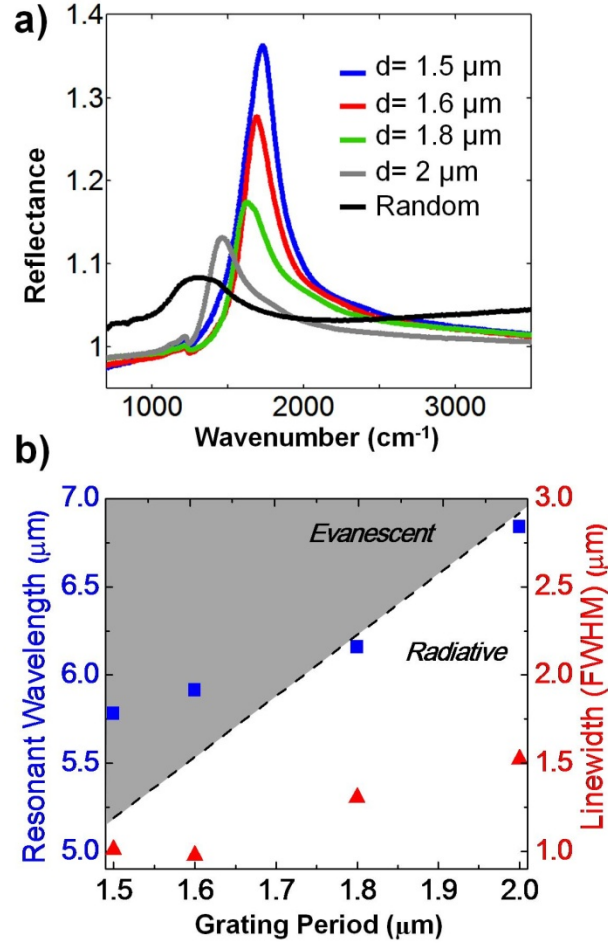


Figure 4-9: Spectral characteristics of periodic nanorod arrays, fabricated using nanostencil lithography are shown. a) Reflectance spectra of the periodic nanorod antenna arrays with 1100 nm length, 230 nm width, 100 nm height and periodicities changing from 1.5 to 2 μm (indicated in the legend) are displayed. Spectrum of 1100 nm long individual nanorod antenna (black curve) is also presented for reference. b) Resonance wavelengths (blue square, left y-axis) and the line widths (red triangles, right y-axis) are shown for varying periodicities. The dashed line separates the evanescent (shaded) and the radiative spectral regions for the first grating order on the silicon/air interface.

from randomized arrays) is also presented for reference (black curve). Slight shifting of the LSP resonance is observed with respect to the ones in reference (Adato et al., 2009) due to the absence of the titanium layer and the variation of the metal thickness. We also note that periodicity is dominant in controlling the resonance frequencies of

the antenna arrays. The effect of the periodicity on the resonance wavelengths and line-widths of the far-field reflectance spectra is summarized in Figure 4.9(b). Here, the dashed line separates the evanescent and the radiative spectral regions for the (1, 0) grating order at the silicon interface for a given periodicity. For periodicities smaller than $d=1.8\ \mu\text{m}$, the diffractive grating order is evanescent and leads to the suppression of the radiative damping. Therefore, significantly narrower far-field spectral response ($1\ \mu\text{m}$ with respect to $3\ \mu\text{m}$ of an individual nanorod) is observed as a result of electromagnetic field confinement within the array. For grating periods $d=1.8$ and $2.0\ \mu\text{m}$, the grating order changes from evanescent to radiative in nature. Hence, broadening of the resonances is observed with increased radiative damping.

The spectra shown in Figure 4.9, including the line widths and the intensities, closely match with the spectra of the nanorod arrays fabricated using EBL. Here, we tuned the collective resonances of the plasmonic arrays to the amide-I and amide-II vibrational bands of the protein backbone, which are $1660\ \text{cm}^{-1}$ and $1537\ \text{cm}^{-1}$ respectively. These collective plasmonic excitations accompanied with enhanced near field intensities are highly suitable for ultrasensitive vibrational nanospectroscopy (Adato et al., 2009). Further studies on these NSL fabricated antennas for spectroscopic application are currently underway in our research group.

4.5 Conclusion

In this work, using nanostencil lithography, we have demonstrated a novel strategy for high-throughput nanofabrication of engineered plasmonic devices. This technique allows fabrication of nanoplasmonic devices with high uniformity and repeatability without using operationally slow and expensive electron/ion-beam lithography tools. Fabricated structures are characterized by scanning electron microscopy and optical measurements. Devices, fabricated using NSL technique are shown to have compa-

rable optical characteristics with respect to the arrays fabricated by EBL. We show that the stencil can be reused for high-throughput fabrication of antenna arrays by simply removing the metal residue with a mild metal etchant. We also show that NSL offers flexibility and resolution to create radiatively engineered nanoantenna arrays for excitation of collective plasmonic resonances. These excitations, by enabling spectrally narrow far-field resonances and enhanced near-field intensities, are highly suitable for ultrasensitive vibrational nanospectroscopy. We believe that NSL can facilitate a significant progress towards the wide usage of plasmonic devices for various applications.

Chapter 5

Nanostencils: Versatility for Fabrication and Patterning

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5.1 Deposited Material Flexibility of Nanostencil Lithography

The evaporation of metals through stencils has been the most common way to exploit stencil lithography. Here we firstly present the relevant literature for the nanostructuring of different materials where resistless processing is required (Table 5.1). In 2004, T. Schallenberg et al. reported the deposition of CdZnSe quantum well islands using nanostencils (Schallenberg et al., 2004). The most important aspect of this work is it is the first time stencils and molecular beam epitaxy (MBE) is combined. In MBE the use of resists or etching processes lead to strong degradation of the material properties which makes NSL a suitable technique for MBE growth. In 2005, C. V. Cojoracu et al. reported using nanostencils for pulsed laser deposition of ferroelectric materials such as BaTiO₃, Ge and lead zirconate titanate (PZT) by PLD (Cojoracu et al., 2006). In 2005 P. Zahl et al. also reported the deposition of C₆₀ fullerenes with 110 nm features on 40 nm wide Cu structures on the substrates (Zahl et al., 2005). In 2006, R. M. Langford et al. reported nanostencil lithography for the deposition of magnetic nickel nanocontacts for studying ballistic magnetoresistance (Langford and

Wang, 2006).

Table 5.1: Deposition of different materials using nanostencils. Modified from (Mena, 2010).

Material	Characteristic Size	Reference
CdZnSe by MBE through GaAs/AlGaAs stencils	300-500 nm	(Schallenberg et al., 2004)
$BaTiO_3$ deposition by PLD	400 nm	(Cojocaru et al., 2006)
PZT deposition by PLD	120 nm	(Shin et al., 2005)
C_{60}	100-400 nm	(Zahl et al., 2005)
Ni	40 nm	(Langford and Wang, 2006)
Antibody and biomolecules on PDMS	100 nm	(Huang et al., 2012)

Nanostencil lithography is a shadow mask technique that allows the patterning of different kind of materials. As shown above, materials like metals, dielectrics, magnetic materials have been successfully deposited through stencils. An important advantage of stenciling is the ability to reuse the stencils many times. The only problem is the clogging of the membranes after material deposition when stencils contain nanometric apertures. In the previous chapter it is shown that there are various wet etching liquids for metals that are highly selective to silicon nitride and allow the cleaning of stencils for different metals. Even though all of the fabricated structures are made of Au in this thesis, similarly other metals could also be patterned. Figure 5-1 shows structures of different metals, Al, Cr, Ti, Ge, Au, and Ag on silicon substrate deposited at 1 Å/s through similar rod shaped nanoapertures.

As seen in Figure 5-1, the deposited structure consists of a central structure surrounded by a halo. It can be seen that germanium has the sharpest structure features

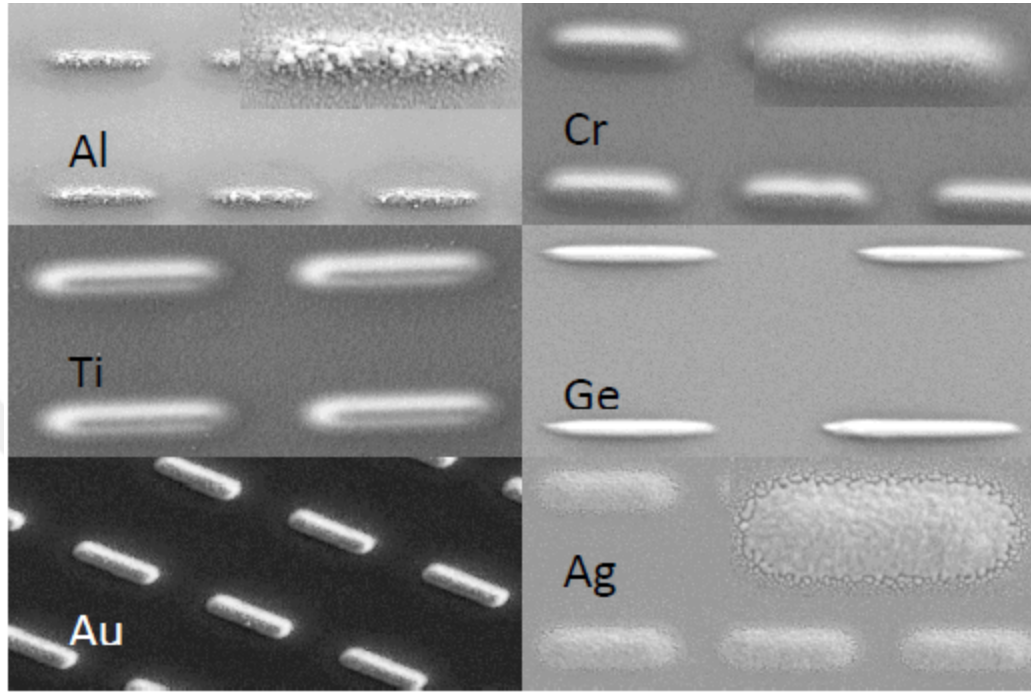


Figure 5.1: Nanopatterning different metals on silicon substrate using similar stencil design. Ge, Au and Cr gives high surface quality structures due to their diffusive properties on silicon.

with no visible halo around them which spread out on the surface in a thin layer as compared to other metals. Individual particles on the structures can be seen very clearly in the case of aluminum and has the broadest halo spread around the structures followed by silver. For gold, the halo spread is smaller than that observed in the case of aluminum. Similar to aluminum, metallic grains scattered in a halo can be seen in the case of gold too. Chromium and titanium have comparable structures with little or no visible halo around the structures but scattered nanoparticles are visible when looked closely. Germanium has no halo around its structures and there are no visible nanoparticles. This is due to the fact that germanium is the least diffusive metal out of all the ones that were used for testing. Aluminum, on the other hand, yielded coarse structures indicating that it is the most diffusive one. In summary, in the case of Au and Ge deposition no significant halo can be observed. These results

are also supported by lateral AFM scans of the deposited metals (Figure 5.2). Overall, the presented results indicate that the halo and geometrical blurring behavior is common for metallic structures deposited through stencils. However, a comparison of the blurring between the materials presented requires further analysis because the depositions are not all done with the same stencils.

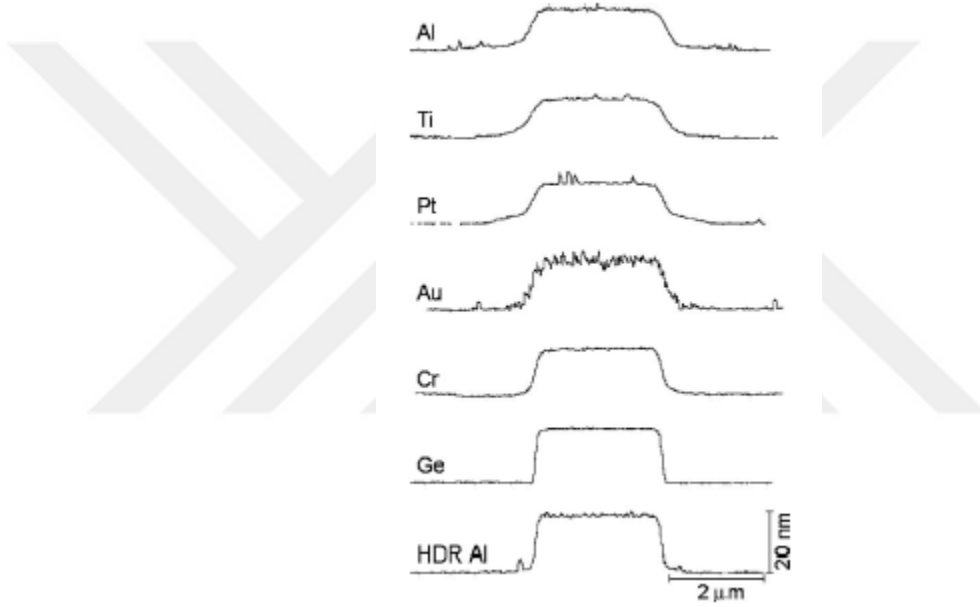


Figure 5.2: AFM scans of different depositions. Adapted from (Rácz and Seabaugh, 2007)

The formation of the halo is mostly related to the atomistic processes involved in metallic thin film growth. The deposition of a structure by evaporation implies the condensation of the atoms on the substrate, heating the substrate a few degrees (up to 40°C) for a conventional silicon wafer. The growth of the structures is driven by both thermodynamics and kinetics. When the atoms arrive to the surface, they remain mobile due to surface diffusion and can join an existing island, form a new nucleation center or eventually be desorbed. The diffusion of atoms during film growth is driven by a gradient in the chemical potential and is a thermally activated process. The surface diffusion activation energy E_d and the diffusion coefficient $D = D_0 \exp(E_d/k_B T)$ are

not fixed constants and may depend on the adatom coverage and the adatom-adatom and adatom-substrate interactions. The activation energy for diffusion of metallic atoms on metals is $0.5 - 1\text{eV}$ (varies for different metals). These different phenomena and factors, like nucleation, diffusion, substrate properties and deposition conditions, affect the dynamics of the adsorbed atoms and probably determine the formation of the halo. The dependence of the surface diffusion activation energy on temperature can be used to minimize the diffusion. It has been observed that diffusion can be suppressed by lowering the substrate temperature. Reportedly, vacuum deposition onto a substrate cooled to liquid nitrogen temperature decreased the spreading of Er dots on SiO_2 by a factor of 2 compared to room temperature. Other than metals, different types of biomolecules can be patterned on the same substrate. In the following, we demonstrate NSL for high throughput patterning of bioprobes with nanoscale features on biocompatible polymer substrate. Nanostencil lithography employs high resolution and robust masks integrated with array of reservoirs. We show that the smallest pattern size can reach down to 100 nm. We also show that different types of biomolecules can be patterned on the same substrate simultaneously. Furthermore, the stencil can be reused multiple times to generate a series of identical patterns. Finally, we demonstrate that biomolecules can be covalently patterned on the surface while retaining their biofunctionalities. Our approach, by offering the flexibility on the nanopattern design and enabling the reusability of the stencil, significantly simplifies the bionanopatterning process, thereby could have profound implications in diverse biological and medical applications.

5.1.1 Multiple Biofunctional Molecular Nanopatterns on Polymer Substrate

Bionanopatterning enables precise immobilization of biomolecules in well defined patterns while keeping their original functionality. Patterned biomolecules with nanoscale

features have great potential in diverse biological and medical applications such as biosensor, proteomics, pharmacology, tissue engineering and cell cultures (Mendes et al., 2007; Christman et al., 2006; Blawas and Reichert, 1998). For example, DNA nanoarrays offer the possibility of measuring the expression levels of large numbers of genes simultaneously and genotyping multiple regions of a genome (Drmanac et al., 2010; Husale et al., 2009). Similarly, high density protein arrays allow screening of larger number of targets with significantly smaller volumes of materials, leading to rapid analysis in proteomics and drug discovery (Lynch et al., 2004; Lee et al., 2004). In addition, patterned biomolecules can provide physical framework that supports cell attachment, as well as biological and chemical moieties that promote and direct cell growth. Such manipulation of cells can be used to study cell behavior and cellular interaction in tissue engineering (Hoover et al., 2008; Wheeldon et al., 2011).

In order to manipulate and pattern biomolecules with micro/nano scale precision, variety of approaches have been implemented. Commonly used methods include dip-pen lithography (Lee et al., 2002), nanocontact printing (nCP) (Truskett and Watts, 2006), inkjet printing (Roth et al., 2004), and electron beam lithography (EBL) (Kolodziej and Maynard, 2012). However, each of these approaches suffers from various limitations with regard to resolution, patterning speed, multiplexing ability, complexity and cost. For example, while dip-pen lithography exhibits high reliability and precise pattern features of tens of nanometers, it is a low throughput technique and falls short in multiplexing capabilities. Nanocontact printing is easy, fast and inexpensive. But patterning dense arrays of different bioprobes at the same time is problematic with this technique. Inkjet printing can print thousands of different materials and rapidly replicate arrays with high throughput. However, its resolution is typically 50-100 μm . As to EBL, although precise geometries and patterns can be achieved, it is a low throughput and costly method. To overcome these

limitations, some other bionanopatterning techniques have been developed during the past few years. For instance, polymer pen lithography uses nanoscale polymer tip arrays to contact print protein patterns in a high throughput manner (Zheng et al., 2009). However, it requires substantial effort to optimize the process since the pattern accuracy and repeatability are related to many factors such as contact force and time. Another method, the parylene shadow mask approach, uses EBL patterned parylene layer as a disposable peel-off template to generate biomolecule arrays (Selvarasah et al., 2008). But the template is disposed every time after use, and a new one needs to be fabricated again using time consuming and costly EBL. Given all these challenges, it is of great importance to find an alternative method that can easily pattern various biomaterials over a large area in a high throughput manner and at low cost.

In this chapter, we demonstrate a novel bionanopatterning approach based on nanostencil lithography (NSL). Instead of evaporating materials, we use the stencil to incubate and pattern biomolecules with nanoscale features. High-throughput patterning of biomolecule nanoarrays can be achieved on biocompatible polymer surfaces like polydimethylsiloxane (PDMS). The stencil we use is patterned silicon nitride (SiN_x) membrane supported by a silicon wafer, as shown in Figure 5.3(a). Our stencil fabrication process results in a truncated pyramid shaped reservoir and a nanopatterned SiN_x mask underneath. Using this unique configuration, we can incubate biosolution in the reservoir. The SiN_x mask shadows the biosolution around the apertures, and biomolecules are patterned through these apertures onto the substrate. Nanoscale protein patterns with feature size down to 100 nm are achieved. We show different kinds of protein arrays can be generated simultaneously on the same substrate by filling each reservoir with different biosolution. We also show that the stencil can be reused many times to generate a series of identical biomolecule patterns. As an appli-

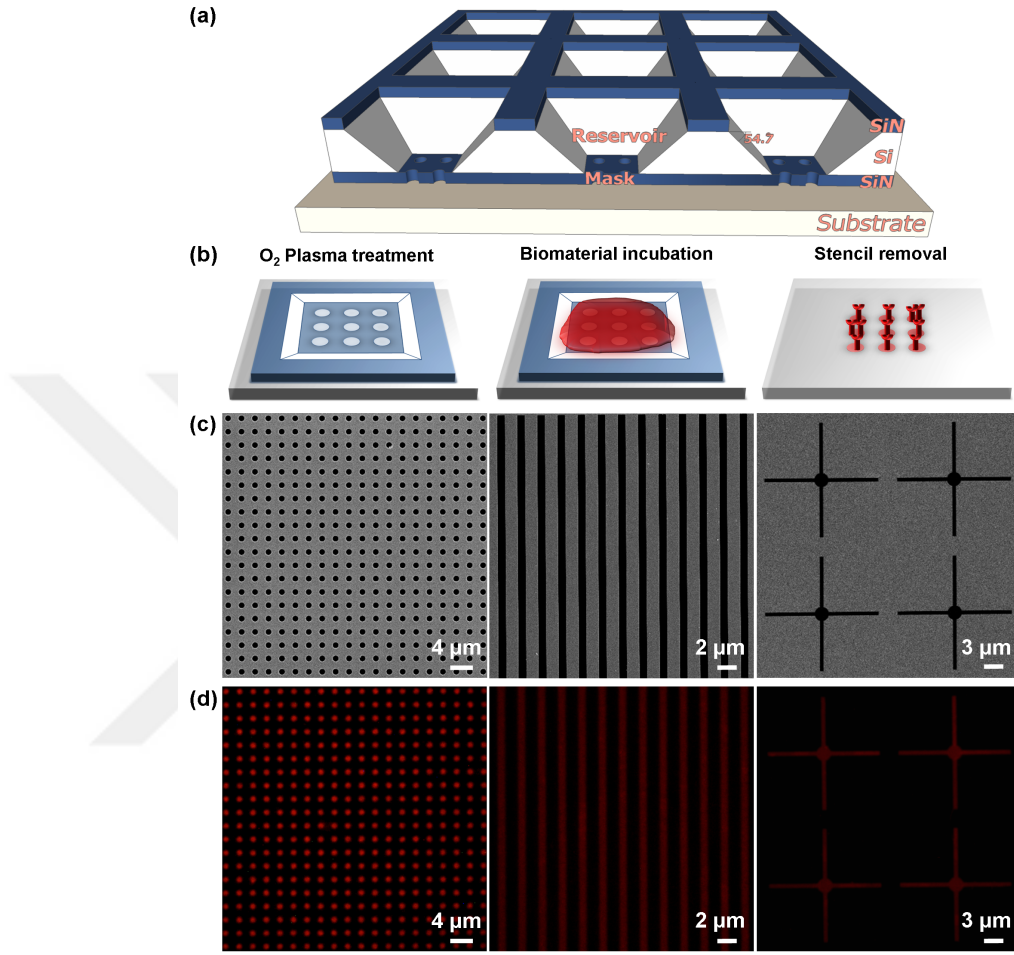


Figure 5-3: NSL technique is used to generate biomolecule patterns. (a) Schematic view of a stencil. The stencil has arrays of reservoirs and a SiN_x mask with nanoapertures under each reservoir. The volume of the reservoir is calculated to be around 0.12 mL. (b) Schematic diagrams of the NSL bionanopatterning technique. Oxygen plasma is applied to make the PDMS surface hydrophilic. Biomaterials are incubated in the reservoir and patterned through the apertures on the mask. Well defined biopatterns are left on the substrate after the stencil removal. (c) SEM images of three different stencil masks are shown. From left to right: a hole-array with 900 nm diameter and 1.5 μm pitch, parallel lines with 800 nm width and 2 μm spacing, and a cross shaped array with 1 μm line width. (d) TRITC labeled anti-mouse IgG is incubated in the stencils. Fluorescence images of patterned antibody are shown. Each array is generated using the corresponding stencil mask shown above.

cation, by incorporating stencil on a modified PDMS surface, we are able to covalently bind monolayer proteins in defined patterns. We also demonstrate that the immobilized proteins preserve their biofunctionalities by measuring the interaction between patterned antibodies and their antigens. This bionanopatterning scheme, enabling the reusability of stencil and simultaneous patterning of a broad range of biomolecular probes, can significantly lower the complexity as well as the cost of biomolecule patterning at nanoscales, and find applications in laboratorial and clinical studies.

Once the stencil is obtained, we can use it to pattern biomolecules. The schematic view of the patterning method is shown in Figure 5-3(b). It is a simple and straightforward process with three steps. First, we attach the stencil onto a PDMS substrate and perform oxygen plasma treatment for 60 seconds. After the treatment, the PDMS area underneath the stencil apertures will be hydroxylated and become hydrophilic. Then the biomolecule solution is spotted into the reservoir and incubated for one hour. After being rinsed and blow-dried, the stencil is peeled off from the PDMS substrate. Removal of the stencil leaves patterned biomolecules on the substrate with shapes complementary to that of the apertures on the stencil. The reason we choose PDMS as the substrate is two-fold. Firstly, PDMS is a biocompatible polymer which has been widely used as template for biomolecular applications. Secondly, PDMS can weakly bond with SiN_x surface due to its surface electro-property and elasticity (McDonald and Whitesides, 2002). The bonding minimizes the stencil-substrate gap and prevents the biomolecule solution from diffusing laterally between the surface and the stencil. As we will show below, the gap-free bonding results in nearly perfect pattern transfer from mask to the substrate with nanoscale resolution.

Electron beam lithography does not only offer us pattern design flexibility, but also the feature resolution and accuracy. Biomolecule patterns with features down to 100 nm can be achieved by using stencil with correspondingly small apertures. To

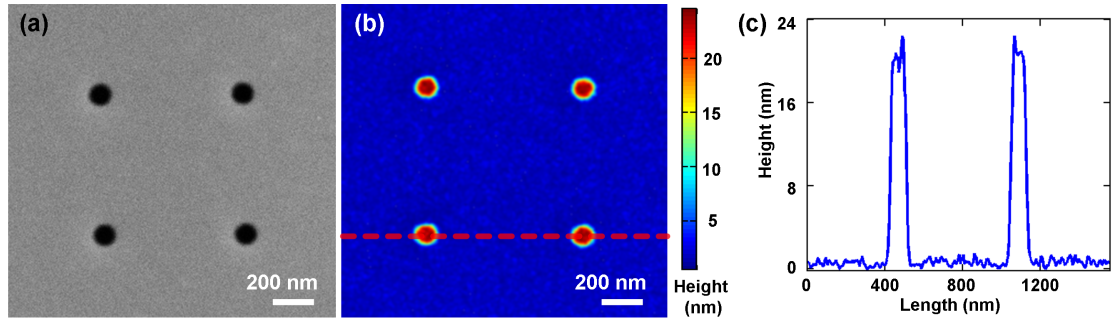


Figure 5-4: Anti-mouse IgG nanoarray with features down to 100 nm is demonstrated. (a) SEM image shows the nanohole mask fabricated on a SiN_x membrane. Hole size is measured to be 105 nm. (b) AFM image of patterned anti-mouse IgG nanoarray is shown. (c) Cross-sectional profile of a patterned row is shown. Data is taken along the red dash line in (b). The widths of the patterns are measured to be around 110 nm

show this capability, we fabricate nanohole arrays on a stencil mask with diameter as small as 105 nm. SEM image of the mask is shown in Figure 5-4(a). Anti-mouse IgG patterns are generated by this stencil in the same way as described above. Since these patterns can not be clearly visualized by optical microscope due to the diffraction limit, atomic force microscopy (AFM) measurement is performed to investigate the detailed profiles of the protein patterns. The AFM image of the protein spot array and its cross section profile are shown in Figure 5-4(b) and (c), respectively. The patterned spots are uniform with clear boundaries. We also observe that the shape of the spot is complementary to that of the apertures on the stencil. The size of the protein spots, measured to be about 110 nm, is nearly the same as the apertures on the stencil. The small difference could be due to the AFM resolution limit. These results prove that there is little lateral diffusion of biomaterials between stencil and substrate since the gap is minimized in our technique. The AFM measurements also demonstrate that our method can preserve the resolution of EBL and generate nanoscale patterns with high accuracy. Given that in our recent work, we demonstrated that the resolution of NSL fabricated structures can be controlled under sub 10 nm (Aksu et al., 2011)

in fabricating plasmonic structures, the feature size of the biopatterns can likely be further reduced by using stencil with smaller apertures.

Multiplexing Capability of NSL

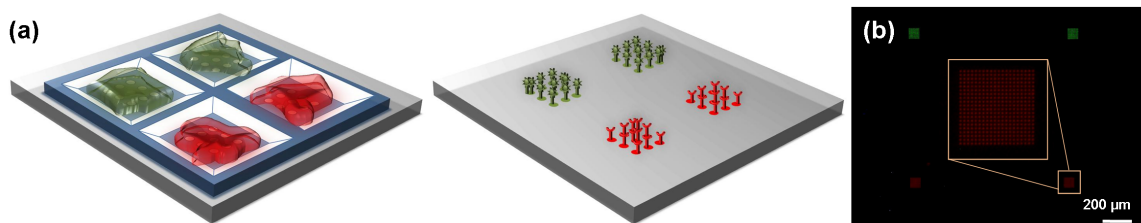


Figure 5-5: The stencil can be used to generate different types of biomolecule patterns simultaneously. (a) Schematic diagram of different biomolecule patterning is shown. First we attach the stencil onto PDMS substrate. Then we load each reservoir with different biomolecule solutions. After the removal of stencil, biomolecules patterns with well defined shapes are achieved. (b) Fluorescence image shows that two different IgG nanoarrays are generated on the PDMS surface. Reds ones are anti-mouse IgG labeled with TRITC and green ones are anti-monkey IgG labeled with FITC. Pseudo color is applied for better illustration. Image in the yellow blanket shows the enlarged feature of the right-bottom array.

One advantage of our patterning method is that different kinds of biomolecules can be patterned simultaneously on the same substrate in a high throughput manner. This multiplexing capability is due to the unique configuration of our stencil. As illustrated in Figure 5-5(a), each stencil contains a number of reservoir arrays that are separated by 1 mm. The architecture of stencil naturally forms barriers among individual reservoirs and prevents solutions from interacting and mixing among them. As a result, different biosolutions can be spotted and incubated in each reservoir, and a variety of biomolecules can be patterned simultaneously on the substrate. To demonstrate this capability we use two antibodies tagged with different fluorophores: anti-mouse IgG labeled with TRITC and anti-monkey IgG labeled with fluorescein isothiocyanate (FITC, from Sigma-Aldrich). Figure 5-5(b) shows the fluorescence signal from the patterned substrate with 2×2 arrays. Each array is about $90 \mu\text{m}$ by

90 μm in size. Pseudo color was applied on the merged image for better illustration. Arrays are well defined and separated by 1 mm. Each feature in the array is uniformly patterned, as shown in the enlarged image. The spacing is set to 1 mm since we load each reservoir manually using pipettes. For applications requiring dense arrays, this spacing can be further reduced by changing the wet etching in stencil fabrication to deep reactive ion etching. The later process leaves vertical sidewalls as opposed to the tilted ones we currently have. With such modification, if the reservoirs are 100 μm by 100 μm and separated by 100 μm , the packing density can scale up to 25 unit/ mm^2 . For loading biosolutions into dense reservoir arrays, the patterning process can be integrated with a standard microarray spotter. Multiple antibody arrays created using this approach could be useful for high throughput immunoassays, molecular diagnostics and drug screening.

Reusability of the Stencil for High-throughput Nanofabrication

Another unique feature of our bionanopatterning approach is the reusability of the stencil. This capability enables high throughput production and is particularly useful when replication of the same design is necessary. Once peeled off from the substrates, the stencil is cleaned in a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) (v/v 3:1) for 5 minutes. After the biomaterial residue and other remnants are stripped away, the stencil is rinsed in water, blow-dried with nitrogen and ready to use again. In some rare cases, mechanical cracks are observed on the stencils. This may result from the peel-off process since the thickness of the membranes is around 70 nm. The life span of the stencil can be improved by further increasing the thickness of the membrane. SEM images in Figure 5-6(a) show the surface of a newly made stencil mask and in Figure 5-6(b) shows its condition before the 4th usage (after cleaning). Both surfaces are clean and uniform. No sign of degradation or deformation is observed after the 3rd usage. The size of the aperture, 900 nm in

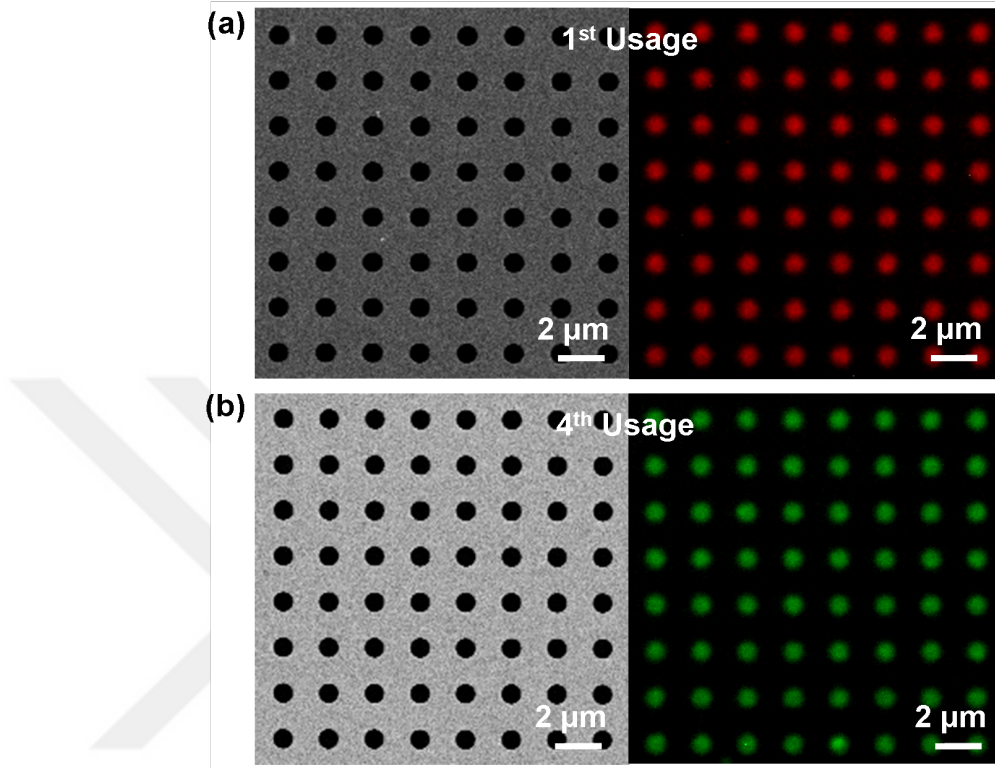


Figure 5-6: Stencils can be reused multiple times. (a) Left: SEM image of a newly made stencil. Right: fluorescence image of the patterned anti-Mouse IgG (TRITC labeled) arrays using this stencil. (b) Left: SEM image of the stencil before the 4th usage. Right: fluorescence image of the patterned anti-monkey IgG (FITC labeled) array.

diameter, is the same for both cases. The stencil was used to pattern TRITC tagged anti-mouse IgG nanospots for the 1st usage and FITC tagged anti-monkey IgG for the 4th usage. Fluorescent images of the patterned antibodies for both cases are shown in the right column of Figure 5-6(a) and (b), respectively. The shape and the uniformity of the fluorescence spots are almost identical. These observations clearly indicate that one design can be replicated many times with a single stencil. The reusability of stencil simplifies the patterning process and lowers the fabrication cost, making our approach highly advantageous compared to the other methods.

Biopatterns Generated by Covalent Linking

For biopatterning techniques to be useful in real applications, two important cri-

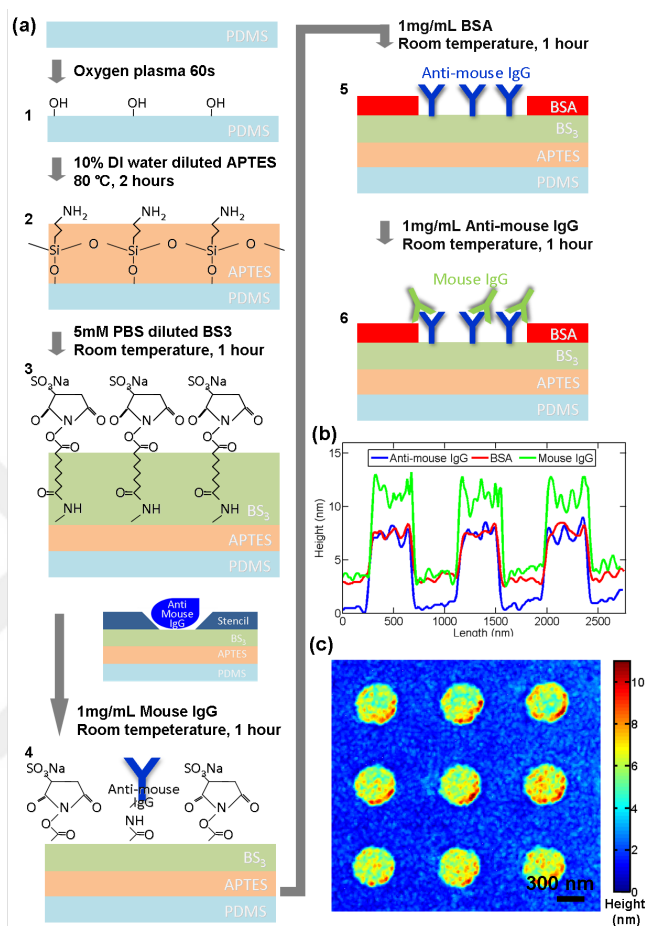


Figure 5.7: Proteins can be covalently patterned by functionalizing the PDMS surface, and the immobilized proteins retain their functionalities for further biointeractions. (a) Schematic diagram for the modification of PDMS surface and the following specific binding test. (b) Cross-section profiles show the thickness changes of the patterns after each interaction. The blue line shows the profile of anti-mouse IgG pattern generated by the stencil. The heights are measured to be 8 nm on average. After BSA occupies the unpatterned PDMS surface, the background rises about 3 nm as shown by the red line. The green line indicates that the mouse IgG is specifically captured only by the anti-mouse IgG patterned area, and the heights are increased by 6 nm on average. (c) AFM image of the nanopatterns after the interaction between the anti-mouse IgG and mouse IgG is shown. Mouse IgG is specifically captured by the anti-mouse IgG patterned areas, showing that the biofunctionalities are well retained after the bionanopatterning process.

teria need to be considered. Firstly, it is highly desired to covalently immobilize biomolecules on surface. Covalent bonds offer both stability and maximal base pairing opportunity by forming a dense and well oriented monolayer (Kim and Kang, 2008). They also reduce nonspecific bindings and diminish sample loss during the course of experiments, allowing for better sensitivity. Secondly, the immobilized biomolecules have to retain their functionalities, so that consecutive bioassays can be performed efficiently. We can successfully achieve these two goals by using our patterning method. As an example, we integrate our stencil on chemically modified PDMS surface for patterning of covalently binded antibody, and test its functionality by interacting with its corresponding antigen. Figure 5.7(a) shows the schematics of the surface modification treatment and a following specific binding test for immobilized anti-mouse IgG. First we treat the PDMS sample with oxygen plasma for 60 s, introducing the hydroxyl groups and making the surface hydrophilic (Figure 5.7 (a)-1). Then we immerse the sample in 10 %(3-Aminopropyl)triethoxysilane (APTES, from Sigma Aldrich) diluted in water at 80°C for two hours. This step modifies the PDMS surface by introducing the amino groups (Figure 5.7(a)-2). After rinsing twice with DI water and blow dry with nitrogen, we cover the sample surface with 5 mM bis(sulfosuccinimidyl)suberate (BS3, from Sigma Aldrich) diluted in PBS. BS3 is a homobifunctional amine-to-amine crosslinker that can covalently bind the amino groups previously formed on the PDMS surface and the ones from the antibody (Figure 5.7(a)-3). The incubation takes one hour at room temperature. Following rinsing in DI water and nitrogen blow drying, we apply the stencil biopatterning method to pattern antibody on the sample. The stencil mask contains array of nanoholes with 420 nm diameter. The reservoirs are loaded with 1 mg/mL anti-mouse IgG and incubated at room temperature for one hour. After washing, blow-drying and peeling off the stencil, we generated covalently bonded antibody nanopatterns on the surface

(Figure 5.7(a)-4). The line profile from AFM measurement is shown in blue curve in Figure 5.7(b). About 8 nm anti-mouse IgG layer is formed on the substrate, which is close to the monolayer thickness. Our biopatterning technique not only achieves high throughput covalently bond biopatterns with monolayer, but also preserves the biofunctionalities of the immobilized antibodies. To demonstrate this, we investigate the interactions between patterned antibodies and their antigen. First we treat the antibody patterned sample with 1 % bovine serum albumin (BSA) in PBS for one hour. BSA passivates the sample surface except for the anti-mouse IgG patterned areas (Figure 5.7(a)-5). As shown by the red line in Figure 5.7(b), the background rises approximately by 3 nm. Then 1mg/mL FITC labeled mouse IgG is coated on the entire substrate and incubated for one hour. The sample is washed with PBS and DI water, and blow dried with nitrogen afterwards. Mouse IgG specifically binds to anti-mouse IgG (Figure 5.7(a)-6), resulting in a 6 nm thickness increase on the anti-mouse IgG patterned area, as shown in green line in Figure 5.7(b). The final AFM image, after mouse IgG immobilization, is shown in Figure 5.7(c). The nanopatterned arrays are still well defined after the binding process. We checked sample under fluorescence microscope, no signal was observed from the unpatterned area, showing a good blocking formed by BSA. We also performed a control experiment whereby monkey IgG was incubated instead of mouse IgG, no binding was observed in that case.

5.2 Design Flexibility of Nanostencil Lithography

Given that EBL is used to create stencils for NSL, we inheritly preserve flexibility and accuracy of EBL in creating plasmonic nanostructures in variety of shapes and arrangements. This can be achieved by simply changing the aperture pattern on the silicon nitride membrane. Figure 5.8(a) shows SEM images of circular gold nano-

antenna arrays fabricated in triangular lattice on silicon substrate. The particles have 200 nm diameter with 600 nm periodicity. The diameters of the nanoparticles are 30 nm larger than the corresponding circular nanoapertures. The shape, size and periodicity distribution of these smaller nanoparticles have been observed to be very uniform over the area of the stencil ($100\ \mu\text{m} \times 100\ \mu\text{m}$). As the dimensions of the particle diminish, the resonances shift towards the visible wavelength regime. High-throughput fabrication of plasmonic substrates supporting resonances at visible spectrum could be important for non-linear photonic and photovoltaic applications. Figure 5-8(b) shows SEM images of Au nanowires with 350 nm width and $50\ \mu\text{m}$ length fabricated on silicon over $50 \times 50\ \text{mm}$ area. The corresponding nano-slits were 300 nm and $50\ \mu\text{m}$ in width and length. No discontinuity or width fluctuation is observed on the wires. The wires fabricated by the stencil technique can carry electrical signals (Selvarasah et al., 2008). In addition, these wires can also be used optically as on-chip plasmonic waveguides for ultra-dense optical interconnects (MacDonald et al., 2008).

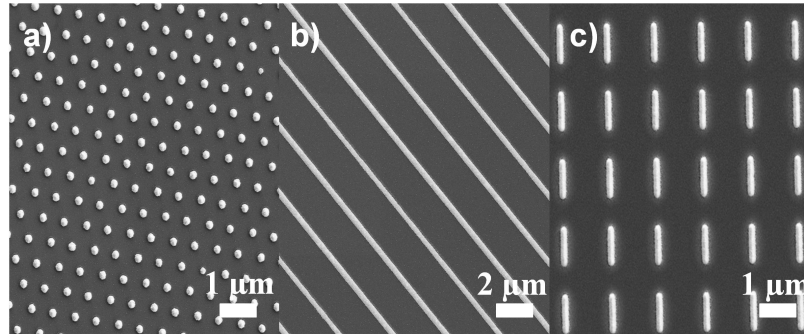


Figure 5-8: Nanostencil lithography allows us to fabricate structures composed of various shapes, dimensions and materials. SEM images of a) circular gold nano-antenna arrays with 200 nm diameter and 600 nm period in triangular lattice, b) gold nanowires with uniform 350 nm width and $50\ \mu\text{m}$ length, c) gold nanorod arrays are shown. All structures are fabricated on silicon using NSL.

After the resolution improvement achieved in Nanostencil Lithography after elim-

inating gap effect (details in Chapter 6), we demonstrated fabrication of engineered dimers such as sharp edged bow-tie antennas as well as oligomeric plasmonic meta-materials that can have inter particle separations as small as 25 nm (Figure 5.9). Such small gaps and asymmetries can induce novel electromagnetic responses such as plasmon induced transparency (Zhang et al., 2008).

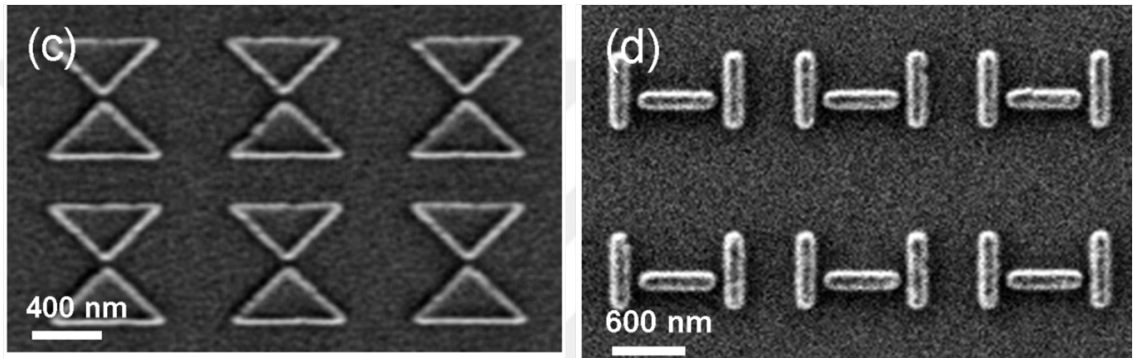


Figure 5.9: Dimers such as sharp edged bow-ties and asymmetric oligomers with inter particle spacings as small as 25 nm could be fabricated using NSL.

In theory any hole larger than atomic size can be used as shadow masks but minimum dimension possible with shadow mask are in the 10 nm range. One special limitation of the shadow masks is the impossibility of donut shaped structures. Using dynamic stenciling this problem can be overcome (Luthi et al., 1999). There are also other tricks to achieve donut design such as using very narrow bridges and relying on deposition diffusion under the mask donut shapes can be patterned. The general solution is to perform shadow mask deposition twice with half masks or using very thin bridges and the gap (Mena, 2010).

5.3 Substrate Flexibility of Nanostencil Lithography

As mentioned earlier, nanostencil lithography is a resist free process thus allows the transfer of the nanopatterns to any planar substrate whether it is conductive, insulat-

Table 5.2: Nanostencil Lithography demonstrated on unconventional substrates. Modified from (Mena, 2010).

Substrate	Characteristic Size	Reference
Free standing beams	300 nm	(Brugger et al., 2000)
Cantilever tips	20 nm	(Champagne et al., 2003)
SW-CNT λ -DNA	500 nm	(Zhou et al., 2003)
ODN-SAMs	700 nm	(Speets et al., 2006)
SW-CNT	100 nm	(Egger et al., 2007)
CMOS device	200 nm	(Arcamone et al., 2008)
PDMS, Parylene-C, LDPE	25 nm	(Aksu et al., 2011)

ing or magnetic. Many researchers have preferred nanostencil Lithography to deposit nanostructures on mechanically or chemically fragile substrates. Here, firstly, some major works of nanopatterning on such non-conventional substrates are presented (Table 5.2).

In 2000, Brugger et al. reported the deposition of metallic dots on cantilever tips (Brugger et al., 2000). In 2003, Champagne et al. reported deposition of 10 nm wide Er dots right on the tip of an AFM cantilever (Champagne et al., 2003). In 2003, Zhou et al. reported nanostenciling on single walled carbon nanotubes and DNA networks to measure the electrical properties of both structures (Zhou et al., 2003). In 2006 Speets et al. reported the nanofabrication on self-assembled monolayers (SAMs) which are widely used for chemical surface modifications (Speets et al., 2006). In 2007, Egger et al. reported deposition of micro- and nanoscale contacts on single walled carbon nanotubes (Egger et al., 2007). In 2008, Arcamone et al. reported the fabrication of nano-electro-mechanical systems on pre-fabricated CMOS

devices using stencil lithography (Arcamone et al., 2008). They could deposit 200 nm sized Al structures precisely aligned to be connected with a CMOS circuit. The flexibility in substrate choice is in sharp contrast to EBL and FIB lithography, which require conductive substrates or addition of a conducting film. Furthermore, resist based lithography techniques limit the shape and the size of the substrate due to the edge-bead formation in spin coating step. Certain applications may require use of non-conductive substrates with irregular shapes. For example, for optical bio-sensing applications at visible frequencies, using either glass or quartz based microscope slides are highly advantageous due to their optical transparency and low-cost. Similarly, at mid-IR frequencies, CaF_2 windows are very suitable. EBL on these insulating substrates requires addition of a conductive film either as a thin ITO layer before the application of EBL resist or as a thin sacrificial metal layer on the e-beam resist. As shown in previous studies, the ITO layer used in the former approach could interfere with the plasmonic responses of metallic nanoparticles (Augu   and Barnes, 2008), while the latter one involves additional fabrication steps. In contrary, using NSL we show here that direct patterning of plasmonic nanoantennas on non-conducting slides can be achieved with a single metal deposition step (Figure 5-10). The optical responses of gold nanorod arrays fabricated on glass and CaF_2 are shown in Figure 5-11. The antennas, intentionally distributed randomly, show distinct LSP resonances. The width and the height of the antennas have been set to 230 nm and 100 nm respectively and the nanorod lengths have been varied from 1000 to 1200 nm. In agreement with the dipole antenna theory, wavelengths of the plasmonic resonances scale linearly with the nanorod length. For a given nanorod length, the antennas deposited on CaF_2 substrate support plasmonic resonances at shorter wavelengths (longer wavenumbers) with respect to the antennas fabricated on glass surface. This is expected since CaF_2 has a lower refractive index ($n_{CaF_2} = 1.40$) than glass ($n_{glass} = 1.51$). Experimentally

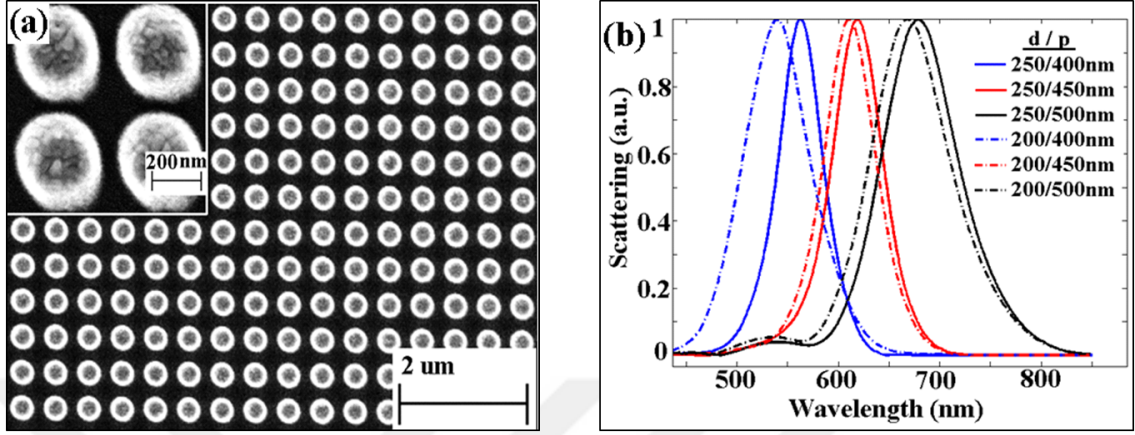


Figure 5-10: (a) SEM image of 300 nm circular gold nano dots with 500 nm periodicity on ITO covered glass. (b) Optical response of the structures in dark field shows strong resonances with narrow linewidths which is suitable for biosensing and photovoltaics

measured resonances are least square fitted to the dipole antenna scaling relation. The estimated refractive index values (1.64 and 1.42 for glass and CaF_2 respectively) closely match to the actual values. We also observed that antennas fabricated on CaF_2 substrates, compared to the ones on glass, show stronger resonances with narrower linewidth. This is also expected due to the lower optical absorption of CaF_2 with respect to glass at mid-IR frequencies.

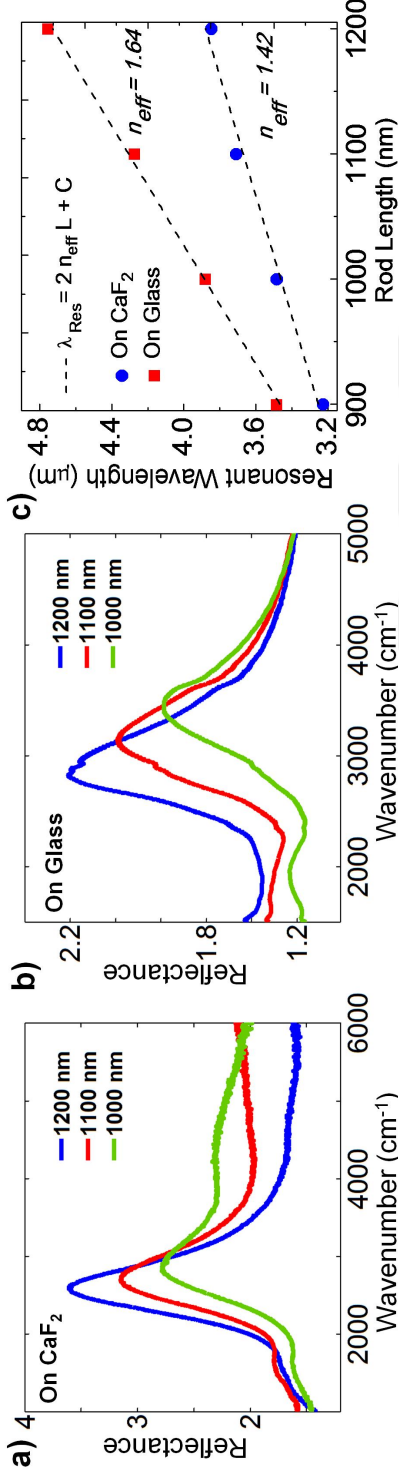


Figure 5.11: Reflectance spectra of randomly distributed nanorods a) on calcium fluoride and b) on glass substrate are shown. Legends indicate the rod lengths. CaF_2 substrate supports plasmonic resonances at shorter wavelengths and shows stronger resonances with narrower linewidths compared to the glass. c) Fundamental ($m = 1$) resonance wavelength on glass (red squares) and on CaF_2 (blue circles) substrates are linearly dependent on the rod length (dashed lines are linear fit). Effective refractive index calculated to be 1.64 for glass and 1.42 for CaF_2 are close to the actual values.

5.4 Conclusion

In conclusion, nanostencil lithography technique allows fabrication of nanoparticles made up of different metals and also patterning of biomolecules with high uniformity, resolution and repeatability in a simple, fast, and low cost fashion. Fabricated structures are characterized by fluorescence microscopy and AFM measurements. Varieties of patterns can be generated using flexible stencil designs, and the pattern features can be replicated with high fidelity. Protein arrays generated by our technique are shown to have feature size down to 100 nm. We show that the stencil can pattern different types of biomaterials. We also show that the stencil can be reused for multiple times by removing the organic residues before each usage. In addition, our technique enables patterning of covalently bond biomolecules while keeping their biological functionalities. We believe this powerful and versatile patterning technique can significantly facilitate the fabrication involving biomaterials, and these patterned nanoarrays could be useful in diverse biological and medical fields. In addition to its high-throughput capability, NSL lithography enables fabrication of plasmonic devices on surfaces otherwise difficult to work with electron/ion beam techniques. Here, we have demonstrated successful fabrication of plasmonic devices on non-conducting surfaces such as glass and CaF_2 . As proof of the versatility of the NSL technique, various nanoscale plasmonic structures such as nanowires and nanodisk are also fabricated. We believe that NSL can facilitate a significant progress towards the wide usage of plasmonic devices for various applications.

Chapter 6

Flexible Plasmonics on Unconventional and Non-Planar Substrates

6.1 High Resolution Nanostencil Lithography with Elastomeric Interfaces

Realization of electronic and photonic components on flexible, stretchable, non-planar and bio-compatible substrates as opposed to the conventional rigid substrates can open doors for next generation of optical devices and integrated circuits with new functionalities (Rogers et al., 2010; Kim et al., 2008; McAlpine et al., 2005). For example, flexible and biocompatible substrates integrated with electronic and photonic circuits can be wrapped around curved surfaces (McAlpine et al., 2007) enabling direct integration of sensor systems with the human body for wireless personal health monitoring. Similarly, stretchable polymeric substrates can lead to actively tunable optical materials and metamaterials for adaptive photonic systems (Pryce et al., 2010). Within the last decade, significant progress has been achieved in flexible electronics. Broad range of novel systems including electronic paper-like display devices (Gelinck et al., 2004), flexible electronics integrated with sensors for artificial skin applications (Someya et al., 2004), conformal bio-integrated electronics for in-vivo brain monitoring (Kim et al., 2010a), electronic eye-type imagers incorporating focal plane arrays on hemispherical substrates have been demonstrated (Ko et al., 2008).

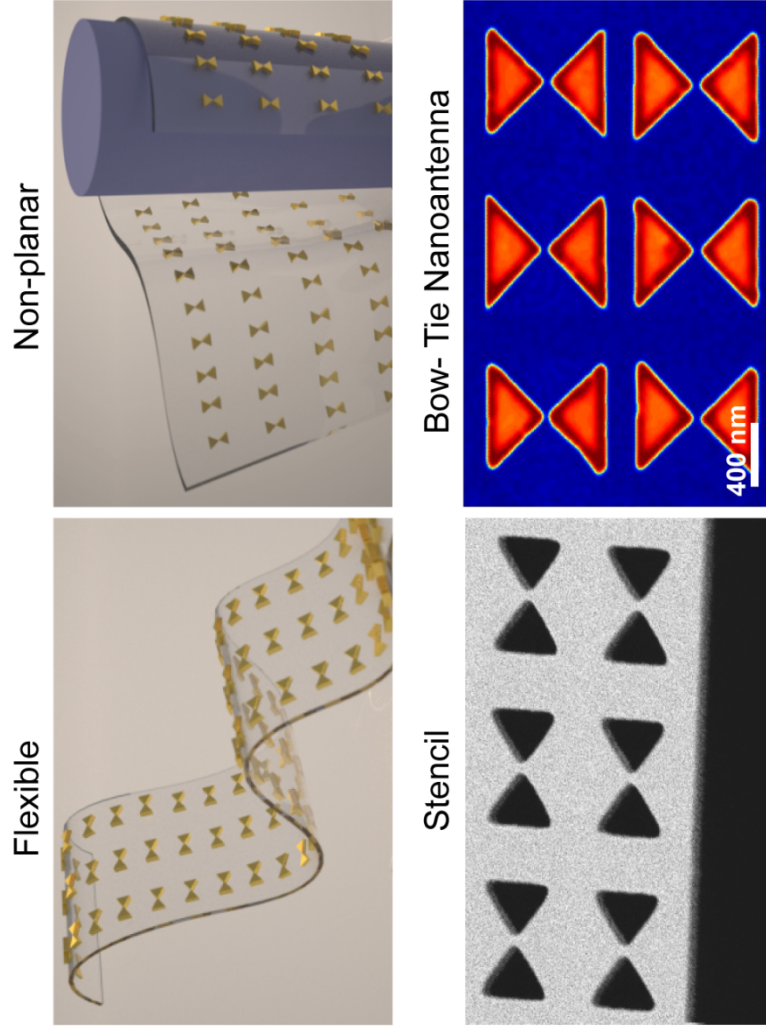


Figure 6.1: Flexible plasmonics and metamaterials on polymeric and non-planar substrates are demonstrated using nanostencil lithography. For the first time, high-resolution fabrication with 10 nm accuracy is achieved at high-throughput and low-cost in a single fabrication step. Remarkable precision is illustrated by fabricating sub-100 nm plasmonic particles with sub-50 nm interparticle distances. We showed optical tuning with mechanical stretching of the polymer substrate. We also showed patterning of nanostructures on curved surfaces, including optical fibers.

Contrary, there is very limited progress in exploiting such functionalities with photonics, particularly at dimensions relevant to nanoplasmonics operating in visible and infrared frequencies. This is mainly due to the difficulty of fabricating nanophotonic structures with dimensions below 100 nm on flexible, non-planar and mechanically compliant surfaces with traditional nanofabrication techniques. Furthermore, their required processing conditions such as operation temperature, use of chemicals (i.e. resists and solvents) are not compatible with polymer based and bio-compatible substrates. The demand for flexible, stretchable, non-planar electronic/photonic systems and multi-functional materials has fueled the research on innovative fabrication methods in recent years (Smythe et al., 2009; Fernandez-Cuesta et al., 2007). Existing novel methods mostly rely on soft lithography techniques (replica molding (Xia and Whitesides, 1998), decal transfer lithography (Childs and Nuzzo, 2002), PEEL (Henzie et al., 2007) etc.), where poly-dimethylsiloxane (PDMS) act as a mold for pattern replication. These techniques have allowed relatively reliable patterning on flexible surfaces, however, each is limited in terms of versatility. They are either complex and require multiple fabrication steps or limited by the material used for patterning and substrate choice. For example, PEEL method described by Henzie et al. involves multiple pattern transfers (from silicon master to PDMS, then from PDMS to photo resist, and from photoresist to nanoholes on thin metal mask) for fabrication of metallic structure on thermal plastic (Figure 6-2). Due to these multiple pattern transfer steps, the resolution of this technique is severely degraded for fabrication of plasmonic structures demanding sub 50 nm interparticle spacing.

Recently, Pryce and Aydin et al. (Pryce et al., 2010) fabricated metamaterials on PDMS substrate by transferring the structures from silicon surface using surface modification. However, the employed surface chemistry procedure (based on mercapto silane) is specific to PDMS substrate and gold. Furthermore, by harness-

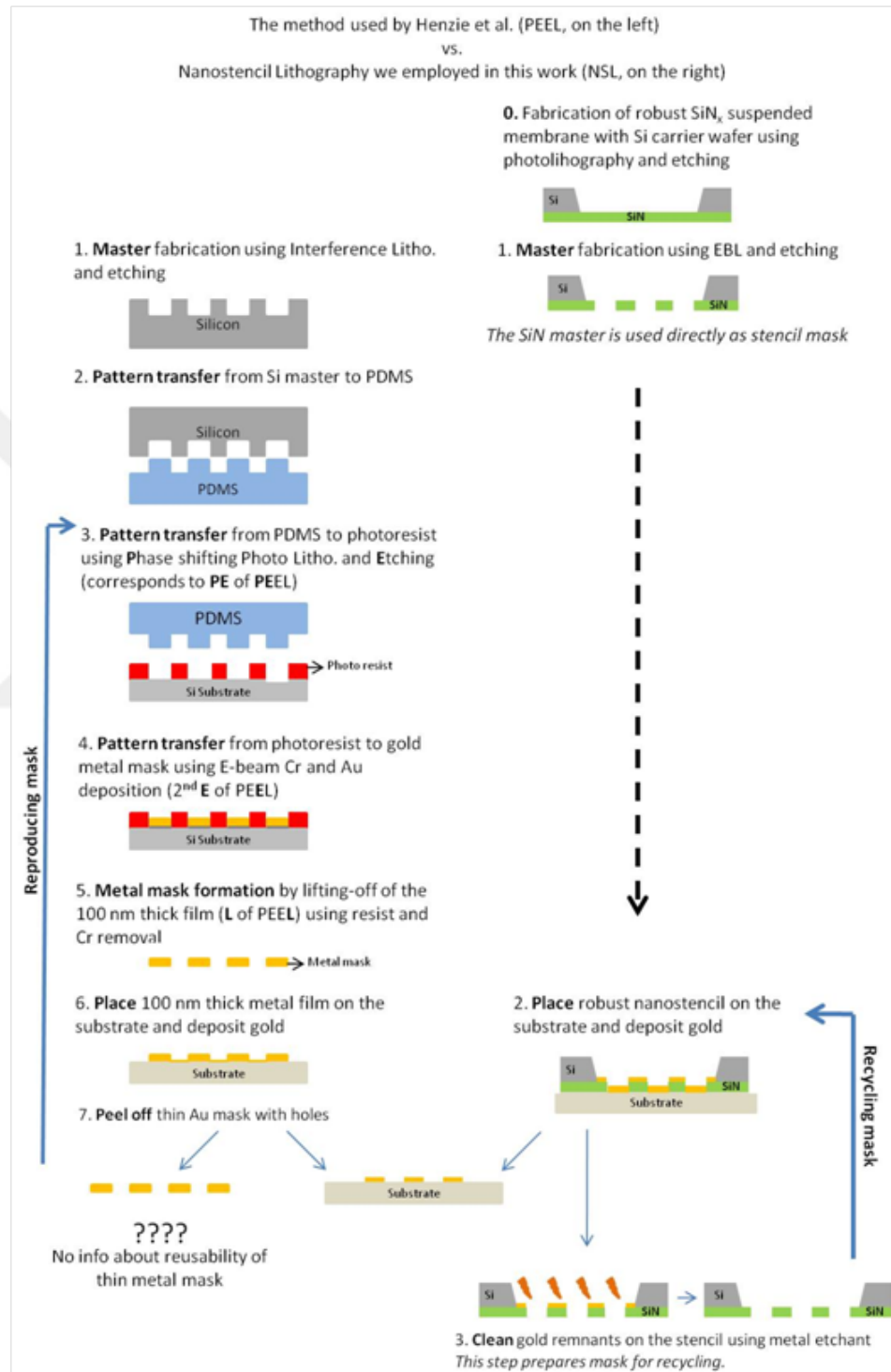


Figure 6.2: Comparison of PEEL (Henzie et al., 2007) with NSL.

ing both the benefits of soft lithography and traditional contact photolithography, Bowen and Nuzzo et al. (Henzie et al., 2007) presented patterning protocols for defining photoresist patterns on highly curved substrates. But it is challenging to fabricate features below $0.1\mu\text{m}$ using their method. Here, we present Nanostencil Lithography (Figure 6-1) that can enable nanopatterning on a wide range of flexible substrates in a single fabrication step (Aksu et al., 2011). As shown in Figure 6-3, once a stencil is placed on a substrate, it behaves like a mask and shadows the applied agent (i.e. organic/inorganic materials) around the aperture. When the stencil is removed, it leaves on the substrate nanoparticles with shapes complementary to that of apertures on the stencil. Figure 6-3(a) and (c) shows fabricated nanostencil and the generated bow-tie shaped metallic nanoparticles, respectively. Recently, we introduced nanostencil lithography for fabrication of variety of nanoplasmonic structure designs including antenna arrays on rigid surfaces such as silicon, CaF_2 and glass (Aksu et al., 2010). In this earlier work, our spectral measurements and scanning electron microscopy images confirmed the feasibility of NSL technique for fabrication of antenna arrays with optical qualities achievable by electron beam lithography (EBL). We also showed that nanostencils can be reused multiple times to fabricate the same pattern with identical optical responses repeatedly and reliably. This capability is particularly useful when high-throughput replication of the optimized nanoparticle arrays is desired.

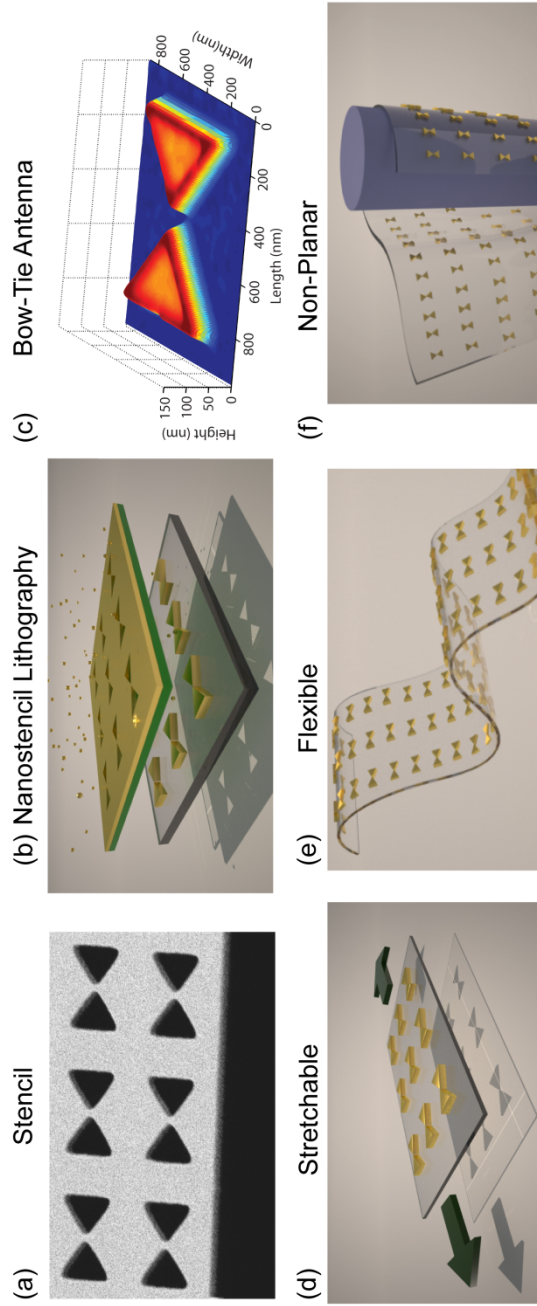


Figure 6.3: Illustration and representative SEM images of functional plasmonic structures. Gap between substrate and stencil plays an important role for fabrication of high quality structures using Nanostencil Lithography (b). Using bowtie shaped stencil (SEM image seen at (a)), bowtie particles with sharp edge profiles and sub-50 nm gap distance could be obtained (AFM image seen at (c)) on flexible, stretchable, bio-compatible, non-planar substrates. These substrates could be used to tune optical properties of plasmonic structures by applying mechanical strain (d). Also flexible films can be directly transferred (e) and wrapped around non-planar surfaces (f).

In this chapter, we demonstrate for the first time nanostencil lithography can be used to achieve functional plasmonic devices on a variety of unconventional substrates including biocompatible PDMS, parylene based polymer thin films as well as plastic food storage roll films purchased from a convenience store. By patterning plasmonic nanoantennas on stretchable polymer films, we show that the optical responses of the antenna arrays can be actively tuned with mechanical stretching of the flexible substrate. We also demonstrate the resolution of nanostencil lithography can be enhanced dramatically by exploiting the adhesive nature of polymeric surface. Controllable adhesion of reusable stencils on the polymer substrate by resulting in minimal stencil-substrate gap eliminates the diffusion and the shadowing problem accompanied with the gap. Consequently, we fabricated nanostructures complementing the size of the nanoapertures on the stencil down to 10 nm accuracy and achieved reliable production of plasmonic dimmers, such as bow-ties with inter-particle separation as small as 30 nm and structure dimensions below 100 nm. Finally, we demonstrate plasmonic structures fabricated on thin flexible films can be directly transferred and wrapped around non-planar surfaces, such as optical fibers. Patterning the facets and the surfaces of the fibers can enable novel functional photonic probes that can monitor the environmental changes in spaces that are either difficult to access.

6.1.1 Analysis of Blurring in NSL and Improving Stenciling Precision

Nanostencil lithography offers great flexibility in fabricating engineered nanostructures for metamaterials and plasmonics. However, there are some inherent limitations to the resolution of NSL. Process flow involves placing the stencil directly on top of the substrate and fixing typically with clips or tapes. This implementation inevitably results in a gap between the stencil and the substrate due to factors such as uneven surface topology and bending/curving of the wafers and stress on the membranes. This behavior is in contrast with resist-based lithography, in which the resist forms

a mask that is adhered to the substrate. This is an advantage that allows the use of stencil lithography on substrates with chemically or mechanically fragile structures that can be damaged by resist processes such as energy radiation, chemical solvents or mechanical contact. It also allows the patterning on high topography structures where resist coating is difficult. However the stencil-substrate gap causes several problems during material (such as metal) deposition. This gap and the associated problems are illustrated in Figure 6.4.

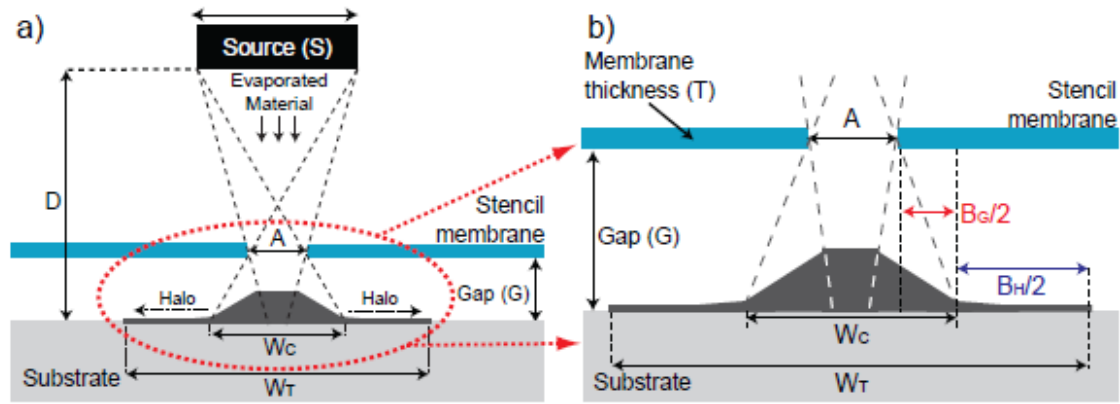


Figure 6.4: Blurring description. B_G occurs due to the shadowing effect and B_H (halo) occurs due to the materials diffusion on the substrate. The material halo surrounding the central structure is difficult to observe because it is an evanescent and very thin layer. Concerning the halo-blurring, currently there exists no model to estimate B_H due to the lack of analysis and understanding of the halo. Adapted from (Mena, 2010)

One problem is linked to shadowing effect (Vazquez-Mena et al., 2008). The finite size of the metal source and the distance between the source and the mask lead to non-directional evaporation resulting in material deposition not only on the area directly under the stencil apertures, but also underneath the stencil membrane. As shown in Figure 6.4(b), due to this problem, fabricated nanostructures have dimensions larger than that of the nanoapertures on the stencil. Furthermore, their vertical

profile is tapered and the thickness is reduced compared to the deposited material. The second problem is linked to the surface diffusion (RÁCZ and Seabaugh, 2007). When the newly deposited materials reach the previously deposited area, they remain mobile. Due to the non-zero stencil-substrate gap, the materials spread laterally to energetically favorable areas and form a thin halo layer around the main nanostructure as shown in Figure 6-4. Increasing the gap, the amount of deposited material the deposition rate and substrate temperature promotes the blurring and size of the halo. These imperfections can ultimately compromise the resolution of NSL and prevent fabrication of nanostructures with sharp edges and small gaps (Mena, 2010).

As we show in the following, these limitations can be overcome by eliminating the gap when nanostencil lithography is implemented on polymeric substrates presenting an external elastic adhesive surface, such as solid PDMS which has repeating units of $-O-Si(CH_3)_2-$ groups (Eddings et al., 2008). This chemical structure leads to a hydrophobic surface with a surface free energy of 20 erg/cm^2 . The low surface energy and the elasticity of PDMS enables sufficient interfacial interactions which can promote weak bonding of PDMS with SiN_x based stencil mask. The bonding minimizes the problems associated with the stencil-substrate gap and results in nearly perfect transfer of the nanoparticle pattern with geometries complementing the apertures on the stencils.

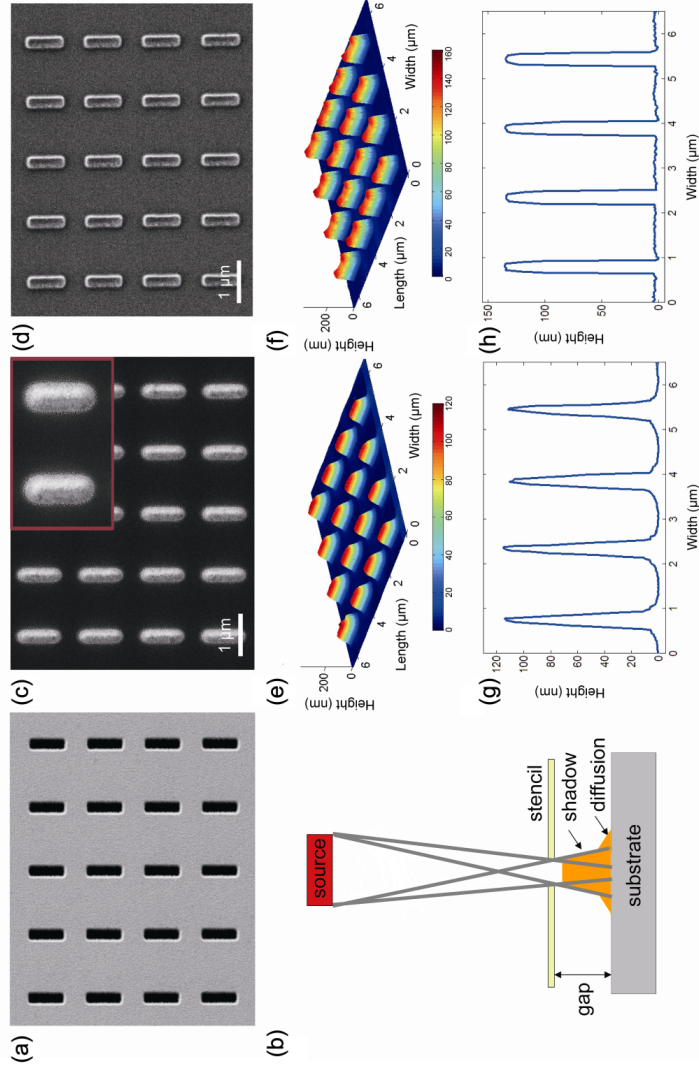


Figure 6-5: (a) SEM image of the stencil mask. (b) The gap between the stencil and the substrate will sacrifice the resolution. Evaporated gold goes under the stencil due to the gap, forming shadow parts. In addition, diffusion occurs on substrate beyond the shadows, resulting in a halo around the structure. (c)-(d) SEM images of the structures deposited on a Si substrate and on the PDMS substrate. Tapered structures and halo can be seen from the inset in (c) for Si substrate. Structures on PDMS, on the other hand, well replicate the apertures on stencil and have sharp edges due to the elimination of the gap effect. (e)-(f) 3D AFM images of the structures deposited on the Si substrate and on the PDMS substrate. (g)-(h) Line profiles obtained from AFM for the structure deposited on Si substrate and on PDMS substrate. Compared to the particles on PDMS, structures on Si have tapered wall profile with less height than evaporated due to the non-directional evaporation and the stencil-substrate gap.

Figure 6-5 illustrates the difference of stencil lithography on rigid silicon (Si) and flexible PDMS substrates. In order to prepare PDMS substrate (Sylgard 184, Dow Corning) mixture (10:1 base to curing agent ratio) is degassed in a desiccator for approximately 30 minutes, and cured at 70°C for 1 hour to promote cross-linking. After placing the stencil masks on the substrate, 150 nm of thick gold was deposited directionally at 3×10^{-6} Torr of chamber pressure using CHA-600S e-beam evaporator. The diameter of the gold crucible is around 2 cm and the evaporation distance between source and samples is 60 cm. After the deposition, the stencil mask and the PDMS substrate were treated with isopropanol, which swells the PDMS to a small extent (Lee et al., 2003). As the PDMS changes size, it increases the strain at the PDMS/stencil interface, causing the PDMS film to peel off. In this way, we can release the PDMS from stencil without damaging the mask or itself. Figure 6-5(a) shows SEM image of the stencil used for fabrication of nanorod arrays on both PDMS and silicon substrates. Figure 6-5(c) shows SEM of the gold nanorod arrays deposited on Si substrate. Compared to the stencil dimensions, the fabricated structures on silicon have larger sizes and ill-defined boundaries due to side depositions (shadows) in the presence of finite stencil-substrate gap. The gold scattering causes more than 50 nm enlargements on each side of the nanostructures. Also, the rods on silicon substrate have round edges with a halo around the particle. The halo formed due to material diffusion is visible in the inset image. Atomic force microscopy (AFM) measurements have been performed to investigate the height and the vertical wall profile of the fabricated nanostructures on both surfaces. Three-dimensional AFM image and line scans of nanorods on silicon are shown in Figure 6-5 (e) and (g), respectively. Since part of the deposited gold scatters on the surface underneath the membrane, the thickness of the nanorods on silicon surface reduces to 120 nm (compared to 150 nm thick material deposited). Also, the deposited structure on silicon has a tapered

vertical profile. On the other hand, the structures fabricated on PDMS are well defined and have sharp edges. Their SEM and AFM images as well as line scan showing vertical profile are given in Figure 6.5(d), (f), and (h), respectively. The size and shape of the nanorods are nearly the same as the apertures on the stencil. The device features are well defined including sharp edges. Neither shadowing nor diffusion of the deposited gold is observed on the polymer substrate since the gap is minimized. The fabricated nanorods have vertical side walls and clear boundaries similar to the nanorods that are fabricated with high-resolution electron beam lithography (Adato et al., 2009). The thickness, measured to be around 140 nm, is closer to the amount of the deposited gold. Repeatability tests are performed with stencil lithography using three identical stencil masks. On each stencil, a pattern containing 50x50 rectangular nanoapertures arrays (with nominal dimensions of 240 nm by 940 nm and periodicity 1.5 μm) are fabricated over 100 μm by 100 μm area and the pattern is replicated in a 3 by 3 array. On three different stencil masks, the average aperture dimensions differ slightly due to variations in fabrication conditions. The aperture dimensions measured using SEM are as follows: 245 nm by 940 nm, 240 nm by 935 nm and 242 nm by 940 nm, respectively. The average dimensions of the deposited nanorods on PDMS are measured using AFM with 4 nm lateral resolution and dimensions are 257 nm by 953 nm, 246 nm by 950 nm and 240 nm by 935 nm, for the corresponding stencil masks, respectively. These measurements indicate that the dimension of the fabricated nanorods nearly matches to that of the corresponding nanoapertures on the stencil, with an accuracy of 9 nm on average. Based on the measurements on these 27 independent sample sets of rectangular nanoparticles, we calculated the standard deviation to be 6.22 nm, which is near the resolution limit of the measurement system (AFM). The same stencil masks are cleaned using gold etchant and reused on three different Si substrates. SEM inspections confirm that the aperture dimensions

show no variation after the cleaning step. The dimensions of the fabricated nanorods on silicon are 327 nm by 1053 nm, 349 nm by 1074 nm and 350 nm by 1070 nm on average, respectively. For Si substrate, the deviation between the dimensions of the nanoparticles and the corresponding nanoapertures are between 82 nm and 139 nm, and on average as large as 113 nm. These results show that by incorporating polymeric interfaces, we can significantly improve the resolution of high-throughput and low cost NSL technique and achieve highly repeatable nanopatterning.

6.2 Flexible Plasmonic Dimers with Sub-50 nm Inter-particle Distances

In metamaterial and plasmonic devices, small gaps and asymmetries can induce novel electromagnetic responses such as plasmon induced transparency and giant near-field intensities that are important for enhanced vibrational spectroscopy and non-linear optics (Schuck et al., 2005; Zhang et al., 2008). Controllable fabrication of sharp edges and small gaps (less than 100 nm) are difficult to obtain with nanostencil lithography on conventional substrates. As shown in Figure 6-6, when implemented on PDMS substrate, nanostencil lithography can enable fabrication of high quality bow-ties with sharp edges. SEM image of the bowtie apertures consisting of two sharp edged triangles with side lengths of 645 nm is given in Figure 6-6(a). The resultant bow-tie nanoparticles with 50 nm gold thickness nicely replicate the apertures on the stencil as confirmed by SEM and AFM images presented in Figure 6-6(b) and (c), respectively.

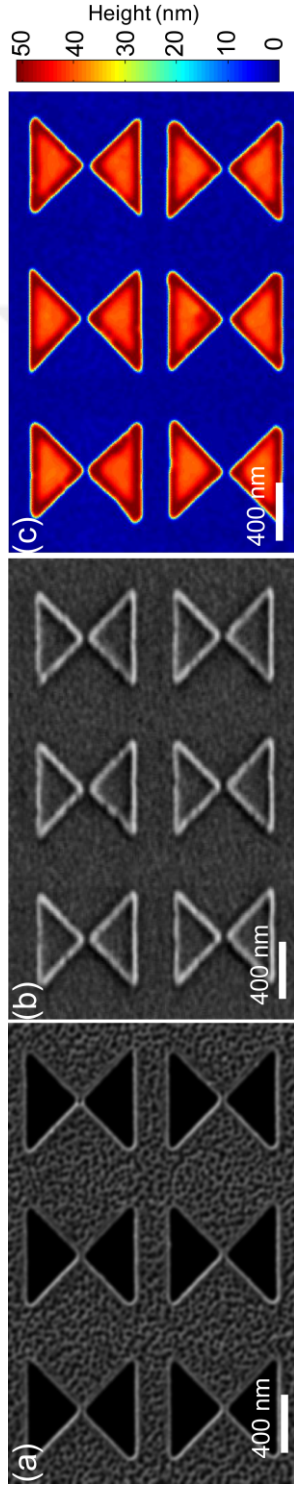


Figure 6.6: (a) SEM image of a bowtie stencil mask. The triangles have side lengths of 645 nm and the dimer separation is about 55 nm. (b) SEM image of bowtie structures fabricated on PDMS substrate. Structures well replicate the stencils down to 10 nm accuracy. (c) AFM images of bow-tie particles shown in (b). The interparticle distance is measured to be 40 nm on average. Sharp edges and small bowtie gaps are confirmed.

Given the high resolution we can achieve on PDMS surfaces, the nanostencil technique could also be utilized to fabricate sub-100 nm sized bow-ties with sub-50 nm interparticle spacing. Fabrication of such structures is very challenging even with high resolution EBL (Schuck et al., 2005). Here, we demonstrated for the first time their fabrication with low cost and high-throughput nanostencil lithography. The top part of Figure 6.7(a) is the SEM image of the nanostencil while the bottom one is the AFM images of the resultant bow-tie nanoparticles with 35 nm interparticle distance and 85 nm side lengths. We also show fine control over the geometrical parameters by fabricating bowtie antenna arrays with interparticle distance changing from 25 nm to 45 nm. In order to optically characterize these structures, visible light is illuminated through a dark field condenser and light scattered from pattern is collected by 100x objective ($N.A. = 0.7$). The excitation source is polarized along the direction connecting the adjacent triangular structures. The structures have resonances at visible wavelengths as shown in Figure 6.7(b). Precise control over the interparticle distance enables fine tuning of the resonance wavelengths. As shown in Figure 6.7(b), when the gap distances decreased with 10 nm steps, clear red shifting of resonance is observed. As metal nanoparticles come in close contact, their optical response changes. Strong near field interactions give rise to new resonances which can be well understood using a hybridization model (Prodan et al., 2003). Hybridization model predicts two modes (in phase and out of phase) that are split in energy. As shown in the charge distribution (inset to Figure 6.7(c)), the dipolar excitations in the bowtie structures are in-phase, where a high field enhancement occurs within the small gap. As the gap size is reduced, a more prominent near-field interaction between the triangular structures is observed which increases the hybridization strength and redshifts the hybrid resonance.

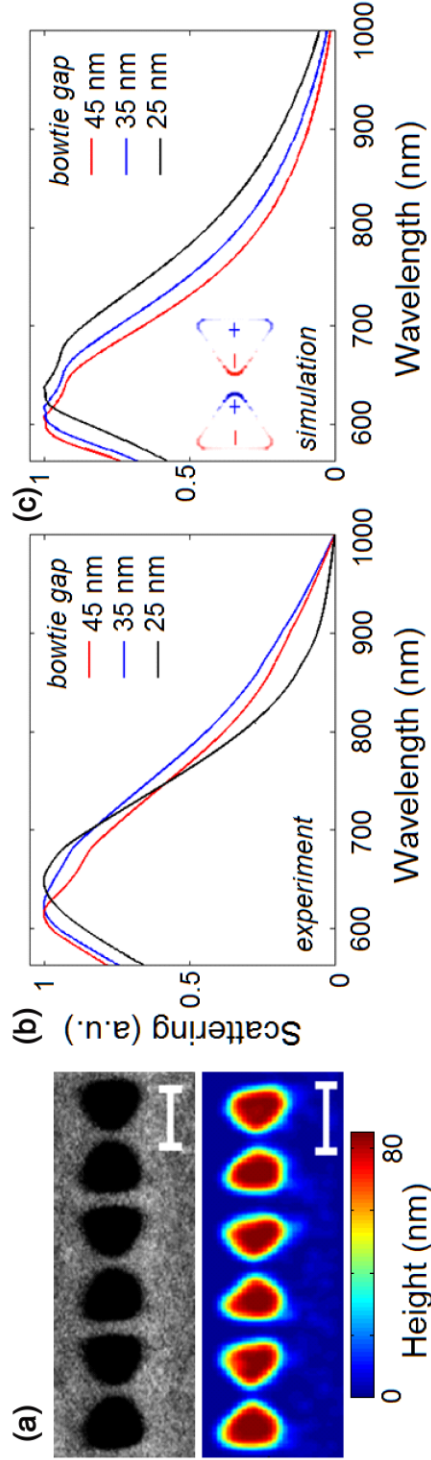


Figure 6-7: (a) SEM image of the nanostencil used (top) and AFM images of the resultant bowtie antennas on PDMS, resonant at visible wavelengths (bottom). Scale bar represents 200 nm. For the nanostencil, the separation distance within the dimer is 25 nm and the side length of a triangle is 100 nm. Bowtie antennas have 35 nm interparticle distance and 85 nm side lengths. (b) Experimentally measured optical spectrum of the bowtie antenna arrays with 85 nm side lengths and interparticle distance changing from 25 nm to 45 nm. Clear red shift of resonance is observed with decreasing the bowtie gap by 10 nm. (c) Numerical calculations of bowtie antennas with the same dimensions as that of the fabricated ones. These calculations confirmed the experimentally obtained resonance locations and the shifts due to the interparticle distance changes. Inset shows charge distribution on bow-tie particles at resonance

The experimental results are justified with the numerical calculations modeled by three dimensional Finite Difference Time Domain (FDTD) method as shown in Figure 6.7(c).

6.3 Flexible Plasmonic Nanoantennas at Mid-IR Wavelengths

Using high-resolution nanostencil lithography, we fabricated infrared plasmonic nanoantennas on a variety of flexible and stretchable polymers including PDMS, parylene-C and plastic food storage roll films based on low density poly ethylene (LDPE). Parylene, which is a family name of poly (p-xylylene) polymers, is widely used in electronics, medicine and pharmacology (Loeb et al., 1977). LDPE is a thermoplastic made from petroleum and widely used in food storage and packaging. All these polymeric materials have absorption bands at certain wavelengths in Mid-IR regime. Figure 6.8 shows the transmission spectrum of bare parylene-C, LDPE and PDMS thin films with thicknesses around $5\text{ }\mu\text{m}$, $13\text{ }\mu\text{m}$ and $100\text{ }\mu\text{m}$, respectively. Among these substrates, LDPE film is the most stretchable film. For fabrication on LDPE substrate, the food storage film has been wrapped around a silicon wafer for convenient patterning. Parylene-C with desired thickness is deposited on an intrinsic silicon wafer with chemical vapor deposition at room temperature (Fortin and Lu, 2003). PDMS film with $100\text{ }\mu\text{m}$ thickness is prepared by spin coating, and as seen in Figure 6.8(c), it strongly absorbs at lower wavenumbers. LDPE thin film and parylene-C shows similar absorption bands at Mid-IR frequencies.

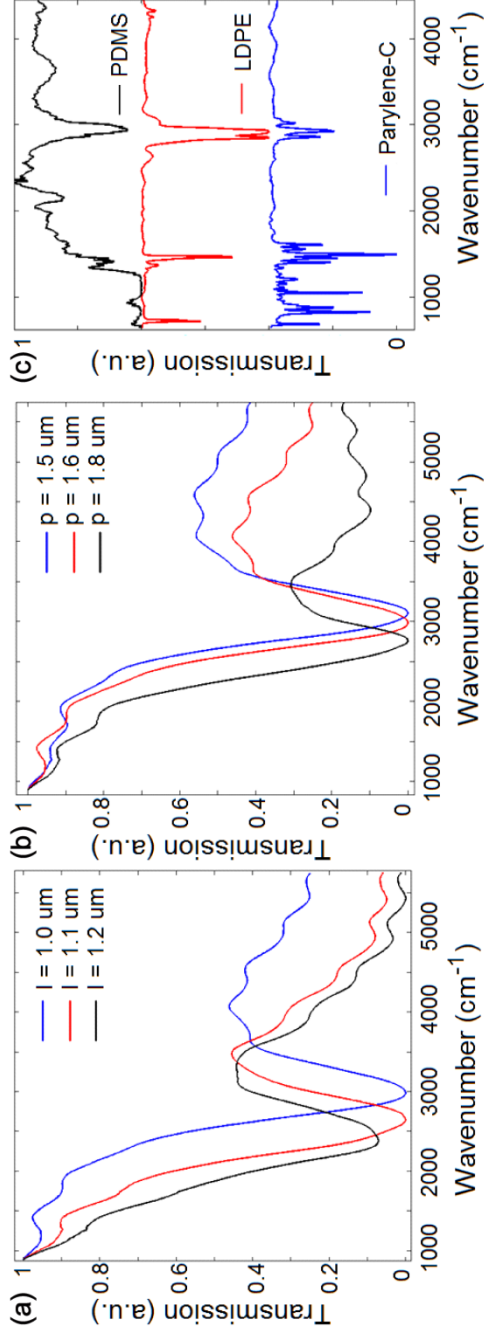


Figure 6-8: (a) Transmission spectra of plasmonic antennas with $1.6 \mu\text{m}$ periodicity and lengths varying from $1 \mu\text{m}$ to $1.2 \mu\text{m}$ on $5 \mu\text{m}$ thick parylene-C film. With increasing antenna length, red shift of resonance is observed. (b) Transmission spectra of plasmonic antennas on $5 \mu\text{m}$ thick parylene-C with $1 \mu\text{m}$ length and periodicities indicated in legend. (c) Transmission spectra of materials used in Mid-IR regime. Polymeric substrates show characteristic absorption bands around 3000 cm^{-1} due to $C-H$ bond stretch. For all spectra, Fourier decomposition technique is utilized in order to remove the interference fringes resulting from thin films.

The optical responses of plasmonic nanoantenna arrays fabricated on parylene-C are presented in Figure 6-8(a)-(b). In a recent article, we showed that the collective excitations of plasmons offer a number of opportunities for creating enhanced near field intensities at nano-tips. To excite collective oscillations, tuning of the localized surface plasmon (LSP) resonance of the antenna with respect to the photonic resonances of the array is critical. LSP resonance is tuned with the rod length while the grating orders are controlled through the periodicity (Adato et al., 2009). Resonance peak wavelengths could be controllably tuned by changing the dimensions of plasmonic structures (such as length, shape, aspect ratio) or by changing the periodicity within the array. Figure 6-8 shows the transmission spectra of the gold nanorod antenna arrays with varying lengths from 1 μm to 1.2 μm and the varying periodicities from 1.5 μm to 1.8 μm . Spectra are obtained using an IR microscope coupled to a *Bruker*TM Fourier Transform Infrared (FTIR) spectrometer with a KBr beam splitter. Light is normally incident on the nanopatterned surface. Transmitted infrared signal is collected using a Cassagrian optics ($N.A. = 0.4$) and coupled into a mercury cadmium telluride (MCT) detector. Post-processing is performed to remove the interference fringes (due to thin polymeric film) and material absorption bands from the resultant spectra. Figure 6-8(a) shows the effect of varying nanorod length when periodicity is kept constant at 1.6 μm . Figure 6-8(b) shows the effect of varying periodicity when the nanorod length is kept at 1000 nm. Similar to nanorods on Si substrate (Adato et al., 2009), nanorods on parylene-C follow the modified antenna theory. Increasing the rod length and periodicity results in red-shifting of the resonance wavelength. These results clearly show that using nanostencil lithography we can fabricate precisely engineered plasmonic nanoantennas structures on flexible/elastic substrates.

6.4 Stretchable Plasmonics for Active Optical Tuning

Patterning materials and plasmonic nanostructures on stretchable elastomeric substrates is particularly interesting as we can actively tune their optical responses by mechanically stretching the flexible substrates (Pryce et al., 2010). So far soft lithography based fabrication approaches have been employed to access polymeric substrates. But these approaches are either compatible with limited variety of material choice or involve multiple fabrication steps. Exploiting wider range of polymers that offer higher durability and stretching at low fabrication complexity requires new approaches. Here we show patterning of nanorod arrays on PDMS and highly stretchable LDPE films in a single fabrication step and demonstrate active optical tuning.

The nanorod antenna arrays in Figure 6-9(a) are fabricated on a 1 mm thick PDMS substrate. Arrays are 945 nm by 240 nm size rods and separated by 1.51 μm . As shown in Figure 6-9(b), mechanical stretching of PDMS in one direction results in a homogeneous periodicity increase (decrease) along the direction parallel (perpendicular) to the applied force. The original periodicity enlarged to 1.83 μm , which indicates 21.3 % stretching. When the applied tension is released, the substrate and the nanorods on it return back to the initial position after relaxation (Figure 6-9(c)). As we can see from Figure 6-8(b) and (c), both under and after mechanical stretching, nanorods are not damaged and they are still perfectly intact with the substrate. To quantify the amount of resonance wavelength tuning, we fabricated similar nanorod arrays on LDPE thin films as this polymeric film is highly stretchable and durable. A homemade mechanical system is utilized for consistent and measurable stretching of the nanopatterned films. An optical microscope coupled to a FTIR system is used to quantify the magnitude of the stretch. After each stretching step, the corresponding change in optical response is measured with FTIR. Figure 6-10 shows the shift on the resonance wavelengths as the LDPE film is stretched. Here the measurements

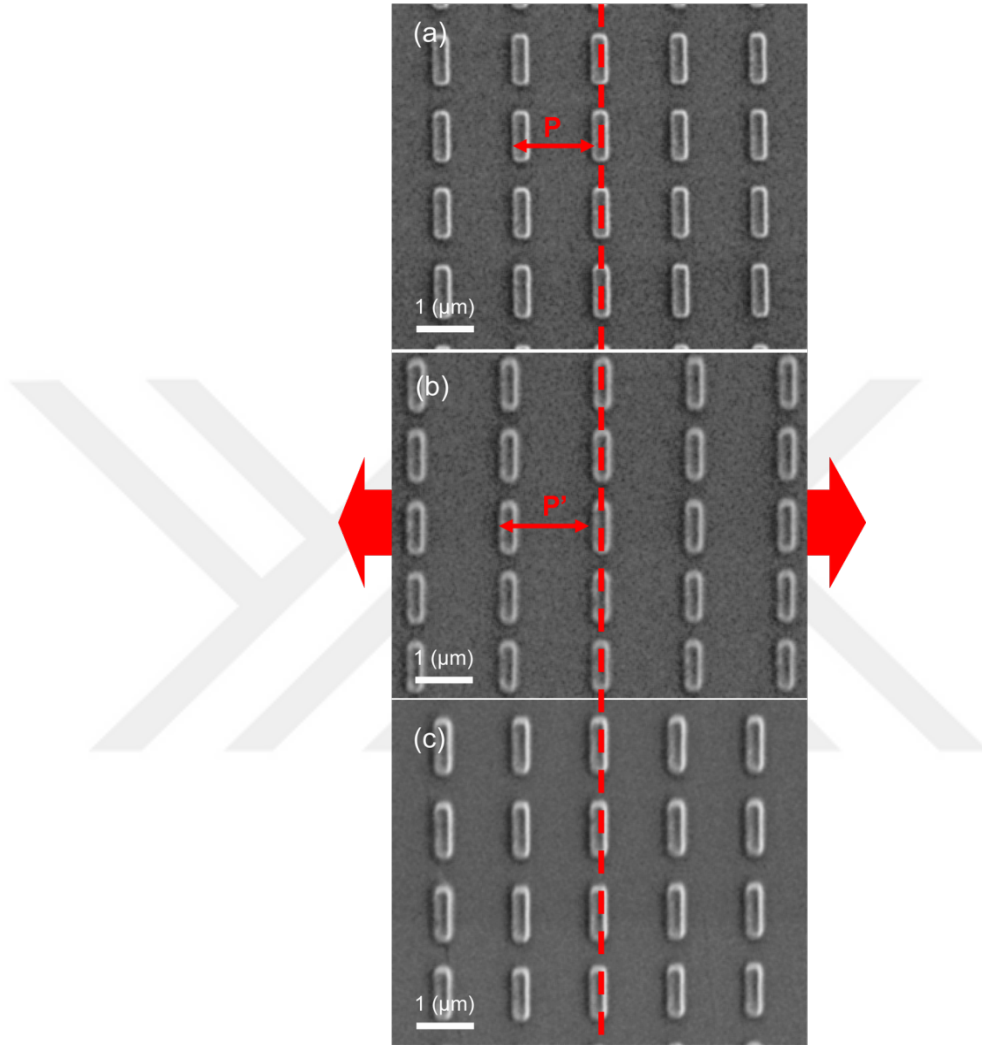


Figure 6.9: (a) SEM image of nanorod antenna arrays on PDMS. Rods are 945 nm in length, 240 nm in width and separated by P , $1.51\mu\text{m}$ (b) SEM image of the antenna arrays when mechanical force is applied on PDMS. The substrate is stretched, resulting in a homogeneous periodicity change along the direction of the applied force. The period is enlarged by 21.3 % to $P'=1.83\mu\text{m}$. (c) SEM images of the antenna arrays when the force is removed. Nanorods return to their initial position without being damaged.

are obtained from a periodic array of gold particles with $1.5\mu\text{m}$ periodicity consisting of nanorods with 1200 nm length, 250 nm width and 70 nm height. The film is mechanically stretched on the plane perpendicular to rod elongation leading to 5 %

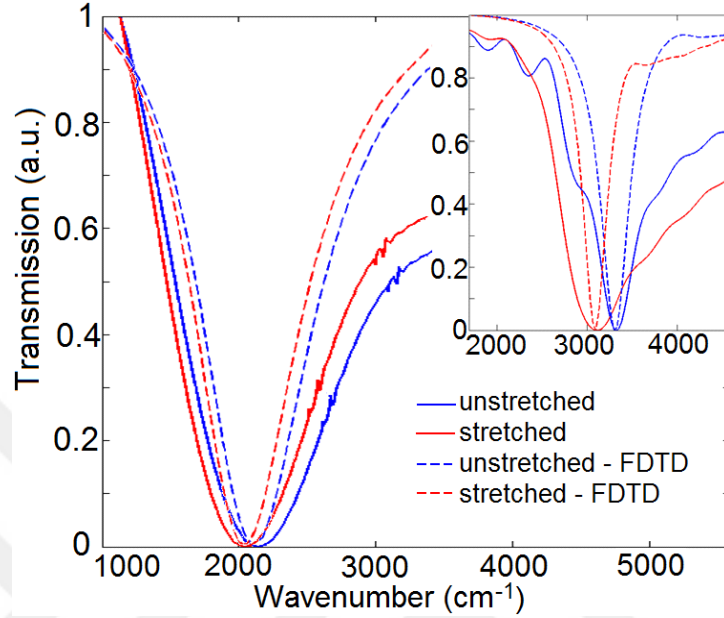


Figure 6-10: Measured and calculated (dashed) transmission spectra of nanorod arrays with $1.5\ \mu\text{m}$ periodicity, $1200\ \text{nm}$ length on a $13\ \mu\text{m}$ thick LDPE film before (blue curve) and after stretching (red curve) are shown. Once the film is stretched (red curve) due to the increase in periodicity only along the direction of the applied force, resonance red shifts by $160\ \text{nm}$. Inset shows a resonance shift for $16\ \%$ strain on LDPE with $900\ \text{nm}$ long gold nanorod arrays (with $1.8\ \mu\text{m}$ periodicity).

enlargement on array periodicity. We observed a $160\ \text{nm}$ red-shifting of the resonance wavelength. We also performed FDTD calculations with periodicities in agreement with the experimentally measured values. As seen in Figure 6-10 (dashed lines), calculated resonance wavenumber clearly overlaps with the experimental data obtained for $5\ \%$ stretching. In calculations, the particle dimensions are the same with the measured dimensions of the fabricated structure, which proves that stretching only changes the periodicity but not the particle dimensions. Inset at Figure 6-10 shows the response of a $900\ \text{nm}$ long gold nanorod arrays (with $1.8\ \mu\text{m}$ periodicity) on LDPE film, when stretched for $16\ \%$ enlargement on periodicity along the rod elongation. The plasmonic resonance wavelength shifts from $3000\ \text{nm}$ to $3230\ \text{nm}$. Performed theoretical calculations prove the periodicity of the particles have changed from 1.8

μm to $2.1\ \mu\text{m}$. Therefore, both SEM images and FTIR results faithfully confirm that we can actively tune the resonance wavelengths without damaging the device.

6.5 Flexible Plasmonics on Non-Planar Surfaces

Ability to fabricate functional nanophotonic devices (such as perfect absorbers, optical cloaks and plasmonic antennas) on curved surfaces can open up novel opportunities (Smythe et al., 2009). But, direct nanopatterning on non-planar surfaces is very challenging with existing technologies as they are inherently two-dimensional. One can overcome this challenge using nanostencil lithography by first generating nanostructures on planar two-dimensional thin flexible polymer films. Then, the film can be used as a carrier to transfer the nanostructures directly to a curved surface. If desired, the carrier polymer can be sacrificially removed (by selective etching) leaving behind only the nanostructures on the non-planar curved surfaces. Nanostencil lithography, which can easily generate patterns on flexible films, is ideal for such a fabrication scheme. For illustration, we show below direct transfer of plasmonic nanoparticles onto optical fibers. Nanopatterning on fiber surfaces can enable functional photonic probes that can monitor the environmental changes in places that are either difficult to access optically (for example in bloodstream and in deep tissues for in-vivo studies; in boreholes for mining/geology) or locations that are dangerous to enter physically (for example, due to chemical/biological toxicity). We fabricated circular gold particles with a $2\ \mu\text{m}$ diameter on $10\ \mu\text{m}$ thick parylene-C flexible thin film over a large area ($400\ \mu\text{m} \times 3\ \text{cm}$) using NSL. Then, under an optical microscope, we wrap the patterned parylene-C around the $300\ \mu\text{m}$ diameter bare fiber optic cable. Optical images of the optical fiber given in Figure 6-11 show successful transfer of the circular gold particles onto the curved surface.

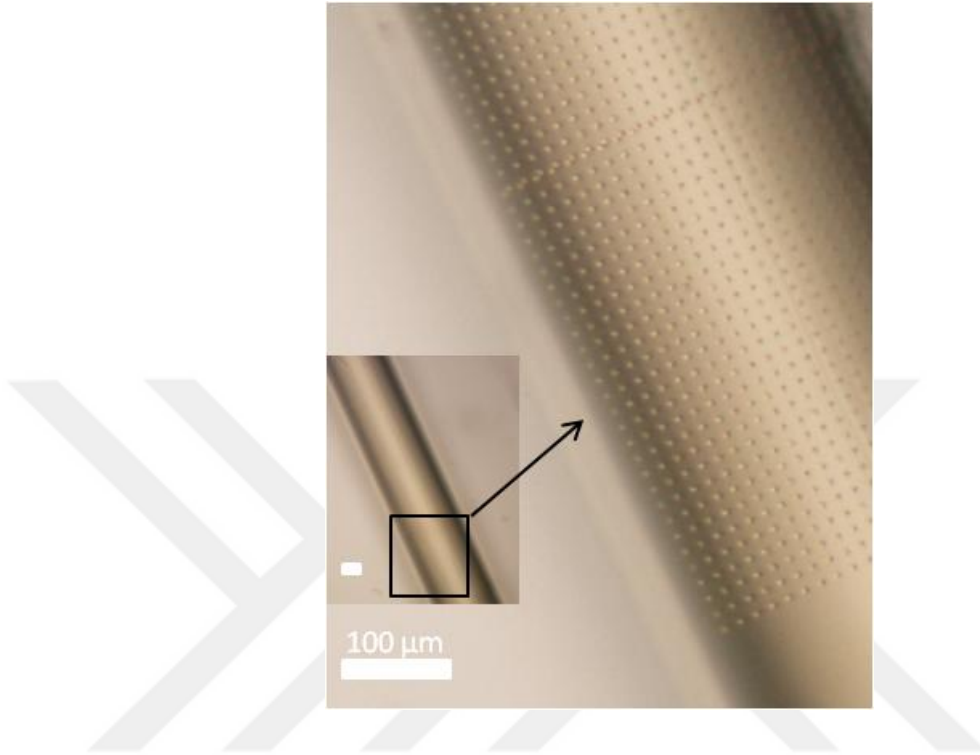


Figure 6.11: Optical microscope images of a fiber optic cable covered with a flexible $10\text{ }\mu\text{m}$ thick parylene-C film patterned with circular gold particles of $2\text{ }\mu\text{m}$ diameter and $10\text{ }\mu\text{m}$ periodicity. Inset shows the same fiber under a lower magnification. The patterned flexible film can be easily wrapped on a curved surface without damaging the plasmonic area.

6.6 Conclusion

In conclusion, we demonstrated for the first time NSL can enable single step, high-throughput, high-resolution and large area fabrication of nanostructures on flexible and elastomeric substrates at dimensions relevant for nanophotonics, plasmonics and metamaterials. The resolution limit of NSL can be improved by using polymeric substrates that have adhesive surface properties, such as PDMS. We showed that NSL can replicate the resolution of gold-standard EBL down to 10 nm accuracy. Consequently, we demonstrated fabrication of high-quality bow-tie antennas with sub- 50 nm gap distance and sub- 100 nm side lengths, and showed precise control of their

interparticle distance. We also showed that nanostencil lithography can be used to access highly durable and stretchable substrates (such as LDPE) for active tuning of plasmonic resonances. With a 5 % periodicity enlargement, due to the mechanical strain applied on LDPE thin film supporting nanorod structures, 160 nm red-shifting of the resonance wavelengths is achieved. We also successfully demonstrated that the nanostructures can be fabricated on curved surfaces by first nanopatterning flexible/elastomeric substrates and then wrapping them around non-planar surfaces. This is illustrated by patterning nanoplasmonic antennas on an optical fiber surface. Integration of plasmonics and metamaterials on non-planar surfaces can open up new functional probes and variety of novel applications. The presented high-throughput fabrication method by offering single-step patterning of features with sub-100 nm dimensions on variety of unconventional substrates could be essential for emerging technologies based on flexible photonics/electronics, as well as for scientific progress in many different fields including biology, material science and sub-wavelength optics.

Chapter 7

Plasmonically Enhanced Vibrational Biospectroscopy using Low-cost Infrared Antenna Arrays by Nanostencil Lithography

Plasmonics is leading to significant advancements and innovations in photonic technologies including biomedicine (Bardhan et al., 2011), energy harvesting (Polman and Atwater, 2012) and telecommunications (Noginov et al., 2011). For biomedical applications, plasmon-based bio nanosensors (Acimovic et al., 2009; Anker et al., 2008) consisting of metallic structures could overcome limitations of conventional biosensors through their unique ability to manipulate light at nanoscale dimensions. Plasmonic biosensors could enable detection of medically important proteins and high throughput screening of their interactions (Chang et al., 2011). One of the powerful and label free optical technique for determining structural and conformational properties of proteins and protein interactions is Infrared (IR) Spectroscopy. However, sensitivity of conventional IR spectroscopy is limited. Thus relatively large quantities of analytes are required to have sufficient absorption signal. Recently resonant plasmonic nanoantennas have been used to enhance the absorption signals of surface bound protein monolayers (Kim et al., 2010b). General concept is to electromagnetically couple the vibrational modes of the proteins to the optical modes of the nanoantennas. Plasmonic antennas boost the interaction between the light and the biomolecules

through the strongly enhanced near fields and increase the sensitivity to attomolar levels (Adato et al., 2009). Such near field interactions can be controlled through the geometry and composition of the metallic nanostructures in arrays (Novotny, 2007). Therefore even slight tailoring of nanoantenna and its arrangement could significantly alter the performance of surface enhanced IR spectroscopy technique. In order to realize precisely tailored plasmonic antennas, we need highly controllable nanofabrication techniques offering flexible design capability. Conventional electron and ion beam based lithography tools enable tremendous nanoscale feature flexibility. However their limitations such as high operational cost and low throughput have motivated development of new nanofabrication techniques. There are a few inexpensive innovative approaches but they lack reproducibility, ability to precisely array and shape control (Cataldo et al., 2011) at nanoscale dimensions. Towards this end, we recently presented that nanostencil lithography (NSL) could be utilized for high resolution, high throughput, and low cost nanofabrication of plasmonic nanoantennas with great design flexibility on conventional as well as flexible and polymeric substrates (Aksu et al., 2010; Aksu et al., 2011). Uniquely, NSL preserves the flexibility of beam based lithography tools for creating nanoantennas in a variety of shapes and arrangements as high-resolution nanostencils are fabricated by e-beam lithography (EBL). We have shown that stencils can be reused multiple times to fabricate series of tailored plasmonic nanoantenna arrays with identical optical responses in a high-throughput fashion.

In this work, we present the first demonstration of NSL fabricated low cost nanoantennas for detecting immunologically important, small-sized protein monolayers and performing antibody assays using plasmonically enhanced vibrational biospectroscopy (Aksu, 2013). We show that 3 nm sized protein monolayers could be detected using infrared nanoantennas fabricated by nanostencils (Figure 7.1). Fabricated arrays con-

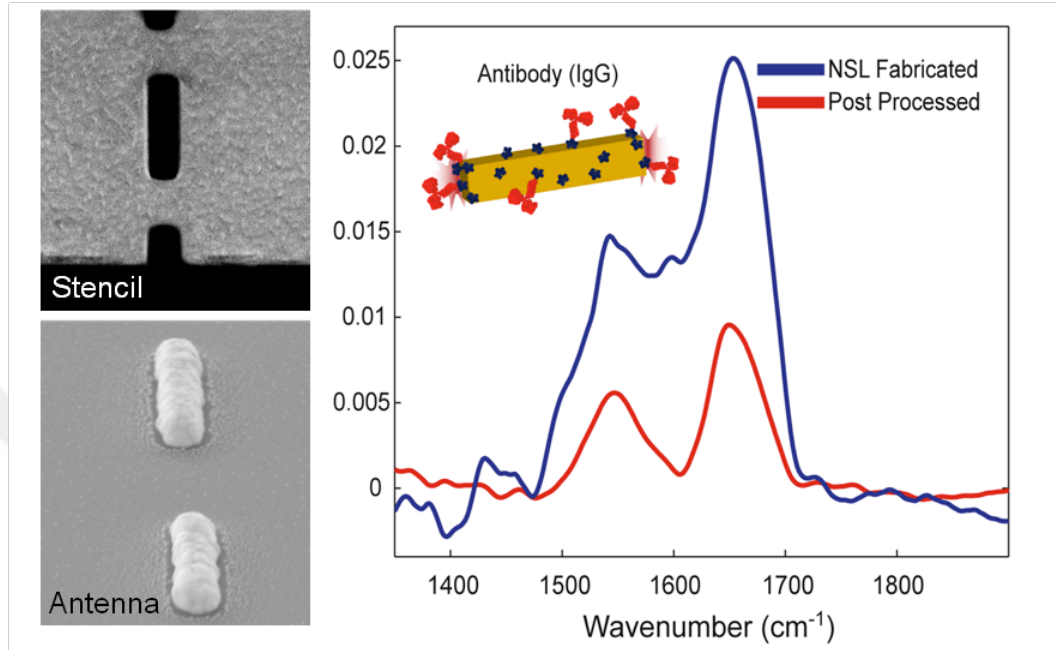


Figure 7.1: Engineered and precisely arrayed nanoantennas manufactured by low cost nanostencil lithography enable plasmonically enhanced vibrational biospectroscopy. These nanoantennas fabricated by reusable stencils lead to strong near field enhancements over large area. Antibody assays and detection of immunologically important small sized proteins with high absorption signals are demonstrated.

sist of precisely arrayed rod shaped gold nanoparticles on silicon substrate and exploit radiative engineering to achieve stronger near field enhancements. Reusable nanostencils enable high throughput and low cost fabrication. However finite gap between the stencil and the substrate results in small sized gold nanoparticle clusters (5 to 20 nm) around the nanorod antenna due to the diffusion of deposited gold (Vazquez-Mena et al., 2008). Earlier works have shown that these scattered small nanoparticles have no observable perturbation on the far field optical responses (Aksu et al., 2010). Here, we investigate the near field characteristics and biosensing performances of the nanoantennas with such scattered nanoparticles around. We introduced a post-processing method to remove these nanoparticle clusters yielding well-defined nanorod antennas. Our theoretical calculations indicate that small nanoparticles around the

nanoantenna enable stronger enhanced near field intensities over larger area compared to the antennas prepared through post-processing. In agreement to these theoretical results, we observe that nanorod antenna arrays directly fabricated using NSL show higher absorption signals for proteins compared to the post-processed ones. This work demonstrates that nanostencil lithography is a promising method for reducing the nano-manufacturing cost while enhancing the performance of biospectroscopy tools for biology and medicine.

7.1 Post-processing Method to Eliminate Blurring Effect

Nanostencil lithography is based on shadow mask patterning (Figure 7.2). Nanostencils placed on any substrate can be used for deposition and implantation of materials as well as etching. NSL is not a photoresist-based lithography, therefore no solvents, baking or energy radiation is needed. Our nanostencil is composed of nanoapertures that are patterned on 100 nm thick SiN_x suspended membrane. The stencils are supported by 550 μm thick silicon carrier wafer for easy handling and transfer. The nanoapertures are defined on the SiN_x membrane by high resolution EBL and dry etching processes. Nanoapertures used in this work are patterned over $300 \times 300 \mu m^2$ membrane area which could be easily scaled up to full wafer. NSL involves only one single deposition step to create nanostructures on any substrate. The patterned side of the stencil is directly placed on the substrate and secured tightly with mechanical clips to minimize the gap in between.

We deposit gold by electron beam evaporator to fabricate plasmonic nanostructures. Directional deposition of 100 nm thick gold is performed in CHA-600S e-beam evaporator without depositing any prior adhesion layer. Unlike EBL, an adhesion layer is not necessary since NSL does not require a lift-off process. Gold pellets with purity of 99.99 % (Kurt J. Lesker Company, USA) are loaded into a 2 cm wide tung-

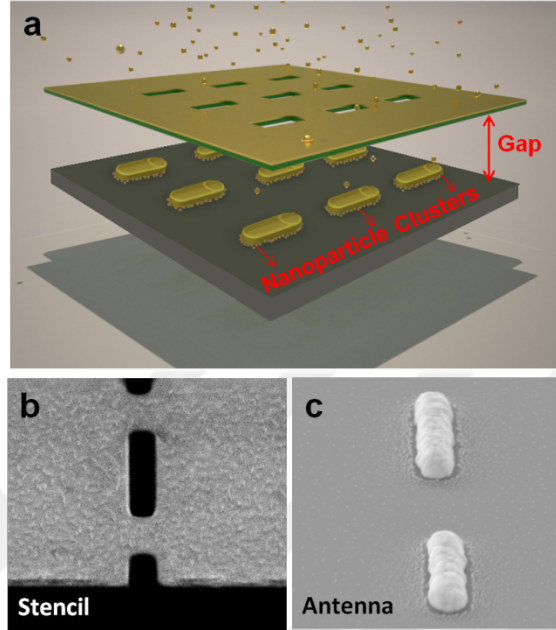


Figure 7.2: Nanostencil lithography is used for low cost nanofabrication of plasmonic antenna arrays. a) Gold deposition scheme is illustrated. Stencil shadows the deposited material. Due to finite gap between stencil and substrate nanoparticle clusters surrounds the nanoantennas. b) SEM images of the nanoapertures on the reusable 100 nm thick SiN stencil. Apertures have 1100 nm length and 250 nm width c) SEM image of gold nanoantennas fabricated on silicon substrate using the nanoapertures shown in b). Gold nanoparticle clusters are scattered around the nanorods.

sten crucible, and the distance between the crucible and stencil is 60 cm. We observed that the pressure inside the evaporator chamber and the gold deposition rate directly influence the resulting antenna quality. Using low pressure ($10^{-7} - 10^{-6}$ Torr) and low deposition rates ($1 \text{ \AA}/\text{second}$) reduce the grain size of the deposited gold and enable well defined nanoantennas with smooth surface. After gold deposition, nanostencils can be cleaned using commercially available Gold Etchant TFA (contains 8 wt % Iodine, 21 wt % Potassium Iodide, 71 wt % water) and reused multiple times allowing cost efficient nanofabrication. Since the nanostencil is fabricated using EBL, NSL offers great versatility in terms of shape and arrangement of nanoparticles. Fab-

rications of sub-100 nm dimeric and oligomeric plasmonic nanoparticles with sub-50 nm gaps as well as 50 μ m long nano wires have been shown on polymeric and semiconductor substrates (Aksu et al., 2011). Furthermore, a wide-range of materials including bio-molecules has been nanopatterned using the nanostencil down to 100 nm sizes without losing their bioactivity (Huang et al., 2012).

To obtain high resolution plasmonic nanoantennas with nanostencil lithography, the gap between the stencil and the substrate should be minimized. However, there is always an inherent gap in between due to the curvature of the wafers and bending of the stencil membranes. This gap results in scattered gold nanoparticles around the designated structures during the metal deposition step (Aksu et al., 2011). Here, we developed a post-processing method to remove these scattered gold nanoparticle clusters. Process involves a dry etching with Argon gas for 20 seconds (10 sccm flow, 35 mTorr pressure and 450 W power) on the patterned silicon substrate. The SEM images of the nanorod arrays before and after processing in Figure 7.3(a) and (b) respectively show the effectiveness of dry etch post-processing. As an alternative we also investigated a wet etching based post-processing on the NSL fabricated nanorods using diluted Gold Enchant TFA. The gold etchant is diluted with DI water from 1:1 ratio to 1:15 ratio (TFA: DI) and best results are obtained with 1:12 ratio. We observed that the removal of scattered gold nanoparticles around the antenna is difficult to control with wet etching post-processing and nanorods are heavily damaged as shown in Figure 7.3(c). Therefore, we investigated dry etching as a post-processing method for obtaining well defined nanostructures.

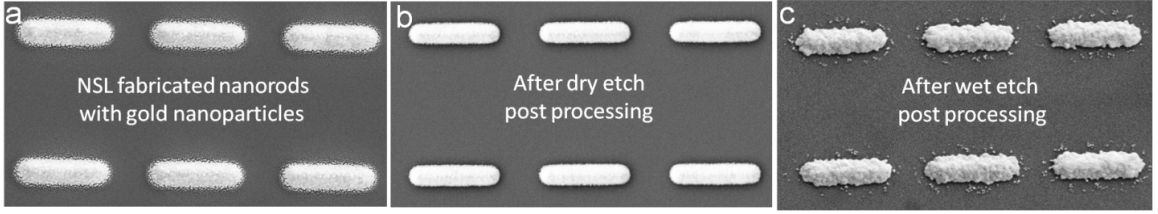


Figure 7-3: SEM images of a) NSL fabricated nanorod antenna arrays. b) and c) show SEM images of nanorod arrays after post-processing with dry etch and wet etch, respectively. Dry etch post-processing is reliable for obtaining well-defined nanostructures with uniform surface. Wet etch post-processing heavily damages the nanorod antenna

7.2 Theoretical Examination of NSL Fabricated Nanorod Antenna Arrays

To investigate the use of nanostencil fabricated antennas for increasing infrared absorption signal of proteins, the suitable nanorod dimensions are first determined theoretically by tailoring the length and the periodicity. Maximum enhanced near fields as well as the best spectral overlap of plasmonic excitations with vibrational bands of the protein backbone around $6\ \mu\text{m}$ wavelength is achieved using $1100\ \text{nm}$ long and $250\ \text{nm}$ wide nanorods with $1.6\ \mu\text{m}$ periodicity in a 50×50 particle array of square lattice. The far- and near-field responses of nanorod antennas are analyzed by finite-difference time-domain (FDTD) solver Lumerical Solutions. The dielectric constants of gold and silicon are taken from Paliks Handbook of Optical Constants. Periodic boundary conditions were used along x- and y- directions. Incident wave is launched from the gold-air interface. Along the direction of the illumination source (z), perfectly matched layer boundary condition was applied. In the simulations, the mesh size is set $2\ \text{nm}$ along the x-, y- and z- directions. We performed simulations on NSL fabricated and post-processed nanorod antenna arrays with optimized geometrical parameters and compared their near field intensity enhancements at $6\ \mu\text{m}$ wavelength.

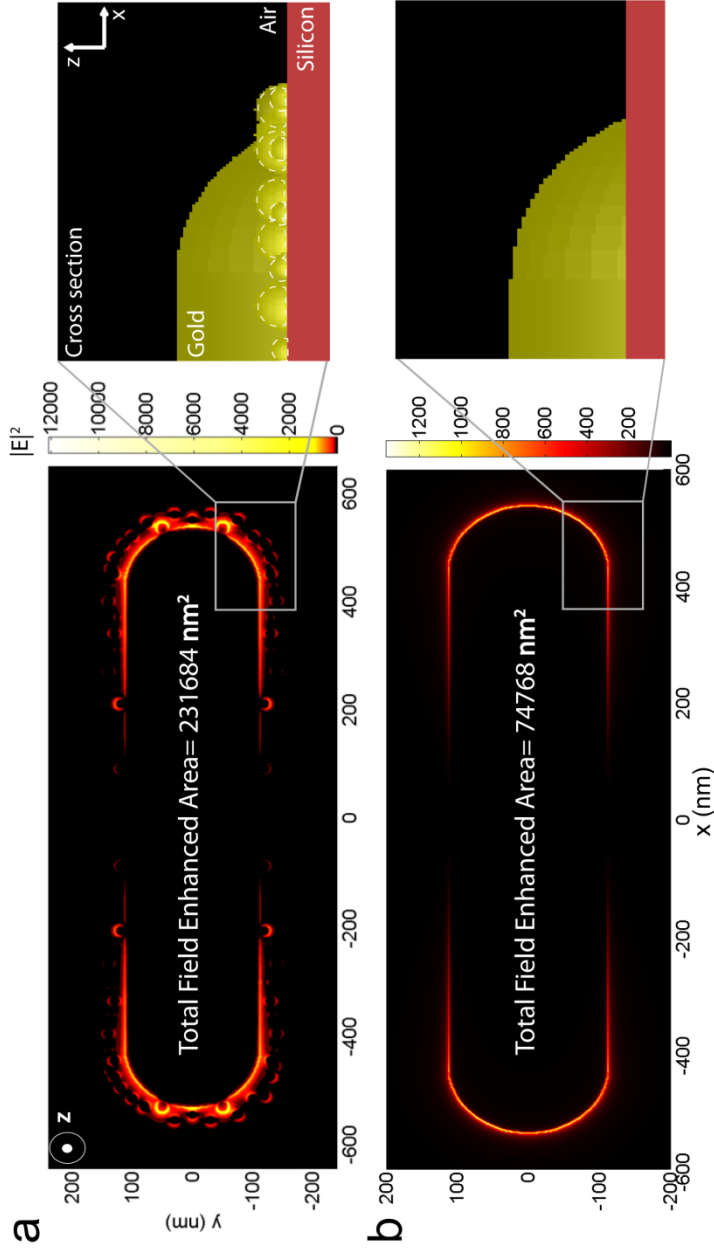


Figure 7.4: Finite-difference time-domain calculations on a) NSL fabricated b) post-processed nanorod antenna arrays. NSL fabricated nanorods are simulated by incorporating nanorods with tiny nanoparticulates (10 and 20 nm diameter) at the gold-silicon interface ($z = 0$). On the left column, field intensity distributions are shown at $z=0$, at $6 \mu\text{m}$ wavelength for both antenna arrays. NSL fabricated nanorods show an order of magnitude higher field enhancement. The total field-enhanced area calculated around the three-dimensional structures is three times larger for NSL fabricated nanorods. The right column shows the cross sections ($y = 0$) of the simulated designs.

NSL fabricated nanorods are designed by imitating the SEM images where nanorod is generated as a half cylinder attached to half hemispheres on both ends. Nanoparticles with 10 to 20 nm size are randomly placed around the nanorod at the substrate air interface (Figure 7.4a). To investigate the effect of spatial distribution of gold nanoparticles around the antenna, simulations with different nanoparticle arrangements have been performed. It is observed that each design has similar near field enhancements. For simulations of post-processed nanorods, the tiny gold nanoparticle clusters around the nanorod are removed (Figure 7.4b). In Figure 7.4, left column shows the near field intensity distribution at silicon gold interface of a) NSL fabricated and b) post-processed nanorods. Field enhancement of NSL fabricated nanorods is an order of magnitude higher (10^4) compared to post-processed ones. These calculations indicate that nanoparticles around the antenna behave as light scattering sites and contribute to the near field enhancement of the antenna. In Figure 7.4 the near field intensity distributions are plotted with the same color scale for two different nanorods. We observed that for the antenna with scattered gold nanoparticles around, not only the maximum intensity is higher but also the field-enhanced area on silicon gold interface is larger. We calculated the field-enhanced area at gold silicon interface ($z = 0$) for two different nanorods using the simulation design shown in Figure 7.4. For calculations we defined a cut off field intensity value as $1/e^2$ of the maximum intensity on post-processed nanorods since this nanorod yields lower field intensity. We then sum up the area where the field intensity is higher than this cutoff value. The calculated field enhanced area is about two times higher for NSL fabricated nanorods ($1.9 \times 10^4 \text{ nm}^2$) than that of the post-processed ($1 \times 10^4 \text{ nm}^2$) ones. Given that the nanorods and the tiny nanoparticles are three-dimensional objects, proteins can bind at their curved surfaces. Therefore we extended the calculation of enhanced area (as described above) along the z direction as follows. In the calculations, step size on

the z-axis is set as mesh size (2 nm). The field-enhanced area at each z value (0, 2, 4 nm) is calculated and these areas are summed up to obtain the total region with field enhancements higher than the selected cutoff intensity. The calculated total area for NSL fabricated nanorods is three times larger than the post-processed nanorods ($2.3 \times 10^5 \text{ nm}^2$ vs $7.4 \times 10^4 \text{ nm}^2$). Given that the detection sensitivity in spectroscopy is linearly proportional with the amount of molecules and the enhanced fields overlapping with them, theoretical calculations indicate that NSL fabricated antennas with scattered nanoparticles are highly advantageous.

7.3 Vibrational Biospectroscopy on Low Cost Infrared Antenna Arrays

In order to demonstrate NSL fabricated low cost nanorod antennas for plasmonically enhanced infrared biospectroscopy, we tested the system with protein monolayer and antibody immobilized bilayers as near field probes. First Protein A/G (Thermo Scientific Pierce) monolayer is physisorbed to the gold nanoantenna substrates (see Experimental Section) forming a monolayer. Protein A/G which is a recombinant fusion protein constituting binding domains of both protein A and protein G with molecular weight of 50.46 kDa has a strong affinity with Fc regions of antibodies. Thickness of a monolayer on gold is measured as 3 nm by ellipsometry. Then anti-mouse IgG from goat (T6653 Sigma Aldrich) are immobilized on protein A/G monolayer. Molecular weight of IgG is 140 kDa. An additional 5 nm thick layer of IgG is detected by ellipsometry. Detecting the protein signatures of monolayer and antibody bilayer is achieved by measuring the reflection spectrum of nanorod antenna arrays before and after protein binding. Optical set-up consists of an IR microscope coupled to a *Bruker*TM Fourier Transform Infrared (FTIR) spectrometer with a KBr beam splitter. Polarized light (along the nanorod) is normally incident on the nanorod-patterned

surface. Reflected infrared signal from antenna arrays is collected using a Cassagrian reflection optics ($N.A. = 0.4$) and coupled into a mercury cadmium telluride (MCT) detector. The collected signal is normalized with the reflection signal from a reference mirror.

The overlap of the plasmonic resonance with absorption bands of protein results in dips in the reflectance spectra where the strength of the dip is directly correlated with enhancement of the protein absorption signal. In Figure 7-5(a) and (b) the reflection spectra before binding any proteins (black dotted curve), after Protein A/G binding (blue curve) and after antibody immobilization (red curve) on the NSL fabricated and post-processed nanorods are shown respectively. In these figures, the dips indicated by vertical dashed lines at amide I (orange, at 1660 cm^{-1}) and amide II (green, at 1540 cm^{-1}) vibrational frequencies are clearly noticeable within the optical spectra collected from the protein coated antenna arrays. Even though protein A/G is a relatively small molecule, NSL fabricated antennas could clearly resolve amide absorption bands. After antibody immobilization, a stronger dip on the plasmonic resonances is observed due to the larger biomass of antibody. To determine the amount of protein absorption signal, the dips in the reflectance spectra are quantified by subtracting the spectra of protein A/G monolayer and antibody bilayers from the initial spectra of nanorod antennas before protein binding ($\Delta R = R_{before} - R_{after}$). Loading the antenna with protein layers results in a slight red shift on plasmonic resonance; therefore for calculating the difference spectrum (ΔR) this shift is corrected. Figure 7-5 (c) and (d) show the difference spectrum of protein A/G monolayer and antibody (IgG) bilayers on the NSL fabricated and post-processed arrays, respectively. The absorption signals of proteins appearing as two peaks (amide I at 1660 cm^{-1} and amide II at 1540 cm^{-1}) are above the noise level for both arrays.

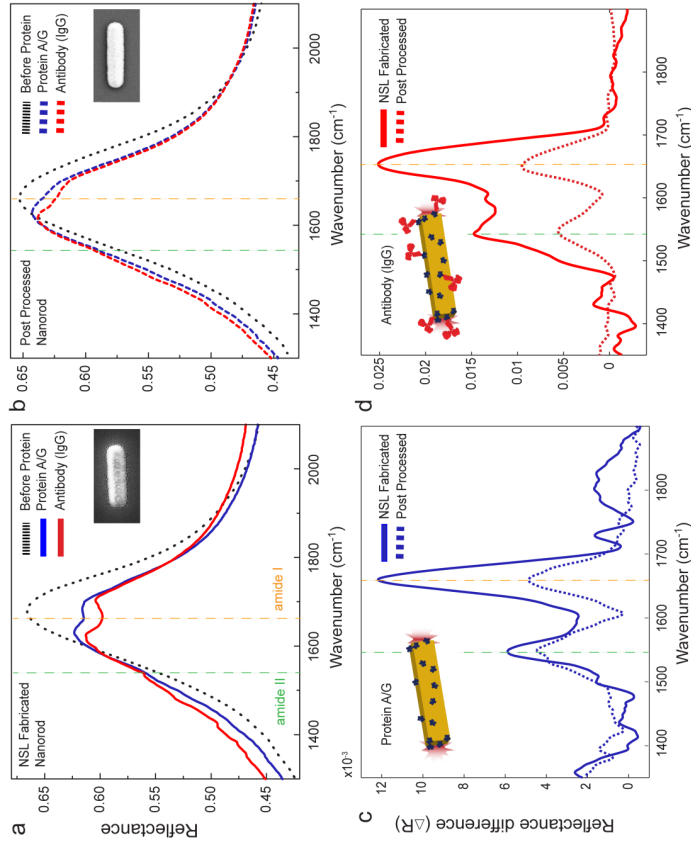


Figure 7.5: Plasmonically enhanced biospectroscopy of protein A/G monolayer and antibody (IgG) is shown. a) Reflectance spectra of NSL fabricated nanorods before protein binding (black dotted curve), after protein A/G (blue solid) and after antibody (red solid) are shown. Inset show SEM image of NSL fabricated nanorod. b) Reflectance spectra of post-processed nanorod antenna arrays before and after proteins are shown. After antibody immobilization stronger dip is observed for both NSL fabricated and post-processed nanorods. Inset shows the SEM image of the post-processed nanorod. c) Reflectance difference between the spectra of nanorod antennas before and after protein A/ G binding is shown for both nanorods. Peaks here correspond to the dips in a) and b). Signal due to amide I is almost three times higher for NSL fabricated nanorods. Similarly, signal due to amide I is almost three times higher for NSL fabricated nanorods.

As shown in Figure 7-5(c), the magnitude of the amide I absorption signal of protein A/G on NSL fabricated antennas (0.012) is nearly three times higher than that of the post-processed antennas (0.004). Similarly Figure 7-5(d) shows the protein absorption signal after antibody immobilization. Absorption signal for protein A/G-antibody bilayer is doubled compared to protein A/G monolayer for both NSL fabricated and post-processed nanorods due to the introduction of larger antibody. The magnitude of the amide I absorption signal of antibody on NSL fabricated antennas (0.025) is nearly three times higher than that of the post-processed antennas (0.009). Removing the nanoparticles around the nanorods using a post-processing reduces the absorption signal for both protein A/G and antibody. These experimental results are in very good agreement with our theoretical calculations, which indicates nearly three times larger enhanced surface area for NSL fabricated nanorods. These measurements demonstrate NSL fabricated low cost nanorod antenna arrays with gold nanoparticle clusters can serve as sensitive biospectroscopy substrates.

Experimental Section

Optical characterization: The reflectance data on the nano rod antenna arrays was collected using an FTIR spectrometer (Bruker, IFS 66/s) and infrared microscope (Bruker, Hyperion 1000). The sample spectra are normalized to a source background. All spectra are collected at a resolution of 4 cm^{-1} and consist of 256 scans co-added with a mirror repetition rate of 40 kHz. Spectroscopic scans are performed under a dry air purged environment to eliminate atmospheric absorption. The thickness of the protein layers was independently characterized through ellipsometer (variable-angle spectroscopic ellipsometer, Woollam) measurements. We obtained thicknesses of 2.85 and 7.92 nm for the protein A/G, protein A/G-IgG bi-layer respectively. The IgG thickness is obtained as 5.10 nm.

Monolayer chemistry and preparation: Before surface functionalization, nanorod an-

tenna patterned silicon chips were cleaned in Plasma Asher with oxygen environment for 10 minutes. Protein A/G at a concentration of 1 mg/ml in PBS (10 mM phosphate buffer) was spotted on the substrate surface and incubated for 1h. A post-incubation wash was carried out to remove unbound protein. To form a protein bilayer of A/G and IgG, IgG (anti-mouse from goat) proteins at a concentration of 1 mg/ml in PBS was subsequently spotted on the A/G-coated bowtie apertures and left to incubate again for 1h. A second post-incubation wash was then carried out.

7.4 Conclusion

In this work we present the first demonstration of Nanostencil lithography fabricated low cost infrared nanoantenna arrays for plasmonically enhanced vibrational biospectroscopy application. Specifically we show detection of 3 nm sized protein monolayers and perform antibody assays using precisely arrayed nanoantennas fabricated by reusable stencils. Due to the inherent gap between the stencil and rigid surface resulting from curved surfaces, we observed tiny metallic nanoparticle clusters around the antenna. We presented a post-processing method to effectively remove these gold nanoparticle clusters without damaging the antenna surface. Our experimental results show that antennas directly fabricated with NSL gives nearly three times higher protein absorption signal than that of post-processed nanoantennas. This observation is supported by theoretical calculations indicating the nanoparticle cluster enables near field enhancements over almost three times larger area. The presented results demonstrates that nanostencil lithography is a promising technique for reducing the nanomanufacturing cost while enhancing the performance of biospectroscopy tools for biology and medicine. As a single-step and low cost nanofabrication technique, NSL could facilitate the manufacturing of biophotonic technologies for real-world applications.

Chapter 8

Summary, Conclusions and Outlook

8.1 Summary of the Results

In this thesis, the systematic fabrication of sub-100 nm metallic nanostructures by nanostencil lithography for plasmonics and metamaterials has been demonstrated. The results presented in this thesis are significant contributions to the application of nanostencil lithography for flexible plasmonics, plasmonically enhanced vibrational biosepectroscopy and nanostencil based biopatterning.

1. Fabrication of plasmonic antenna arrays operating both in the visible and infrared frequency regime is demonstrated.
2. The fabricated nano antenna arrays observed to have identical optical responses with standard e-beam lithography fabricated plasmonic nano antenna arrays.
3. As a unique advantage, nano stencils that are used for plasmonic structure fabrication could be used for 12 times (at least) and show no degradation and clogging for future usages. This behavior is particularly important when high-throuhput fabrication of photonics devices is needed.
4. Collective plasmonic behavior of NSL fabricated engineered plasmonic nano antenna arrays are investigated compared against EBL fabricated antenna arrays. No significant difference is observed. This result indicates that using NSL high optical quality plasmonic structures could be fabricated in high throughput fashion.
5. The versatility of nano stenciling is investigated. Using nano stencils, bio patterning down to 100 nm sizes without loosing bioactivity of deposited immunologically

important protein could be achieved.

6. Unlike many other polymer based and colloidal lithography techniques, NSL is confirmed to achieve wide range of plasmonic nanostructure shapes and arrangements in a high precision.

7. Unlike conventional beam based lithography methods, it is demonstrated that using NSL we could utilize polymeric or non planar surfaces for nanophotonic/ plasmonic application for next generation of application.

8. Analysis of blurring issue in NSL is investigated. The blurring problem is overcome by eliminating the gap using polymeric substrates that have self surface sticking properties. Sub-10 nm resolution (very close to EBL precision) is achieved on polymeric substrates.

9. Plasmonic dimers and oligomers with sub-50 nm gap distances and sub-100 nm sizes that have variety of interesting optical properties could be fabricated in high throughput fashion reliably

10. Using NSL, stretchable plasmonic nano devices could be realized for active optical tuning and adaptive photonics systems.

11. To overcome blurring effect in NSL, a post processing method is suggested. The results indicate that well defined plasmonic antennas with smoother surfaces could be achieved.

12. The first plasmonically enhanced vibrational biospectroscopy application is demonstrated using NSL fabricated low cost, large area infrared antenna arrays.

13. For the first time, detailed theoretical investigation on NSL fabricated nano structures is demonstrated with this thesis. Effect of blurring in NSL for biospectroscopy and near field enhancements is demonstrated. The results indicate that NSL fabricated nano antennas with scattered gold nanoparticles around present more sensitive spectroscopy results.

8.2 Conclusions

In this thesis work, using nanostencil lithography, we have demonstrated a novel strategy for high-throughput nanofabrication of engineered plasmonic devices. This technique allows fabrication of nanoplasmonic devices with high uniformity and repeatability without using operationally slow and expensive electron/ion-beam lithography tools. Fabricated structures are characterized by scanning electron microscopy and optical measurements. Devices, fabricated using NSL technique are shown to have comparable optical characteristics with respect to the arrays fabricated by EBL. We show that the stencil can be reused for high-throughput fabrication of antenna arrays by simply removing the metal residue with a mild metal etchant. We also show that NSL offers flexibility and resolution to radiatively engineer nanoantenna arrays for excitation of collective plasmonic resonances. These excitations, by enabling spectrally narrow far-field resonances and enhanced near-field intensities, are highly suitable for ultrasensitive vibrational nanospectroscopy.

In addition, nanostencil lithography technique allows fabrication of nanoparticles made up of different metals and also patterning of biomolecules with high uniformity, resolution and repeatability in a simple, fast, and low cost fashion. The nano patterning ability is characterized by fluorescence microscopy and AFM measurements. Varieties of patterns can be generated using flexible stencil designs, and the pattern features can be replicated with high fidelity. Protein arrays generated by our technique are shown to have feature size down to 100 nm. We show that the stencil can pattern different types of biomaterials. We also show that the stencil can be reused for multiple times by removing the organic residues before each usage. In addition, our technique enables patterning of covalently bond biomolecules while keeping their bio-

logical functionalities. In addition to its high-throughput capability, NSL lithography enables fabrication of plasmonic devices on surfaces difficult to work with electron/ion beam techniques. Here, we have demonstrated successful fabrication of plasmonic devices on non-conducting surfaces such as glass and CaF_2 . As proof of the versatility of the NSL technique, various nanoscale plasmonic structures such as nanowires and nanodisk are also fabricated.

We also demonstrate for the first time NSL can enable single step, high-throughput, high-resolution and large area fabrication of nanostructures on flexible and elastomeric substrates at dimensions relevant for nanophotonics, plasmonics and metamaterials. The resolution limit of NSL can be improved by using polymeric substrates that have adhesive surface properties, such as PDMS. We showed that NSL can replicate the resolution of gold-standard EBL down to 10 nm accuracy. Consequently, we demonstrated fabrication of high-quality bow-tie antennas with sub-50 nm gap distance and sub-100 nm side lengths, and showed precise control of their interparticle distance. We also showed that nanostencil lithography can be used to access highly durable and stretchable substrates (such as LDPE) for active tuning of plasmonic resonances. With a 5 % periodicity enlargement, due to the mechanical strain applied on LDPE thin film supporting nanorod structures, 160 nm red-shifting of the resonance wavelengths is achieved. We also successfully demonstrated that the nanostructures can be fabricated on curved surfaces by first nanopatterning flexible/elastomeric substrates and then wrapping them around non-planar surfaces. This is illustrated by patterning nanoplasmonic antennas on an optical fiber surface. Integration of plasmonics and metamaterials on non-planar surfaces can open up new functional probes and variety of novel applications. The presented high-throughput fabrication method by offering single-step patterning of features with sub-100 nm dimensions on variety of unconventional substrates could be essential for emerging technologies based on flex-

ible photonics/electronics, as well as for scientific progress in many different fields including biology, material science and sub-wavelength optics.

Finally, in this work we present the first demonstration of nanostencil lithography fabricated low cost infrared nanoantenna arrays for plasmonically enhanced vibrational biospectroscopy application. Specifically we show detection of 3 nm sized protein monolayers and perform antibody assays using precisely arrayed nanoantennas fabricated by reusable stencils. Due to the inherent gap between the stencil and rigid surface resulting from curved surfaces, we observed tiny metallic nanoparticle clusters around the antenna. We presented a post-processing method to effectively remove these gold nanoparticle clusters without damaging the antenna surface. Our experimental results show that antennas directly fabricated with NSL gives nearly three times higher protein absorption signal than that of post-processed nanoantennas. This observation is supported by theoretical calculations indicating the nanoparticle cluster enables near field enhancements over almost three times larger area. The presented results demonstrates that nanostencil lithography is a promising technique for reducing the nanomanufacturing cost while enhancing the performance of biospectroscopy tools for biology and medicine. As a single-step and low cost nanofabrication technique, NSL could facilitate the manufacturing of biophotonic technologies for real-world applications.

8.3 Outlook

The results and experiments carried in this thesis have also risen new questions and challenges. The role of surface diffusion on the blurring still needs further analysis and understanding which is essential to improve the resolution of stencil lithography. Modeling and simulation of blurring effect for different deposited materials and substrates would be effective to improve the pattern quality and resolution of fabricated

nanostructures.

Enlarging nano patterned area is also fundamental for the applications and throughput of the technique. Since the stencils for nanopatterning require thin stencil membranes, the area that could be patterned with nanoapertures is limited. Further work could enable more compliant and robust stencils to increase the throughput.

Additional research on applications of nanostencil lithography will provide answers to questions about potential of nanostencil lithography for other photonic applications and open new fields of opportunity for this technique.

Another important point is to enable compatibility of nanostencil lithography with conventional industrial fabrication processes. Especially dynamic deposition of materials with controllable stage at nanometer precision could facilitate and enhance the three dimensional fabrication using NSL.

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PUBLICATIONS

Book Chapters

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2. H Altug, A A Yanik, R. Adato, S Aksu and A Artar. *Plasmonics for Ultrasensitive Nanaospectroscopy and Ultrasensitive Optofluidic-Plasmonic Biosensors*. In: Plasmonics and Plasmonic Metamaterials: Anlysis and Applications. World Scientific. eds: I Tsukerman and G Shvets. 2010.

Selected Journal Publications

1. S Aksu et. al. Plasmonically enhanced vibrational biospectroscopy using low-cost infrared antenna arrays by nanostencil lithography. Submitted to *Advanced Optical Materials*. 2013.

2. M Huang, B Galarreta, A Artar, R. Adato, S Aksu and H Altug. Reusable nano stencils for creating multiple biofunctional molecular nano patterns on polymer substrates. *Nano Letters*, 12(9):4817-4822. 2012.
3. S Aksu et. al. Flexible plasmonics on unconventional and nonplanar substrates. *Advanced Materials*, 23(38):4422-4430. 2011.
4. T-Y Chang, M Huang, A A Yanik, H-Y Tsai, P Shi, S Aksu, M F Yanik and H Altug. Large scale plasmonic microarrays for label-free high-throughput screening. *Lab Chip*, 2011, 11, 3596-3602.
5. S Aksu, A A Yanik, R Adato, A Artar, M Huang and H Altug. Highthroughput nanofabrication of plasmonic infrared nanoantenna arrays for vibrational spectroscopy. *Nano Letters*, 10:2511-2518. 2010.

Patents

1. Plasmonic nano antenna arrays for vibrational nano spectroscopy, methods of use and methods of high-throughput nano fabrication. *Provisional PCT Application No. US2010/053757*