Electrodeposition of metal nanostructures for plasmonic sensing

Mueller, Aaron David

2019

Mueller, A. D. (2019). Electrodeposition of metal nanostructures for plasmonic sensing. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/106468>

<https://doi.org/10.32657/10220/47994>

**ELECTRODEPOSITION OF METAL NANOSTRUCTURES
FOR PLASMONIC SENSING**

AARON DAVID MUELLER

SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING

2019

**ELECTRODEPOSITION OF METAL NANOSTRUCTURES
FOR PLASMONIC SENSING**

AARON DAVID MUELLER

School of Electrical and Electronic Engineering

A thesis submitted to the Nanyang Technological University

in fulfillment of the requirement for the degree of

Doctor of Philosophy

2019

STATEMENT OF ORIGINALITY

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other University or Institution.

3/4/2019

Date

Aaron D Mueller

SUPERVISOR DECLARATION STATEMENT

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

4 April 2019
Date

Professor Zhang Dao Hua

AUTHORSHIP ATTRIBUTION STATEMENT

This thesis contains material from four paper(s) published in the following peer-reviewed journal(s) where I was the first and/or corresponding author.

Much of Chapter 3 is published as Mueller AD, Tobing LYM, Zhang DH. Reliable Fabrication of High Aspect Ratio Plasmonic Nanostructures Based on Seedless Pulsed Electrodeposition. *Adv Mater Technol.* 2019; 1800364:1–9

The contributions of the co-authors are as follows:

- Dr. Tobing conceived the idea for electrodeposition of nanostructures onto ITO.
- I decided to use pulsed electrodeposition, the code for which was developed by Dr. Tobing and me.
- I performed the electrodeposition.
- Dr. Tobing performed the EBL and development.
- Dr. Tobing and I performed SEM measurements together.
- I collected the spectral data, and Dr. Tobing helped with the analysis of the nanostructure spectra.
- I wrote the manuscript. Dr. Tobing and Prof. Zhang made revisions.
- Prof. Zhang supervised the work.

Chapter 4 is published as Mueller AD, Tobing LYM, Zhang DH. Combining sonicated cold development and pulsed electrodeposition for high aspect ratio sub-10 nm gap gold dimers for sensing applications in the visible spectrum. *Nanoscale*. 2018; 5221–8.

The contributions of the co-authors are as follows:

- Dr. Tobing performed the EBL and development.
- I performed the electrodeposition.
- Dr. Tobing and I performed SEM measurements together; I analyzed the SEM images to determine structural dimensions.
- Alana Soehartono performed characterization of the structures in refractive index liquids.
- I collected the spectral data, and Dr. Tobing helped with the analysis of the nanostructure spectra.
- I wrote the manuscript. Dr. Tobing and Prof. Zhang made revisions.
- Prof. Zhang supervised the work.

Parts of Chapter 5 have been published as Mueller AD, Tobing LYM, Luo Y, Zhang DH. Vertical growth of plasmonic nanostructures via electrodeposition on a conductive oxide. ICMAT 2017. *Procedia Engineering* **215**, 60-65.

The contributions of the co-authors are as follows:

- Dr. Tobing conceived the idea for electrodeposition of nanostructures on ITO
- Dr. Tobing and I performed electrodeposition and SEM together.
- I performed the simulations
- I wrote the manuscript; Dr. Tobing and Prof. Zhang revised the manuscript.
- Prof. Zhang and Prof. Luo supervised the work.

Other parts of Chapter 5 will be submitted as Mueller AD, Tobing LYM, Soehartono AM, Zhang DH. Evolution of the Localized Plasmonic Longitudinal Mode and Sensing Characteristics as a Function of Height.

Contributions of the authors are as follows

- Dr. Tobing conceived the idea for electrodeposition of nanostructures on ITO
- Dr. Tobing and I performed electrodeposition and SEM together.
- I performed the simulations
- Alana Soehartono performed characterization of the structures in refractive index liquids and collected some of the data.
- I collected some of the data and wrote the text
- Prof. Zhang supervised the work.

3/4/2019

Date

Aaron D Mueller

ACKNOWLEDGEMENTS

First and foremost I would like to thank my PhD supervisor Professor Zhang Dao Hua. I am very grateful for both the support and freedom he has given me in my studies. His positive attitude and helpful suggestions have been key to the completion of this work.

Second, I would like to thank my other mentor, teacher, collaborator, and friend Landobasa Tobing. He has taught me more about things as diverse as nanofabrication and philosophy than anyone I've previously known. This project would not have been successful without his guidance and encouragement.

On this note, I would also like to thank Lando's TL kakis Stevanus and Chee Keong for their help and encouragement. I would like to thank my labmates for their support and company, especially Xu Zhengji, Qiu Shupeng, Qian Li, Tong Jinchao, Liu Lin, Suo Fei, Hu Hao, Liu Dongjue, Huang Yao, and Chen Qiran. Additionally I would like to thank the laboratory technicians for their help and humor, especially Anthony Chong, Mr. Yeoh, Ms. Yvonne, Poh Chee, Ms. Debbie, and Hasman. Also, the N2FC fabrication staff have been great, I'd like to give a shout out to Shamsul, Zul, Mak Foo Wah, Ling Ling, Kwok Fai, and Irene Chia.

I am also deeply appreciative to have such an understanding family, mom, dad, and grandparents, supporting my move halfway across the world to stay in school even longer, haha.

I owe the biggest debt of gratitude to my wife and collaborator Alana Soehartono. I definitely couldn't have done this without your help and support. Thank you also to my daughters Ariani and Alia for giving me something good to look forward to when I come home at night.

TABLE OF CONTENTS

Abstract.....	xxiii
List of Figures.....	xxiv
List of Tables	xxx
Nomenclature and Abbreviations	xxxi
Chapter 1 Introduction	1
1.1 Motivation.....	1
1.2 Objectives	5
1.3 Major Contributions.....	6
1.4 Thesis Organization.	8
Chapter 2 Background.....	11
2.1 Plasmonics	11
2.1.1 Maxwell's Equations	11
2.1.2 Optical Properties of Metals	14
2.1.3 Plasmon Classification	15
2.2 Plasmonic Biosensing	20
2.3 Experimental Methods	26
2.3.1 Electron Beam Lithography	27
2.3.2 Electrochemical deposition	30
2.3.3 Characterization Methods.....	39

2.3.4	Finite Difference Time Domain Simulations	40
Chapter 3	Development of Electrodeposition Process	49
3.1	Introduction.....	50
3.2	Results and Discussion	52
3.3	Alternate Deposition Modalities	66
3.3.1	Deposition of Negative Patterns	67
3.3.2	Deposition onto other substrates.....	72
3.3.3	Concluding remarks on alternate deposition modalities.....	76
3.4	Conclusion	77
Chapter 4	High Aspect Ratio Sub-10-nm Gap Gold Dimers	79
4.1	Introduction.....	79
4.2	Experiment.....	82
4.2.1	Nanopatterning	82
4.2.2	Electrodeposition.....	83
4.2.3	Characterization.....	84
4.3	Results and Discussion	84
4.3.1	Fabrication of square dimer with high aspect ratio gaps	84
4.3.2	Plasmonic characteristics of gold square dimers.....	90
4.3.3	Bulk Sensing Performance	93
4.4	Conclusions.....	96
Chapter 5	Evolution of the Longitudinal Mode and Sensing Characteristics as a Function of Height	99
5.1	Effect of height on nanostructure resonance properties.....	100

5.1.1	Square dimer simulations	104
5.1.2	Rotationally symmetric structure simulations	112
5.2	Growth of nanostructures of various heights and comparison of sensitivities.....	114
5.3	Conclusions.....	123
Chapter 6	Conclusion and Recommendations	125
6.1	Conclusions.....	125
6.2	Recommendations.....	127
Author's Publications		129
Journals		129
Conference Proceedings.....		130
References.....		131
Appendix A	Supporting Information for Fabrication and Measurements	143
A.1	Pulse Waveforms for Nanostructures in Chapter 3	143
A.2	Supporting Information for Dimer Measurements in Chapter 4.....	144
A.2.1	Detailed Measurement of Lateral Dimensions	144
A.2.2	Dimer Height Measurements.....	147
A.2.3	Calculation of the Refractive Index of AZ5214E.....	151

ABSTRACT

In this thesis, a cost-effective method for top-down fabrication of metallic nanostructures with deep-subwavelength dimensions is explored, finding use in plasmonic sensing applications. Currently, few methods exist for the fabrication of such metallic structures with deep sub-optical-wavelength feature sizes. The two-step process of electron beam lithography followed by electrodeposition has emerged as a viable fabrication scheme for such devices, saving both time and precious metal by avoiding physical deposition in a vacuum chamber. The development of a process which uses a transparent conductive layer of indium tin oxide rather than a metal seed layer is reported. The simulation and fabrication results of various types of high aspect ratio periodic structures, chosen for light localization and polarization invariance, are presented and analyzed, including structure morphology and the accompanying process limitations. In the case of gammadion crosses, electrodeposition produces structures with transmission spectral resonance exhibiting a Q -factor as high as 11.1 in the visible spectrum, a 65% increase over the planar counterpart. Moreover, dimers grown with this method were found to have consistently sub-10-nm and even sub-5-nm gaps. As this process can produce tall nanostructures, plasmonic modal evolution with height is investigated, along with effects on refractive index sensitivity. Tall v -shaped split ring resonator structures were found to have a sensitivity of close to 400 nm/RIU in the optical spectrum, much higher than the theoretical maximum predicted for simple localized resonance.

LIST OF FIGURES

Figure 1.1 Biosensor schematic, from [6].....	2
Figure 2.1 (a) Transparency to radiation above and below the plasma frequency, (b) real (ϵ') and imaginary (ϵ'') parts of the plasma permittivity, and (c), reflection and transmission near the plasma frequency, adapted from [10].....	16
Figure 2.2 (a) Surface plasmon polaritons excited by a prism and by a nanohole grating, evanescently decaying away from the surface, (b) dispersion relation for an ideal metal and (c) reflection measurement shows a dip at the incidence angle where the dispersion relation is satisfied due to momentum matching, adapted from [10]. ...	17
Figure 2.3 (a) Localized surface plasmon resonance of a nanosphere and scattering and absorption cross sections of a metallic nanosphere with radius (b) $R < 15$ nm and (c) $R > 15$ nm, adapted from [10].	18
Figure 2.4 Scatter plot of the data in Table 2.1 in yellow, along with the theoretical maximum in Equation (2.25) in blue. The point circled in orange represents a shell structure, whereas those with orange squares represent use of longitudinal modes, adapted from [68].....	23
Figure 2.5 Schematic of single alkanethiol (dodecanethiol in this case)molecule bonded to gold substrate. The head group can be chosen to fit nearly any surface chemistry or target analyte. From [86].	26
Figure 2.6– Exposure and development processes for positive, negative, and image reversal resists.....	28
Figure 2.7–Electron beam process for AZ5214E photoresist at 20kV accelerating voltage. (a) Different resist tones for different exposure dose range. At small doses, the resist exhibit positive-tone characteristics. At large doses, the resist molecules are cross-linked, making the AZ resist negative-tone. In between positive and negative regime, through post-exposure annealing, it is possible to have image-reversal tone for the AZ resist. (b) Image-reversal tone characteristics as a function of baking temperature, bake time, and development time.	29
Figure 2.8– Electron beam sensitivity for ZEP520A resist at 20kV accelerating voltage based on sonicated cold development process.....	30
Figure 2.9 Two phases in contact.	32
Figure 2.10– Model of double layer region with specifically absorbed ions [90]	33
Figure 2.11– Example of current density vs overpotential various α	35
Figure 2.12– Realistic example of the current density as a function of electrode potential [93].....	36

Figure 2.13–Schematic of typical electroplating process	38
Figure 2.14–Hyperspectral imaging (a) A schematic of the imaging system, and (b) example scans of arrays of v -shaped SRRs of various opening angle and arm length. 40	
Figure 2.15–Hyperspectral imaging, recording the 10x10 average spectral profiles of a structure (red) and the bare substrate (green) for normalization	40
Figure 2.16–Schematic of Yee cell used in FDTD method	41
Figure 2.17–Propagation of fields and lateral boundary conditions used for simulation of periodic structures with x -oriented electric field (top row) and y -directed electric field (bottom row).....	41
Figure 2.18–Screenshots of simulation views in Lumerical FDTD for an arbitrary structure, a C6 star on ITO substrate in this case. (a) The perspective view. (b) The top (x - y) view showing the use of symmetric BCs in the x direction and antisymmetric BCs in the y direction. (c) The side (x - z) view	43
Figure 2.19–Screenshots of perspective views of two structure groups in Lumerical (a) The rounded quadrilateral as first added, and (b) the same structure with the constituent parts shown as different colors: teal for the rectangles (faces), orange for the cylinders (edges), and magenta for the spheres (corners). (c)-(f) A partial (180°) circular toroid as the number n of constituent cylinders per 360° is decreased from 100 to 12.	44
Figure 2.20– xy (top row) and perspective (bottom row) screenshots of v -SRR structures in Lumerical FDTD. (a), (b) A simple structure composed of three rectangular prisms. (c)-(f) a more physical rounded structure, consisting of three rounded-top polygon quadrilaterals and extra cylinders and partial circular toroids to fill in the gaps, with the extra parts shown in purple in (e)-(f). (g), (h) Concentric v -SRR shapes, with the outer material being dielectric and the inner gold, on ITO substrate (purple)	46
Figure 2.21–Screenshot of the Lumerical FDTD user interface with the object tree expanded on the left and the four views on the right.	47
Figure 3.1– Schematics of the dual-substrate electrodeposition holder: (a) top view, (b) side view, and (c) side view	53
Figure 3.2– (a) Illustration of current density pulse shape and parameters and (b) 2 seconds of each of the waveforms used in this work.....	53
Figure 3.3– Reflection spectra at various positions on samples (a) $S1$, (d) $S2$, and (g) $S3$, with reflection images inset, and corresponding SEM images for (b)-(c) $S1$, (e)-(f) $S2$, and (h)-(i) $S3$. The thick line in the spectra represents the mean of the measurements, with the shaded blue area encompassing ± 1 std. dev. The dashed curve represents the ideal normalized reflectivity based on optical constant data. The inset images depict a square area of side $51.68\ \mu\text{m}$	55
Figure 3.4– Reflection spectra at various positions on samples (a) $S4$, (d) $S5$, and (g) $S6$ with reflection images inset and , and corresponding SEM images for (b)-(c) $S4$, (e)-(f) $S5$, and (h)-(i) $S6$. The significance of the lines and shaded regions is the same as the previous figure. The inset images depict a square area of side $51.68\ \mu\text{m}$	57
Figure 3.5– Reflection spectra at various positions on samples (a) $S7$ and (d) $S8$ with reflection images inset, and corresponding SEM images for (b)-(c) $S7$, and (e)-(f) $S8$.	

The significance of the lines and shaded regions is the same as the previous figures. The inset images depict a square area of side $51.68\ \mu\text{m}$	59
Figure 3.6– Schematic of the electrodeposition setups for the two nanostructure samples and their dummy substrates. Before depositing the nanostructures, the $n=10$ dummy sample surface was ITO, but the $n=21$ dummy sample surface had an additional layer of gold.	60
Figure 3.7– SEM micrographs of various electrodeposited structures: (a) square dimers of side length $s = 80\ \text{nm}$ and nominal gap $g = 30\ \text{nm}$, (b) six-fold rotationally symmetric stars ($s = 100\ \text{nm}$), (c) four-fold internally rotationally symmetric gammadion crosses ($s = 100\ \text{nm}$), and (d) four-fold externally rotationally symmetric v -SRR ($s = 100\ \text{nm}$, $\theta = 60^\circ$). All scale bars represent $400\ \text{nm}$	61
Figure 3.8– Transmission spectra of (a) square dimer, (b) C_6 -symmetric star structure, (c) gammadion resonator, and (d) fourfold rotationally symmetric v -SRR array (C_4 v -SRR with $\theta = 45^\circ$ and $\theta = 60^\circ$) for planar ($h = 30\ \text{nm}$) and electrodeposited ($h = 70 \pm 5\ \text{nm}$) structures. The resonance modes are indicated by the solid, hollow, and double arrows.....	64
Figure 3.9 Comparison of positive and negative techniques: (a) deposition using positive technique, with sacrificial area on the same sample, (b) deposition using the negative technique, and (c) final structure examples for a given EBL exposure pattern.	67
Figure 3.10 SEM images of the gold film electrodeposited onto NS6 at (a) lower and (b) higher magnification	69
Figure 3.11 SEM images of (a) hexagonal and (b) square tessellation patterns, with higher magnifications inset.....	70
Figure 3.12 SEM images of the annular cavities, where the three numbers separated by dashes in each subfigure signify the relative EBL dose, the circle radius, and circle line width	71
Figure 3.13 SEM images of the annular cavities, where the three numbers separated by dashes in each subfigure signify the relative EBL dose, the circle radius, and circle line width	72
Figure 3.14 Example of deposition of concentric square annuli onto high sheet resistance ITO substrate.....	73
Figure 3.15 –Results of deposition of nanostructure arrays onto $2\ \text{k}\Omega/\square$ ITO substrate. (a) u -shape SRRs and (b) C_5 star shapes	73
Figure 3.16 –Gold deposition onto the $2\ \text{k}\Omega/\square$ ITO substrate: (a) the height marker, (b) the dummy area, (c) the dummy area at higher zoom, and (d) a square pattern at oblique incidence	74
Figure 3.17 – SEM images of the large areas of titanium after electrodeposition.....	76
Figure 4.1 (a) Schematic of the square dimer array on ITO substrate with the unit cell indicated by the dashed square. Top-view SEM micrograph of square dimers with sub-10-nm gaps fabricated by (b) physical vapor deposition and (c) electrodeposition method. The scale bars represent $100\ \text{nm}$	86
Figure 4.2 Oblique-incidence SEM images of the fabricated dimer arrays with normal-incidence SEM images inset. (a)-(c) Design square dimension of 80nm with gap	

decreasing from 40nm to 20nm and (d)-(f) the same as above but with square dimension of 60nm. The inclination angle for the oblique images is 25°. All scale bars are 400 nm.	87
Figure 4.3 (a) Zoomed out version of the array shown in Fig. 1 (e), with $s = 60\text{nm}$ and $g = 30\text{nm}$, showing the regularity of the fabricated array. The scale bar represents 2 μm	87
Figure 4.4 Averages of the normalized measurements with error bars based on the standard deviations, plotted with respect to design gap size, for both the 60nm and 80nm iterations. Above, side length the measurements in the x (s_x) and y (s_y) and directions. Below, the normalized gap measurements. Jitter was added to the abscissa for clearer viewing.	89
Figure 4.5 Boxplots showing the distribution of measured dimer heights. Individual data points are also shown, with added jitter. Whiskers are extended to the measured extrema.	90
Figure 4.6 Transmission responses of high aspect ratio (on 20 $\Omega/\square$ ITO) and planar (on 50 $\Omega/\square$ ITO) square dimer structures ($s = 80\text{ nm}$, $g = 30\text{ nm}$) under x and y polarizations.	91
Figure 4.7 Transmission response of the square dimer structures under x and y polarizations. Here, the parameters s and g refer to the nominal square side length and gap, respectively, as illustrated schematically in Figure 4.1.	92
Figure 4.8 Comparison of electrodeposited deposited and planar dimer transmission spectra in air and in two resists: (a) $s80g40$ electrodeposited array, (b) $s80g40$ planar array, (c) $s80g30$ electrodeposited array, and (d) $s80g30$ planar array. In all spectra, the resonance wavelength is denoted with a circle.	94
Figure 4.9 Transmission dip minima plotted against cladding refractive index for the two dimer arrays. The regression lines for the points are also shown.	95
Figure 4.10 (a) Transmission spectra of dimers with side length $s=80\text{ nm}$, gap $g=30\text{ nm}$, and height $h\sim 140\text{ nm}$ in air and various refractive index liquids, and (b), a plot of the dip location versus refractive index, indicating the sensitivity with the slope of the line of best fit	96
Figure 5.1 Spectral effects from a moderate increase in height. (a) Simulation and (b) experimental transmission spectra for square dimers with a design side length of 80 nm and gap of 30 nm ($s80g30$). The simulated dimers have dimensions matching the experimental measurements presented in Chapter 4. (c) Simulation and (d) experimental transmission spectra for C6 star shaped structures with design arm length of $s=100\text{ nm}$. (e) Simulation and (f) experimental transmission spectra for gammadion cross structures is arm section length of $s=60\text{ nm}$. Heights of structures in nm are displayed adjacent to their corresponding curves. Arrows show shift of relevant transmission minima.	101
Figure 5.2 Graphical representation of the blue shifts shown in the spectra of the previous figure	102
Figure 5.3 (a) Transmission spectra for periodic dimers $s80g20$, with heights from 20 nm to 140 nm in increments of 10 nm, and (b) Differences in transmission for dimers whose heights differ by 10 nm, where the subscripts indicate height in nm	105

Figure 5.4 (a) Transmission spectra for periodic dimers $s80g20$, with heights from 20 nm to 140 nm in increments of 10 nm, and (b) Differences in transmission for dimers whose heights differ by 10 nm, where the subscripts indicate height in nm	106
Figure 5.5 Heatmaps of the transmission under x -polarization of square dimers with various side lengths s and gaps g , with heights from 20 nm to 1000 nm. (a) $s80g20$, (b) $s80g30$, (c) $s80g40$, (d) $s100g20$, (e) $s100g30$, and (f) $s100g40$. White lines have been added to trace the evolution of the longitudinal modes with height.	107
Figure 5.6 Heatmaps for absorption, reflection and transmission for $s80g20$ under x -polarization, with heights from 20 nm to 1000 nm.....	108
Figure 5.7 Simulation results of y -polarization transmission spectra for low ($h=30$ nm), moderately tall ($h=120$ nm), and tall ($h=1000$ nm), square dimers with gaps of 20, 30, and 40 nm. (a) square dimension $s=80$ nm dimers and (b) square dimension $s=100$ nm dimers	110
Figure 5.8 Heatmaps of y -polarization spectra for dimers with heights from $h=20$ nm to $h=1000$ nm (a)-(c) $s80g30$ and (d)-(f) $s100g30$	111
Figure 5.9 Heatmaps of spectra for $C6$ stars with $s=80$ nm and period $p=240$ nm in the x and y directions, for heights from $h=30$ nm to $h=1000$ nm.....	112
Figure 5.10 Heatmaps of spectra for gammadion cross structures with half arm length $s=60$ nm, for heights from $h=30$ nm to $h=1000$ nm	113
Figure 5.11 Layout of the EBL pattern for deposition of structures using various numbers of pulses	115
Figure 5.12 Compilation of screenshots of various scans from Cytoviva and ENVI software, with one dose from T21 enlarged for clarity.....	116
Figure 5.13 SEMs of T27square dimers with EBL pattern having side length $s=100$ nm, $g=20$ nm, and periods $p=4s$, at 65% dose at (a) normal and (b) oblique incidence. The scale bars represent 500 nm.....	117
Figure 5.14 SEMs of $C3$ stars with EBL pattern arm length $s=100$ nm and periods $p=3s$: (a) 75% dose pattern at normal incidence, and periods (b) 65% dose at oblique incidence. The scale bars represent 500 nm.....	117
Figure 5.15 Measured transmission spectra for $C6s80$ structures from various samples. The measured and estimated heights (in nm) are shown in the legend	118
Figure 5.16 Measured transmission spectra for $C6s80$ with air cladding and PMMA cladding (offset), with dashed and dotted lines connecting distinguishable modes ...	119
Figure 5.17 Simulation of square dimer array. (a) On the top, a schematic representation of the array, and on the bottom, of one unit cell, and (b) transmission spectra for structure heights of 40nm, 120nm, and 400nm, offset vertically, with dielectric coating thickness of 0nm (none) to 20nm, from [177].	121
Figure 5.18 Spectral measurements of the non-rotationally symmetric array of v -SRRs with arm length $s=100$ nm, opening angle of 40° , and period of $p=3s$ measured in air and in different refractive index solutions. (a) x -polarized and (b) y -polarized spectra, and dip position and best fit lines for (c) x -pol and (d) y -pol spectra.....	122
Figure 5.19 An extension of Figure 2.4. Scatter plot of the LSPR sensitivity data in other works (from Table 2.1) in yellow, along with the theoretical maximum in	

Equation (2.25) in blue. The orange squares with black outline represent the ν -SRR data from T27 as shown above in Figure 5.18. Adapted from [68]...... 123

LIST OF TABLES

Table 2.1. List of various geometries for LSPR along with their resonance wavelengths and refractive index sensitivities, from [68]	23
Table 3.1. Sample designations and pulse parameters. The total deposition times and current ON times are given in the last two columns. A current density of $j_{ON} = 3$ mA/cm ² was used for all samples.	54
Table 4.1. Measured dimensions of dimers, in nm, and aspect ratios	88
Table 4.3 Summary of Q factors.	93
Table 5.1. Slopes $d\lambda_R/dh$ of white lines in Figure 5.5, denoting the slope of the j^{th} longitudinal resonance	108
Table 5.2. Sample names, number of pulses, and surface material of dummy substrate	115
Table 5.3. Measured resonances in air (λ_{R0}) and in PMMA (λ_{R1}), the gray cells correspond to resonance locations that did not have obvious dips with zero derivative.	120

NOMENCLATURE AND ABBREVIATIONS

EBL	Electron beam lithography
FDTD	Finite difference time domain
FOM	Figure of merit
FOMC	Figure of merit-contrast
LSPR	Localized surface plasmon resonance
SAM	Self-assembled monolayer
SEM	Scanning electron microscopy
SPR	Surface plasmon resonance
SRR	Split-ring resonator

Chapter 1 INTRODUCTION

1.1 Motivation

Diagnostic testing is a crucial component of primary healthcare, with results influencing decisions concerning treatments, referrals, and hospital admissions. Despite decreases in rates of deaths across all categories besides suicide [1], deaths from diseases that are not diagnosed early or monitored properly are still a major issue [2]. A diverse and growing number of so-called point-of-care (POC) tests aim to change this. Well-known examples of medical tests moving towards POC include portable ultrasound, pulse-oximetry, and blood glucose monitoring in diabetic patients. Such tests, performed close to the patient (as opposed to a laboratory in a separate facility) and yielding quicker if not immediate results, offer the potential to improve patient outcomes by optimizing decisions about prescriptions and referrals, improving efficiency, and decreasing costs [3]. Optical biosensors, enabling direct, real-time, and label-free detection of many biological and chemical species, offer numerous advantages as an alternative to traditional analytical techniques, including high specificity and sensitivity, small size, and potential cost-effectiveness [4–6].

Figure 1.1 Biosensor schematic, from [6]

Science and engineering have bolstered many of the recent advances in medicine. In particular, technologies from various areas in the burgeoning field of nanoscience are enabling even more possibilities. The integration of nanotechnology into POC diagnostic testing is an obvious choice, in line with the POC requirement for smaller sample and device sizes [3,7]. One important technology which has captivated much research attention for use in chemical and biological sensors is that of (localized) surface plasmon resonance (SPR and LSPR) [8–11]. The small sample and device size makes them ideal candidates for integration with microfluidic channels [12–14], and easily multiplexed sensing [15,16].

Although (non-localized) SPR remains the leading plasmonic investigative method, its implementation is made more difficult by the more involved Kretschmann excitation scheme, the need for tight optical alignment, and sensitivity to ambient temperature [17]. Several commercial plasmonic setups are available [18]; however, other than OpenSPR from Nicoya Lifesciences, Inc. [19], they all use SPR, as opposed to LSPR. Lowering the fabrication cost of LSPR substrates is key to enabling more widespread adoption of and a greater market share for LSPR-based sensing devices.

LSPR sensing platforms have been validated in metal nanoparticles fabricated through both top-down and bottom-up (self-assembly) approaches [20]. Due to higher

reproducibility, the former is much preferred to the latter, despite the associated increase in costs. Because these methods involve optical excitation and measurement, costs may be kept lower by using visible-range sources and detectors and by minimizing the use of devices such as polarizers. Top-down approaches for fabrication of well-ordered metal nanoparticles with subwavelength feature size is typically carried out by physical deposition, such as e-beam evaporation, through a predefined template, followed by lift-off of the excess metal. However, the equipment is expensive, and the process is time-consuming. Moreover, most of the metal, often expensive noble metals such as gold or silver, is wasted in the process.

We propose a better way of metal deposition—electrochemical deposition. For this purpose, we explore a combination of electrodeposition and electron beam lithography (EBL) to produce (potentially high aspect ratio) plasmonic nanostructures. Prior experimental research into the fabrication of such structures using the two-step process of EBL and electrodeposition has been performed by other groups [21–23], but in most cases, a metal seed layer was used to make the surface conductive. This layer is detrimental to performance in plasmonic applications because it behaves as a plasmonic “short circuit” between the individual structures. Hence, the fabrication process requires an extra step of plasma etching in order to remove the layer. We propose using indium tin oxide (ITO) to coat glass as a basis for electrodeposition of such plasmonic nanostructures for numerous reasons. Its electrical conductivity renders it amenable to electrodeposition, its transparency at visible wavelengths allows the use of transmission spectra of supported structures, and its inability to sustain plasmons at the wavelengths of interest means that it does not have to be removed following the electrodeposition step.

In addition to wasting less precious metal, the electrodeposition process is fast, up to 17.5 nm/s, two orders of magnitude faster than physical deposition. Moreover, like seeded growth of colloidal nanoparticles in solution, the metal quality of the electrodeposited metal is much better. Finally, due the nature of the process, growing vertically from the substrate, electrodeposited structures are capable of achieving higher aspect ratios than those fabricated with physical deposition.

1.2 Objectives

The main objective of this work is the development of processes utilizing seedless electrodeposition through a nanopatterned for the fabrication of well-ordered metallic nanostructures of various shapes and sizes. After determining optimal process parameters, this work aims to show the limits of the process, such as minimum lateral feature size and maximum height. Because the structures are capable of being grown taller than those grown using physical deposition, the resonance modes, particularly longitudinal modes and their interaction with transverse modes are explored in simulations and experimental results. Furthermore, for applications in plasmonic sensing, the sensitivities for the tall structures are compared to their short counterparts.

1.3 Major Contributions

The major contributions of this thesis are as follows:

1. In this work, the development of a reliable process for fabricating arrays of metallic nanostructures using seedless electrodeposition onto ITO is demonstrated. Moreover, two alternate processes were developed: (1) electrodeposition through a positive resist template, utilizing a sacrificial dummy substrate plated in parallel with the nanostructures for better current control, and (2) electrodeposition around a negative resist template, for which a dummy substrate is not required. This includes the choice of using pulsed versus DC current, and the optimization of the corresponding pulse parameters.
2. This work also demonstrates that, in addition to bulk nanostructures, seedless electrodeposition may also be used to grow patterns of metallic nanoparticles and to sparsely coat large areas with nanoparticles of relatively uniform size.
3. This work shows that the developed seedless electrodeposition process may be used to deposit tall metallic nanostructures having sub-10-nm gaps, in this case in arrays of square dimers. It is also shown how, due to the inherent growth mechanisms, smaller gaps and higher aspect ratios are achievable using electrodeposition over alternative processes such as electron beam evaporation. Moreover, these tall structures exhibit experimentally higher refractive index sensitivity than their planar counterparts, which attributable to the growth quality this method entails.
4. Because the proposed fabrication technique may be used to grow nanostructures taller than other methods, this work investigates the spectral

mode evolution of some metallic nanostructures in simulations and experiments, in the case where structure height is varied from almost planar to very tall (extremely tall in simulations). The evolution is shown to be a complex process, influence both by height and by refractive index of the cladding. It is demonstrated that tall structures are capable of supporting longitudinal modes, which have higher refractive index sensitivity than their planar counterparts. Recommendations are given for utilizing this possibility of taller structures to achieve better refractive index sensitivity in practice.

1.4 Thesis Organization.

This thesis is organized into seven chapters, organized in the following manner:

Chapter 1 is the introductory Chapter. It contains the motivation for pursuing the work contained in the thesis, the objectives and major contributions of the thesis, and a summary of thesis chapter organization.

Chapter 2 is a background Chapter. It covers plasmonics basics, starting with Maxwell's equations and material considerations, showing how they lead to different types of physical phenomena collectively referred to as "plasmonics". It further covers various definitions plasmonic refractometric sensitivity found in the literature. The chapter finishes by discussing experimental methods used for carrying out the thesis work, including electron beam lithography (EBL), electrodeposition, and characterization methods. It also includes information on simulations carried out using the finite difference time domain method.

Chapter 3 details the investigation of using pulsed electrodeposition for coating of gold on ITO-coated glass. In this Chapter, optimal pulse parameters are found which yield high quality gold films. Results are then shown of nanostructures from two samples grown using these pulse parameters to grow dimers and other structures exhibiting various degrees of rotationally symmetry. Additionally, the Chapter outlines other deposition techniques explored in parallel with the main fabrication strategy of the thesis. These include both electrodeposition onto the same substrate but using a template defined with a negative resist and results of electrodeposition onto another substrate.

Chapter 4 discusses in more detail how the combination of sonicated cold development of an EBL pattern with the pulsed electrodeposition parameters

determined in the previous Chapter can be used to grow high aspect ratio dimers with consistently sub-10-nm gaps. Furthermore, it is demonstrated that these tall structures, having better metal film quality than their planar counterparts deposited with physical deposition, exhibit an increase in bulk refractive index sensitivity by 45%.

Chapter 5 discusses the resonance modes of square dimers, and various rotationally symmetric and non-rotationally symmetric structures as height is increased. It is shown that, given the interplay of various transverse and longitudinal modes, height and mode selection are not trivial, but under the right conditions, very high aspect ratio metallic nanostructures can display superior refractive index sensitivity.

Chapter 6 is the concluding Chapter, in which the thesis is summarized, and recommendations for future directions for this work are outlined.

Chapter 2 BACKGROUND

2.1 Plasmonics

A plasma, a neutral gas of ions and electrons, is good model for materials where the main contribution to the permittivity and conductivity is from free or mostly free electrons. This includes materials such as cold plasma (e.g. as an approximation of the ionosphere), for conduction band electrons in a metal, and for heavily doped semiconductors [24]. Plasmons are the quanta of collective oscillations of the free electron gas density. Depending on the conditions out of which they arise, they can have various forms, such as the volume (bulk) plasmon, surface plasmon polariton, and localized surface plasmon. In order to understand the difference between these, we must first look at Maxwell's equations.

2.1.1 Maxwell's Equations

Our starting point will be the macroscopic form of Maxwell's equations, which, given bulk constituent parameters and subject to certain boundary conditions, govern the behavior of the electric and magnetic fields. If we assume time-harmonic ($e^{-j\omega t}$ time dependence) fields in the absence of source charges or current densities, they take the form

$$\nabla \cdot \mathbf{D} = \rho \quad (2.1)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (2.2)$$

$$\nabla \times \mathbf{E} = j\omega\mathbf{B} \quad (2.3)$$

$$\nabla \times \mathbf{H} = \mathbf{J} - j\omega\mathbf{D}, \quad (2.4)$$

where ρ is free charge [C], $\mathbf{J}$ is conduction current density [A/m²], $\mathbf{D}$ is the electric flux density [C/m²], $\mathbf{B}$ is the magnetic flux density [T = Wb/m²], $\mathbf{E}$ is the electric field intensity [V/m], $\mathbf{H}$ is the magnetic field intensity [A/m], ω is frequency [rad/s], and j is the imaginary unit. respectively. If we limit our attention to linear, isotropic media, then the constitutive relations relating the field intensities and field densities can be written as

$$\mathbf{D} = \varepsilon_0 \varepsilon_r \mathbf{E} \quad (2.5)$$

$$\mathbf{B} = \mu_0 \mu_r \mathbf{H}, \quad (2.6)$$

where $\varepsilon_0 \cong 8.854 \times 10^{-12}$ F/m and $\mu_0 = \frac{1}{4\pi} \times 10^{-7}$ H/m are the free space permittivity and permeability, respectively, and ε_r and μ_r (both dimensionless) are the material-specific and possibly frequency-dependent relative permittivity and relative permeability, respectively.

Another important equation which relates the electric field to the conduction current density is Ohm's law, $\mathbf{J} = \sigma \mathbf{E}$, where the conductivity σ may range from negligible for dielectric materials such as air or glass to very large ($\sim 10^7$ S/m) for common metals. We may wish to use one parameter to encompass both the

displacement and conduction current responses to the electric field, in which case, we can rewrite (2.4) as

$$\nabla \times \mathbf{H} = -j\omega\varepsilon_0\varepsilon(\omega)\mathbf{E}, \quad (2.7)$$

where we have defined the frequency-dependent complex dielectric function $\varepsilon = \varepsilon_r + j\sigma/\varepsilon_0\omega$. Here the real part may represent the polarization response due to bound charge, and the imaginary part may represent the response due to free charge. While this characterization is more accurate at low frequencies, the distinction is less clear at optical frequencies [25]. We may combine Maxwell's curl equations to arrive at the *wave equation*, written here in terms of the electric field,

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}, \omega) = -\omega^2\varepsilon_0\varepsilon(\omega)\mu_0\mathbf{E}(\mathbf{r}, \omega), \quad (2.8)$$

$$\mathbf{q}[\mathbf{q} \cdot \mathbf{E}(\mathbf{q}, \omega)] - q^2\mathbf{E}(\mathbf{q}, \omega) = -\varepsilon(\mathbf{q}, \omega) \frac{\omega^2}{c_0^2}\mathbf{E}(\mathbf{q}, \omega), \quad (2.9)$$

in the spatial and Fourier domains, respectively. Here, c_0 is the speed of light in a vacuum and $\mathbf{q} = [q_x \ q_y \ q_z]^T$ is spatial frequency. We allow for the possibility of spatially dispersive media by explicitly writing ε as a function of $\mathbf{q}$. By definition, transverse waves satisfy $\mathbf{q} \cdot \mathbf{E} = 0$, leading to the generic dispersion relation

$$q^2 = \varepsilon(\mathbf{q}, \omega) \frac{\omega^2}{c_0^2}. \quad (2.10)$$

However, for longitudinal waves, we see that the two terms on the left side of Eq. (2.9) cancel, implying

$$\varepsilon(\mathbf{q}, \omega) = 0. \quad (2.11)$$

This means that longitudinal plasma oscillations can occur only at frequencies where ε is zero.

2.1.2 Optical Properties of Metals

As stated previously, many optical properties of metals can be explained by a plasma model, in which a gas of free electrons of number density n_e moves in a background of stationary positive ions. The assumptions made by this model are that some aspects of the band structure are taken into account via the electron mass m_e , and that the electron motion is collision-damped with a frequency $\gamma = 1/\tau$. The relaxation time τ is typically on the order of 10 fs at room temperature. These assumptions yield a simple expression for the dielectric function:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + j\gamma\omega}, \quad (2.12)$$

where $\omega_p = q_e \sqrt{n_e / \varepsilon_0 m_e}$ is the plasma frequency of the free electron gas. When we consider the Drude model for conductivity, namely

$$\sigma(\omega) = \frac{\sigma_0}{1 - j\omega\tau}, \quad (2.13)$$

where $\sigma_0 = q_e^2 n_e \tau / m_e$ is the DC conductivity, we recover the form of our original complex dielectric function:

$$\varepsilon(\omega) = 1 + \frac{j \sigma(\omega)}{\varepsilon_0 \omega}. \quad (2.14)$$

2.1.3 Plasmon Classification

While the word *plasmon* encompasses a variety of plasma-like oscillations of free electrons, they are generally divided into three canonical categories, based on the excitation, material geometry and size, and nature of the electric field describing their behavior. The three types of plasmon resonances considered here are the bulk plasmon, surface plasmon polariton, and localized surface plasmon.

2.1.3.1 Bulk Plasmons

Large three-dimensional (bulk) metal structures are capable of sustaining bulk plasma oscillations internally. They correspond to the condition in Eq. (2.11). Assuming the plasma dielectric function of Eq. (2.12) in the case of zero damping, they occur at the plasma frequency ω_p , given by

$$\omega_p^2 = \frac{n_e q_e^2}{m_e \epsilon_0}, \quad (2.15)$$

where n_e is the number density of free electrons, q_e is electron charge, and m_e is the effective mass of the electron which accounts for the band structure of the metal. This is the most fundamental plasmon supported by the metal, depending only its intrinsic material parameters. It is at this frequency that that real part of the plasma permittivity is zero. Below the plasma frequency, metals absorb and reflect incident radiation. Above the plasma frequency, metals become transparent. This is shown below in Figure 2.1. Bulk plasmons are longitudinal modes. They cannot be excited by an incident photon; however, they can be excited by impact from a particle.

Figure 2.1 (a) Transparency to radiation above and below the plasma frequency, (b) real (ϵ') and imaginary (ϵ'') parts of the plasma permittivity, and (c), reflection and transmission near the plasma frequency, adapted from [10].

2.1.3.2 Surface Plasmon Polaritons

The next type of plasmons we consider are termed surface plasmon polaritons (SPPs). They propagate along the plane between a metal and a dielectric and have an in-plane wave vector given by the expression

$$k_{SPP}(\omega) = k_0 \sqrt{\frac{\epsilon_d \epsilon_m(\omega)}{\epsilon_d + \epsilon_m(\omega)}}, \quad (2.16)$$

where $k_0 = \omega/c_0$ is the free space wavenumber and $\epsilon_m(\omega)$ and ϵ_d are the dielectric constants of the metal and surrounding dielectric, respectively. The wave decays exponentially normal to the surface, with a decay length on the order of a few hundred nanometers in the dielectric. Depending on the metal loss at the excitation frequency, the SPP propagation length is typically between 10 and 100 μm in the visible region. A schematic of SPP excitation and propagation is shown in Figure 2.2(a).

Figure 2.2 (a) Surface plasmon polaritons excited by a prism and by a nanohole grating, evanescently decaying away from the surface, (b) dispersion relation for an ideal metal and (c) reflection measurement shows a dip at the incidence angle where the dispersion relation is satisfied due to momentum matching, adapted from [10].

From Figure 2.2 (b), we see that the SPP dispersion relation lies to the right of the light line, and thus cannot be directly excited by an incident photon. With a need to match the energy $\hbar\omega$ and momentum $\hbar k$, several methods for SPP excitation exist, including coupling by a prism or grating (as illustrated in Figure 2.2(a)), by particle impact, or by a near-field source as in SNOM (scanning near-field optical microscopy). Based on Figure 2.2 and Eq. (2.16), we note that $k_{SPP} \rightarrow \infty$ for $\omega \rightarrow \omega_{SPP}$, which occurs when $\epsilon_m = -\epsilon_d$. If the dielectric is air, then this happens at the frequency for which $\epsilon_m = -1$.

2.1.3.3 Localized Surface Plasmons

The final type of plasmon resonance considered here is the localized surface plasmon resonance (LSPR), in which the electron cloud of a nanometric metallic particle is resonantly excited due to the increased particle polarizability at certain frequencies. These resonance enable highly enhanced near fields which are confined much more tightly to the metal surface than SPPs, tens of nanometers at optical

frequencies as opposed to hundreds. The LSPR of a nanosphere and its associated spectra are illustrated in Figure 2.3.

Figure 2.3 (a) Localized surface plasmon resonance of a nanosphere and scattering and absorption cross sections of a metallic nanosphere with radius (b) $R < 15$ nm and (c) $R > 15$ nm, adapted from [10].

The simplest geometry for which an analytical solution to the problem of scattering by a small particle exists is that of a sphere. If the radius a of the sphere is much smaller than the wavelength of incident radiation, then we may solve the Laplace equation for the electric potential under the quasi-static limit, i.e.

$$\nabla^2 \Phi = 0 \text{ with } \mathbf{E} = -\nabla \Phi, \quad (2.17)$$

subject to continuous boundary conditions

$$\Phi_{in}|_a = \Phi_{out}|_a \text{ and } \epsilon_m \frac{\partial \Phi_{in}}{\partial r} \Big|_a = \epsilon_d \frac{\partial \Phi_{out}}{\partial r} \Big|_a, \quad (2.18)$$

where $\mathbf{E} = E_0 \hat{\mathbf{z}}$, ϵ_m , and ϵ_d are the driving electric field, metal dielectric function, and dielectric function of the surrounding dielectric, respectively. The dipole moment of a particle in an electric field can be written in terms of its polarizability, viz. $\mathbf{p} = \alpha \mathbf{E}_0$. By comparing the expression for the scattered electric field outside the sphere with that for the dipole moment $\mathbf{p} = q\mathbf{d}$ in the limit as $d \rightarrow 0$, we find that the polarizability of the nanosphere is

$$\alpha = 4\pi a^3 \varepsilon_d \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}. \quad (2.19)$$

Scattering and absorption cross sections can be determined from electric field scattered by the dipole. In terms of the dimensionless size parameter $q = k_0 a$, they are [26,27]

$$\sigma_{sc} = \sigma_{geom} Q_{sc} = \sigma_{geom} \cdot \frac{8}{3} q^4 \left| \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \right|^2, \quad (2.20)$$

$$\sigma_{abs} = \sigma_{geom} Q_{abs} = \sigma_{geom} \cdot 4q \operatorname{Im} \left[\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \right]. \quad (2.21)$$

Here, $\sigma_{geom} = \pi a^2$ is the geometrical cross section, and the dimensionless quantities Q_{sc} and Q_{abs} are known as the scattering and absorption efficiencies, respectively. The resonance occurs when the denominator of the polarizability is minimized. For an ideal lossless metal, this means that it becomes zero when $\varepsilon_m = -2\varepsilon_d$. If the sphere is in air, then $\varepsilon_m = -2$. The quasi-static approximation is applicable when $k_0 a \ll 1$. When the sphere size approaches the order of the wavelength of the incident radiation, Mie theory [28,29] can yield exact expressions for the scattered field in terms of a sum of vector spherical harmonics, the lowest order of which represents the dipole described above. Interparticle scattering may also play a significant role in the optical properties.

Outside of spheres, analytical solutions, whether in the quasi-static approximation or using Mie theory, exist for few other geometries, such as prolate and oblate spheroids [30,31]. Therefore, for predicting the optical and plasmonic performance of more complicated geometries, computational methods such as the finite difference time domain (FDTD) method [32], finite element method (FEM) [33],

and discrete dipole approximation (DDA) [34] are often used. For simulating plasmonic nanostructures in this work, the FDTD is employed. This is discussed in Section 2.3.4.

2.2 Plasmonic Biosensing

Optical biosensing is an umbrella term encompassing many types of platforms and physical phenomena for transduction, such as those shown in Figure 1.1. These platforms include substrates with nanostructures or waveguides [35–39], solutions with nanoparticles [40], optical fibers with special cladding [41,42] or tapers [43,44], and photonic crystal fibers [45–47], among others. Common transduction phenomena include fluorescence [48,49]; colorimetric sensing [50,51]; Raman scattering [52–54]; measurement of light absorbance, reflectance, or transmission for refractive index sensing using SPR or LSPR [11,12,16,55–60].

An important figure of merit in plasmonic sensing applications is the bulk refractive index sensitivity. Here, “bulk” refers to the dielectric environment both close to and far from the metal surface. A change in the surrounding dielectric index, due to, for example, an increase in the concentration of a known solute, should lead to a change in the plasmonic spectrum. Bulk sensitivity, for a given spectral feature (a peak or a dip), is simply the ratio of the change in wavelength of the feature to the change in bulk refractive index, $S = \eta_B = \Delta\lambda/\Delta n$, which typically has units of nm/RIU. Alternatively, some authors may use energy (frequency) instead of wavelength, in which the units used are eV instead of nm. In terms of bulk sensitivity, traditional SPR has been shown to be much more sensitive to changes in the bulk solution than LSPR, for reasons including that the evanescent field of the plasmon

resonance for SPR extends much farther into the dielectric than that for LSPR. However, for actual affinity-based biosensing, where the analyte to be detected is near the surface of the metal, the sensing performance of LSPR rivals that of SPR, despite the ~20 times higher bulk sensitivity and Figure of Merit (*FOM*, described below) of SPR; this is attributed to more efficient use of the evanescent field for LSPR [17]. Bulk sensitivity, because it is experimentally the easiest type of sensitivity to characterize, is often used as a measure of sensing potential for structures exhibiting LSPR resonance [59,61,62].

Homola [63], using the SPP dispersion relation $k_{SPP} = k_0[\epsilon n^2/(\epsilon + n^2)]^{1/2}$, and Miller [64], using the dipole resonance condition for an ellipsoidal particle, have shown that, for SPR and LSPR, respectively, the sensitivities can be calculated analytically as [17]

$$\frac{\partial \lambda_{SPR}}{\partial n} = -2\epsilon' / \left[n^3 \frac{\partial \epsilon'}{\partial \lambda} \right], \quad (2.22)$$

$$\frac{\partial \lambda_{LSPR}}{\partial n} = 2\epsilon' / \left[n \frac{\partial \epsilon'}{\partial \lambda} \right]. \quad (2.23)$$

Here, ϵ' is the real part of the metal dielectric function $\epsilon = \epsilon' + i\epsilon''$, and n is the refractive index of the surrounding medium. Moreover, according to Miller, between 500 nm and 800 nm, the approximately linear dependence of ϵ' on λ results in a linear relation between λ_{LSPR} and n [64], namely

$$\frac{\partial \lambda_{LSPR}}{\partial n} = \frac{2}{n} \left(\lambda_{LSPR} + \frac{\epsilon_0}{m} \right), \quad (2.24)$$

where ε_0 and m are the parameters used in the linear approximation of the real part of the metal dielectric function $\varepsilon' \approx m\lambda + \varepsilon_0$. Thus, as done by many others [61,64–67], bulk sensitivity will be characterized by the line of best fit for several points in a plot of resonance wavelength versus surrounding refractive index.

An upper limit on the refractive index sensitivity was analytically derived by Zalyubovskiy et al. [68] in the quasi-static approximation, and it was shown to be independent of particle shape. This limit is given by

$$S \leq \frac{\lambda_0}{n} f \frac{2}{1+q}, \quad (2.25)$$

where f is the energy confinement ratio of the analyte-perturbed volume to the dielectric bulk ($f \leq 1$), and

$$q = -\frac{\partial(\omega\varepsilon')/\partial\omega}{\varepsilon'}. \quad (2.26)$$

is the ratio of energies stored in the metal and dielectric ($q > 1$ in vis-NIR away from absorption peaks). This yields a vis-NIR upper limit of

$$S < \frac{\lambda_0}{n}. \quad (2.27)$$

The resonance wavelength and sensitivities of several structures, taken from the tabulated data in [68] are shown below in Table 2.1, along with a plot to show their comparison to the theoretical maximum in Figure 2.4. Three experimental data points in this plot lie above the theoretical maximum. The circled point represents a shell structure with a non-metal interior, which may contribute to increased sensitivity. The two points enclosed by boxes represent plasmon resonance sensing using a

longitudinal mode, in which one of the structural dimensions becomes on the order of the wavelength of light, thereby yielding a higher sensitivity.

Geometry	λ_0 [nm]	S [nm/RIU]	Geometry	λ_0 [nm]	S [nm/RIU]
Prism [69]	630	205	Disk [70]	1200	633
Rattles [65]	650	285	Shell [71]	720	408
Pyramids [72]	600	200	Star [73]	800	232
Rice [74]	1460	802	Tube [75]	650	250
Rod [76]	720	170	Branch [67]	1141	703
Rod [77]	1100	850	Crescent [78]	1083	368
Rod [67]	1096	540	Ring [79]	1050	550
Rod [80]	840	260	Shell [79]	1250	750
Rod [15]	830	700			

Table 2.1. List of various geometries for LSPR along with their resonance wavelengths and refractive index sensitivities, from [68]

Figure 2.4 Scatter plot of the data in Table 2.1 in yellow, along with the theoretical maximum in Equation (2.25) in blue. The point circled in orange represents a shell structure, whereas those with orange squares represent use of longitudinal modes, adapted from [68]

A second measure of sensing performance often used encompasses the linewidth of the resonance, with smaller linewidths enabling more easily discriminated shifts.

This unitless measure is known as the Figure of Merit (FOM), $FOM = FOM_B = \eta_B/\Gamma$,

where Γ is the resonance linewidth, usually measured as full width at half maximum (FWHM). The FWHM and FOM can also be analytically derived as above [17]. Another spectral feature influencing peak detection and discrimination is the contrast (e.g. prominence) of the peak, measured as the difference between the peak (or dip) maximum and minimum, with higher contrast being better. Some authors have incorporated this into a modified FOM , known as $FoMC$, which is simply $FoMC = FOM \cdot C$, where C is the unitless contrast [59]. Another proposed measure of figure of merit, which considers the relative peak intensity changes at the wavelength of maximum intensity change $dI/d\lambda$, is the, $FOM_B^* = \left(\frac{dI/dn}{I}\right)_{max}$ [81,82], is more suitable for complex spectra which do not exhibit a simple Lorentzian shape.

In addition to bulk sensitivity characterization, another measure of sensor performance more specific to LSPR is the analyte or surface sensitivity, which is a measure of how much the spectral peaks or dips shift in the presence of a thin coating material of different refractive index than the bulk surroundings. Like the sensitivity measures for the bulk, but assuming a coating with a constant refractive index (e.g. $n=1.5$ for biological samples), a couple useful quantities are the surface sensitivity $\eta_S = \Delta\lambda_{LSPR}/\Delta t$ [81], where l is the layer thickness in nm, and another figure of merit as proposed by Becker $FOM_{layer}^* = \left(\frac{dI/I}{dt}\right)_{max}$ [82]. Furthermore, Becker proposes that a good comparison among different types of nanostructures, which have different evanescent decay lengths in the surrounding media, is given by the defined value $\lim_{t \rightarrow 0} FOM_{layer}^*$. Still others insist on a better measure of surface sensitivity, which can account for bulk index sensitivity, analyte thickness, and analyte refractive index. Li et al. propose using a so called second order sensitivity, measured with respect to a particular spectral peak or dip, given by $\frac{\partial^2 \Delta\lambda}{\partial n_a \partial t}$, where n_a is the refractive index of the

analyte [83]. They show that this is analytically equivalent to $\frac{2m}{l_d} e^{-2t/l_d}$, where l_d is the decay length of the LSPR mode in the surrounding medium, and m is a sensitivity factor which is equivalent to bulk sensitivity for infinite analyte thickness. Often in the literature, the focus is on the limit of detection (LOD), which is the lowest quantity or concentration of a substance that can be distinguished from the absence of that substance with a statistical confidence level. Thus, many groups plot refractive index shift versus the logarithm of concentration of a given analyte in solution.

However, biological and chemical sensing often require detection of a single (bio-) molecule in the presence of numerous other interfering species, for which specific adsorption is required [13]. In one incarnation of achieving specific adsorption of an analyte, the gold surface is covered by a self-assembled monolayer (SAM) of alkanethiols (with a general formula $\text{HS}(\text{CH}_2)_n\text{X}$), where X can be any appropriately chosen head group. The strength of the sulfur-gold bond originates from several forces, including the strong semi-covalent bond of sulfur to the gold surface (homolytic bond strength ~ 184 kJ/mol [84], compared to the C-C single bond with strength of 348 kJ/mol [85]). Additionally, self-assembly is aided by the hydrophobic van der Waals interactions between the methylene carbons on the alkane chains [86]. Using an appropriate cross-linking chemistry, an appropriate targeting molecule can be attached to the ends of the SAM chains. This targeting molecule is chosen such that the only molecule that will bind to it is the desired target analyte. For example, if we desired to detect a specific antigen, we may attach its corresponding antibody to the end of the SAM chains. Assuming that the antigen layer has a different refractive index than the surrounding bulk solution, the change in refractive index Δn should be detectable using a plasmonic sensing scheme. Because LSPR has much tighter confinement to the surface than traditional SPR, it is much better suited to applications

such as this, where SAM and analyte length is on the order of several nanometers. This scheme is illustrated schematically in Figure 2.5.

Figure 2.5 Schematic of single alkanethiol (dodecanethiol in this case) molecule bonded to gold substrate. The head group can be chosen to fit nearly any surface chemistry or target analyte. From [86].

2.3 Experimental Methods

In this section, we briefly discuss background information about experimental methods of fabrication, including electron beam lithography and electrodeposition. Specific parameters for the fabrication processes used in the works discussed in this thesis will be detailed later.

Prior to any further processing on our part, the starting materials thus far as purchased or otherwise received have been mostly dielectric substrates with a conductive coating and some conductive substrates. After scoring and cleaving the substrates into appropriate sizes, roughly 1.5 cm² squares, our process for fabricating the high aspect ratio metallic nanostructures consists of two parts. First, we must define the two-dimensional area to be grown vertically on the substrate. This is performed using electron beam lithography (EBL). At the end of this step, the surface of the sample is a binary pattern. The portions to be electroplated are exposed, while

the remaining area is covered by resist. Experimental aspects of these two main steps, EBL and electroplating, will be discussed in the following subsections.

2.3.1 Electron Beam Lithography

Electron beam lithography is an essential nanofabrication technique in which nanopatterns are created by programmatically scanning an electron beam across a sample to write nanometric two dimensional patterns. At the writing stage of the process, the sample consists of a conductive substrate coated by a layer of resist, which is sensitive to the electrons. The sections of resist that are bombarded by electrons from the beam experience a change in solubility. A *positive tone* resist exhibits an increase in solubility, the mechanism of which is the scissions of long polymer chains. On the other hand, a *negative tone* resist experiences a decrease in solubility owing to the increased cross-linking of polymer chains. After the patterns are written into the resist, a suitable developer is used to dissolve the more soluble portions of the resist, leaving a nanopatterned resist template on top of the substrate. The next step in many nanofabrication procedures is often metallization via electron beam evaporation or sputtering, followed by lift off to remove remaining resist. Sometimes, the desired structure is the remaining resist itself. The main steps in performing EBL are as follows:

1. Clean the surface of the sample.
2. Spin coat the resist. Final resist thickness depends on viscosity, spinning time, and spinning speed. The thickness is inversely proportional to the square root of the spinning speed.
3. Bake the coated sample.

4. Place the sample in the EBL machine and, after calibration and setup, perform the exposure. Remove the sample from the EBL machine.
5. Develop the resist, i.e. dissolve the soluble part of the resist using the appropriate chemical developer.

There is a third type of resist behavior besides strictly positive or negative. Some resists, known as image reversal resists [87–89], maybe used in either the positive or negative mode. When used for positive mode patterning, the process is the same as the steps listed above. However, in negative (image reversal) mode, there is an additional step to be performed between steps 4 and 5 above, which involves exposing the whole sample at once (flood exposure) to UV light. The exposure and development processes for the three types of resists are summarized in the figure.

Figure 2.6– Exposure and development processes for positive, negative, and image reversal resists

As a prerequisite for different types of electrodeposition processes, the ability to write patterns into both positive and negative resists is essential. However, as the required exposure dose for negative-tone e-beam resist can be 10-20x higher than that for the positive-tone e-beam resist, we explore the use of “image reversal” AZ5214E photoresist for our negative patterning. Although originally intended for

photolithography, where ultraviolet rays break the molecular bonds at specific deposited energy, the molecular bond in AZ5214E resist can also be broken by an electron beam. In addition, the image-reversal process allows the writing of negative patterns at 10% of the dose required by the typical negative-tone e-beam resist, which saves e-beam writing time. The fabrication of the nanostructures in this research utilized two resists, AZ5214E and ZEP520A. Their contrast curves, which depict the experimentally obtained normalized residual resist thickness electron beam exposure dosage, are shown in the following figures, along with the image reversal bake characteristics of AZ5214E, for an electron energy of 20 keV.

Figure 2.7—Electron beam process for AZ5214E photoresist at 20keV accelerating voltage. (a) Different resist tones for different exposure dose range. At small doses, the resist exhibit positive-tone characteristics. At large doses, the resist molecules are cross-linked, making the AZ resist negative-tone. In between positive and negative regime, through post-exposure annealing, it is possible to have image-reversal tone for the AZ resist. (b) Image-reversal tone characteristics as a function of baking temperature, bake time, and development time.

Figure 2.8– Electron beam sensitivity for ZEP520A resist at 20kV accelerating voltage based on sonicated cold development process.

2.3.2 Electrochemical deposition

In electrochemical deposition, metallic cations from aqueous solution are reduced and deposited onto an electrode. The chemical process of this reduction can be represented by the general equation

where $M_{(aq)}^{z+}$ represents a metallic ion with oxidation state +z in aqueous solution and $M_{(s)}$ represents the solid metal deposited on the electrode. This deposition can be achieved by one of two means, differentiated by the source of the electrons: (1) an electrodeposition process, also known as electroplating, using an external power supply or (2) an electroless deposition process using an aqueous reducing agent without an external power supply. Often, the terms electroplating and electrodeposition are used synonymously, though there may be slight difference in meaning. In addition to electroplating, electrodeposition may also refer to electrophoretic deposition or underpotential deposition. However, in this work, the terms electroplating and electrodeposition are used interchangeably.

In the context of electrodeposition, an *electrochemical cell* refers to a system of two electrodes separated by an electrolyte in aqueous solution. There will generally be a measurable electrical potential difference between the two electrodes which depends on several factors including the electrode materials and electrolyte solution composition. While it is possible to assign an approximate absolute potential to each electrode individually, this is difficult and is not generally done. Instead, the equilibrium potential of electrochemical *half cells* are usually given, according to the

metal/electrolyte combination at one electrode with respect to a standard electrode. Common aqueous reference electrodes include the standard hydrogen electrode (SHE) and the more experimentally convenient saturated calomel electrode (SCE), among others [90].

2.3.2.1 The metal-solution interface at equilibrium

Although Eq. (2.28) here as a one-way reaction, the metal/solution interface at each electrode involves bidirectional transfer in the absence of any externally applied voltage or current, i.e.

Reaction from right to left is known as *reduction*, and that from left to right as *oxidation*. At this kinetic equilibrium, the metallic electrolyte concentration and the half cell equilibrium potential are related to one another by the Nernst equation [91]

$$E_{eq} = E^0 + \frac{R T}{z F} \ln[M^{z+}] , \quad (2.30)$$

where E^0 is the standard electrode potential of the M/M^{z+} electrode, R is the gas constant, $F = 96485 \text{ C mol}^{-1}$ is the Faraday constant, and the square brackets represent the concentration, or more specifically, the activity of metal ions in the solution. The interface between the metal and the solution, however, is not as simple as metal one side and solution on the other, as shown in Figure 2.9.

Figure 2.9 Two phases in contact.

The charged interphase that develops between the metal and the solution is a complex interplay between the excess charges in the metal, the ions in solution, and the dipolar nature of water molecules. Practically, it behaves like a capacitance between the charged species and the oriented dipoles. Arising from surface charge densities σ^M in the metal and σ^S in the solution, it is often called the double layer capacitance C_{dl} , although it is realistically more than two layers. A simple model for this behavior consists of several layers on the solution side, minimally consisting of an *inner layer* and a *diffuse layer* [90]. The inner layer (closest to the electrode) contains molecules and ions that are *specifically adsorbed* onto the surface. It is also known as the *compact*, *Helmholtz*, or *Stern layer*. The species in this layer are centered on a distance x_1 , known as the *inner Helmholtz plane* (IHP), from the electrode with a charge density of σ^i . Completely solvated ions, constituting a charge density of σ^d only approach the electrode up to a distance x_2 , known as the *outer Helmholtz plane* (OHP), from the electrode. The charge densities are related to one another as

$$\sigma^S = \sigma^i + \sigma^d = -\sigma^M, \quad (2.31)$$

although the absolute signs of the charge densities may change depending on the direction of any externally supplied current. This model is shown in Figure 2.10. It must be stressed that this is a simplified model and that more sophisticated models do exist but are outside the scope of this report.

Figure 2.10– Model of double layer region with specifically adsorbed ions [90]

2.3.2.2 Application of external voltage or current

When current I flows through the electrode as part of an electrochemical cell, whether the current is applied directly or is the result of an applied voltage, there will be an increase in the potential of the electrode to $E(I)$, such that the so-called *overpotential* can be written as [92]

$$\eta = E(I) - E_{eq} . \quad (2.32)$$

The overall electrode reaction consists of several partial reactions, each of which requires energy to proceed. The four possible partial reactions, and thus four possible rate-determining steps. The *charge transfer reaction* refers to the transport of charge carriers across the double layer, and this is the only partial reaction that is directly influenced by electrode potential. *Mass transport* processes involve the transfer of reagents between the bulk solution and the interphase region and are accomplished by a combination of diffusion near the interphase and migration (drift) in the bulk

solution. Additionally, *chemical reactions* occurring in solution or at the interface may require energy to proceed. The fourth and final type partial reaction which needs to be considered is *crystallization*, which involves incorporation or removal of metal ions from the metal lattice of the electrode [90,91]. Thus, the total overpotential is [91]

$$\eta = \eta_{ct} + \eta_{mt} + \eta_r + \eta_c , \quad (2.33)$$

with the overpotential components on the right-hand side of Eq. (2.33) referring to charge transfer, mass transport, reaction, and crystallization, respectively.

Though not explicitly used in calculations related to the electrodeposition process used to for the research described in this work, we include a few simple relationships between current and overpotential. There have been many developments in characterizing the relationships between these quantities since the advent of modern electrochemistry. The first was an empirical relationship between overpotential and current given in 1905 by Julius Tafel as [91]

$$\eta = a + b \ln(j) , \quad (2.34)$$

where a and b are constants and j is current density. From this equation, we can see that, at least for a certain regime, the current density depends exponentially on the overpotential. By using a quantity known as the transfer coefficient α , introduced by Erdey-Gruz and Volmer in 1930, to take care of the potential-dependent part of the Gibbs free energy, a more complete (and bipolar) relationship is given by the Butler-Volmer equation [91]:

$$j = j_0 \left[\exp \left(\frac{(1 - \alpha) z F \eta}{R T} \right) - \exp \left(- \frac{\alpha z F \eta}{R T} \right) \right] \quad (2.35)$$

The charge transfer coefficient α is in the range of 0 to 1, and is often 0.5, corresponding to a symmetric energy barrier. Plots of Eq. (2.35) is shown below in Figure 2.11 for various values of α .

Figure 2.11– Example of current density vs overpotential various α .

Although it is not suggested by the equation or by the plot, the current will not increase indefinitely with increasing overpotential. The amount of current that can flow from solution to the electrode is limited by the mass transfer, whereby the metal ions reacting at the electrode are no longer able to reach the electrode at a sufficient rate. An example of a more realistic plot of current density for potential is shown in the figure, in this case, for copper.

Figure 2.12– Realistic example of the current density as a function of electrode potential [93]

These equations are useful for characterizing electrochemical reactions; however, for electroplating, we are often more interested in the amount of substance plated. Assuming that all of the current passing through the electrode is converted into metal ions deposited on that electrode, we can employ a simple equation which actually precedes much of modern electrochemical analysis. The equation is summarized from Faraday's laws of electrolysis as

$$m = \frac{Q M}{F z} , \quad (2.36)$$

where m is the mass of substance deposited, Q is the total amount of charge passed through the electrode, and M is the molar mass of the substance. From this we can easily see that the amount of substance deposited is directly proportional to the total charge passed.

Often we are interested not in the mass of the substance deposited but in the volume, or more specifically, the thickness d for a given plated area A , such that $V = A d$. If we use the mass density $\rho = \frac{m}{V}$ and assume a constant current I passed for time t , then we have that $Q = I t$, then we can recast Eq. (2.36) as

$$d = \frac{(I t)m}{\rho A F z} . \quad (2.37)$$

While electroplating, we may prefer to know the plating rate, e.g. in units of nm/s. This is easily found from Eq. (2.37) as

$$rate = j \left(\frac{M}{\rho F z} \right), \quad (2.38)$$

where we have replaced I/A by the symbol for current density j .

In performing electrodeposition, there are a couple of distinctions or classifications that can be made about a given process. One classification is based upon the source type of the external power supply. Controlled-current electrodeposition fixes the value(s) of the current and allows potential to adjust based on changes in the electrochemical cell, whereas controlled voltage electrodeposition fixes the value of the overpotential at the working electrode. Another classification is the time dependence of the external power signal, for example direct current (DC) vs. pulsed.

At the beginning of this section, we mentioned that the potential is measured at an electrode with respect to a reference electrode. In electrodeposition, there are often three electrodes involved: the working electrode (cathode), the reference electrode, and the counter electrode (anode), also known as the auxiliary or sacrificial electrode. In order to plate metal onto the working electrode, metal ions come from the solution. To replace the ions in solution, metal from the counter electrode dissociates into the solution. This process is shown schematically in Figure 2.13 for a metal cathode, copper anode, and Cu_2SO_4 electrolyte solution. The reference electrode is not a necessity for electroplating. It does however allow characterization of the potential of

the cathode half cell only, whereas measurements made between the anode and cathode will include effects of the potentials of both electrodes. For more thorough characterization of electrochemical experiments and for performing controlled-voltage electrodeposition, the reference electrode is mandatory. Controlled-current electrodeposition, on the other hand, may be performed without the use of a reference electrode. All of the work presented in this thesis utilized a two-electrode setup with controlled current.

Figure 2.13–Schematic of typical electroplating process

Electrodeposition was carried out using a Keithley 2400 Source Meter Unit (SMU). For direct current deposition it is sufficient to use the SMU manually, in local mode: setting, starting, and stopping the current using the buttons on the front. However, for pulsed electrodeposition, it is necessary to use the device in remote mode, connected to a computer using either GPIB or serial interface, and programmed using SCPI commands. We communicated to the SMU through the serial interface, sending commands and recording data using a MATLAB serial object. Using the

SMU in remote mode this way also permitted collection of the current and voltage data from each electrodeposition process.

2.3.3 Characterization Methods

This work is primarily concerned with the fabrication, through EBL and electrodeposition, and plasmonic behavior of arrays of metallic nanostructures. For characterization of the physical properties of the nanostructures, the Raith e_Line used for EBL is also used for surface electron microscopy (SEM) of the nanostructures. By default, this is at normal incidence with respect to the substrate, i.e. looking from above the nanostructures. This allows analysis of the pattern fidelity and the structure shape, size, and morphology, in the transverse dimension. Additionally, we use two custom tilted holders that allow for oblique incidence SEM, one with a fixed inclination angle of 25° , and the other with a variable angle that we use at 45° . Using these, we are able to characterize the height of the structures, as described later in the thesis.

For spectral characterization, we use the Cytoviva hyperspectral imaging system, which utilizes a diffraction grating for recording the spectrum of each pixel in a line scan of the sample on a microscope. For obtaining transmission and reflection spectra, the spectra of the structures are normalized with respect to bare substrate and a mirror, respectively, in order to negate the effects of a non-uniform source intensity. A schematic of the system is shown in Figure 2.14. Using ENVI software that comes with the system users can point and click at points shown in the scans (Figure 2.14(b)), displaying the spectra and recording them as text files for processing by other software. The recording of spectra for two points, structure and bare substrate, using spectral average of 10×10 pixels, is shown in Figure 2.15.

Figure 2.14–Hyperspectral imaging (a) A schematic of the imaging system, and (b) example scans of arrays of v -shaped SRRs of various opening angle and arm length.

Figure 2.15–Hyperspectral imaging, recording the 10x10 average spectral profiles of a structure (red) and the bare substrate (green) for normalization

2.3.4 Finite Difference Time Domain Simulations

Because the geometries of all the structures used in this work lack analytical solutions for LSPR phenomena, we utilized commercial Finite Difference Time Domain (FDTD) software (Lumerical [94]) to perform simulations where applicable. The finite difference time domain method solves the full vectorial form of Maxwell's equations in differential form on a discrete spatial and temporal grid. The electric and magnetic fields are computed in a leapfrog fashion, on grids that are slightly offset, as shown below in the schematic of a Yee cell in Figure 2.16

Figure 2.16–Schematic of Yee cell used in FDTD method

All the fabricated structures presented in this work are periodic arrays covering square areas of side $10\ \mu\text{m}$ or $100\ \mu\text{m}$. Thus, in the most general case, the simulations were set up to have periodic boundary conditions in the x and y directions, with a $-z$ -directed source propagating toward the substrate at normal incidence to the substrate. When the structures exhibit mirror symmetry parallel (perpendicular) to the injected electric field, then symmetric (antisymmetric) boundary conditions are used. This is illustrated below in Figure 2.17 and later in Figure 2.18(b). Symmetric and antisymmetric boundary conditions are useful because they reduce the volume simulated by a factor of half for each direction along which they are applied.

Figure 2.17–Propagation of fields and lateral boundary conditions used for simulation of periodic structures with x -oriented electric field (top row) and y -directed electric field (bottom row)

For sensing, we are often interested in measuring the reflection or transmission spectra. One way to simulate this in FDTD is to have a plane wave source injected (say in the $-z$ direction) toward the structure, with field monitors (z -normal planes) P_R and P_T located above the source and below the structure, respectively. Lumerical provides such monitors which measure the transmitted power normalized to the injected power at each wavelength. Lumerical's recommendation to ensure a distance of at least half of the longest simulation wavelength used between the structures and the FDTD simulation boundary is helpful for accurate simulations, but it leads to longer simulation times. An alternative is based on the methodology used for computing the absorption (σ_{abs}) and scattering (σ_{scat}) cross sections for single nanoparticles.

Lumerical includes a type of source known as a Total Field Scattered Field (TFSF) source, which is a plane wave that injects from one chosen plane and is absorbed (subtracted) in another. Also included in Lumerical are analysis groups consisting of six planar field monitors in the form of a rectangular prism. A box placed within the TFSF region can be used to calculate the power absorbed at each wavelength, and one placed outside of it can be used to calculate the power scattered. Based on the lateral size of the TFSF source, the absorption and scattering cross sections can then be computed. For this work, these analysis groups were adjusted for periodic simulations by using only the field monitor planes directed parallel to the source and extending them to the edge of the FDTD region. An example of this can be seen in Figure 2.18(c), a screenshot of the side (x - z) view in Lumerical of a simulation of a gold nanostructure on top of an ITO substrate (purple).

Figure 2.18—Screenshots of simulation views in Lumerical FDTD for an arbitrary structure, a C_6 star on ITO substrate in this case. (a) The perspective view. (b) The top (x - y) view showing the use of symmetric BCs in the x direction and antisymmetric BCs in the y direction. (c) The side (x - z) view

The side view shows the injection plane of the TFSF source above the nanostructure, and the absorption (subtraction) plane of the source below the structure. Assume the four planes here labeled M_i , $i = 1, 2, 3, 4$, have source normalized transmission T_i in the $+z$ direction. The scattered power, normalized with respect to the injected power is given by $S = -T_4 + T_1$, and the normalized absorption is given by $A = -T_2 + T_3$. The power monitors used in the Analysis group here can be used to calculate the transmission and reflection as $T = -T_2$ and $R = 1 + T_3$, from which, along with A above, we can verify the relation $A + R + T = 1$. Note that we must add 1 to T_3 in the expression for R due to the injected plane wave propagating downward through the M_3 monitor, contributing a normalized power of -1 .

Lumerical FDTD includes by default a number of primitive shapes such as extrusions of 2D shapes (triangle, rectangle, polygon, circle, ring, and custom area defined by one or two planar curves), spheres, pyramids, etc. The software also provides users with a number of built-in Structure Groups, which is a group of primitive shapes with a set of input parameters and a script to set up the overall structure; moreover, it allows users to create their own structure groups. Some examples of the Structure Groups included in the software are a quadrilateral with rounded edges and corners, a (partial) circular toroid, and two- and three-dimensional lattices of spheres. The first two are illustrated below in Figure 2.19. Note that for structures such as the partial circular toroid (Figure 2.19(c)-(f)), the external surfaces of which are not completely continuous, the approximation by a finite number of constituent structures becomes invalid as the structural discontinuities become on the order of the FDTD mesh size.

Figure 2.19—Screenshots of perspective views of two structure groups in Lumerical (a) The rounded quadrilateral as first added, and (b) the same structure with the constituent parts shown as different colors: teal for the rectangles (faces), orange for the cylinders (edges), and magenta for the spheres (corners). (c)-(f) A partial (180°) circular toroid as the number n of constituent cylinders per 360° is decreased from 100 to 12.

To more accurately simulate the spectral response of the structures fabricated as a part of this work, many structures were constructed to have sharp edges on the (ITO) substrate and rounded edges and corners otherwise. Sharp corners are well known to host local plasmonic hotspots and would thus introduce spurious modes in the simulations which would not be present in the as-fabricated structures. It is relatively straightforward to make a hybrid between the all-rounded quadrilateral and a pure rectangular prism (“Rectangle”) by removing the spheres and cylinders along the bottom face, which rests directly on the substrate. This was the basis for the structure groups used to simulate the C_n star structures (as in Figure 2.18 for the C_6 structure) and the dimer structures. This user-generated structure group is called ‘rdtoppolyquad’, for “rounded-top polygon quadrilateral”.

A more complicated structure to model properly is that of the v-shaped split-ring resonator, or v-SRR. A simple, non-rounded structure for this could be constructed from 3 rectangular prisms, as shown below in Figure 22.20 (a)-(b), for the left arm, right arm, and connecting central piece. In order to simulate a structure more similar to those fabricated, a rounded v-SRR structure group was made, as shown in Figure 22.20 (c)-(f). In addition to the three rdtoppolyquads replacing the rectangles, it was also necessary to include cylinders at the edges and partial circular toroids at the corners on the base of the v shape to fill in empty space and maintain a smooth exterior. These extra pieces are shown in purple in Figure 22.20 (e)-(f). Finally, in order to simulate how the resonance would change for analyte sensing, we simulate the rounded v-SRR with a dielectric coating, as shown in Figure 22.20 (g)-(h), where the structure group includes two rounded v shapes, the outer one composed of dielectric and the inner of gold. With the correct setup script, this proved to be an easy

way to maintain uniform thickness t_{coat} of a conformal coating on the resonator when simulating.

Figure 22.20— xy (top row) and perspective (bottom row) screenshots of v -SRR structures in Lumerical FDTD. (a), (b) A simple structure composed of three rectangular prisms. (c)-(f) a more physical rounded structure, consisting of three rounded-top polygon quadrilaterals and extra cylinders and partial circular toroids to fill in the gaps, with the extra parts shown in purple in (e)-(f). (g), (h) Concentric v -SRR shapes, with the outer material being dielectric and the inner gold, on ITO substrate (purple)

Another point to note about modeling in Lumerical FDTD is that when there are structures which physically overlap in the simulation region, the one listed last in the object tree has precedence. An example is shown for a v -SRR below in Figure 2.21. The object tree is on the right side of the screenshot. Hierarchically, the two structures in the object tree are the cladding ('clad') and the rounded v -SRR with conformal coating and substrate ('vRound'). The cladding, here simulated as a dielectric with refractive index 1.33 to represent an aqueous background, occupies the upper portion of the simulation region, and the substrate, part of the vRound structure group, occupies the lower portion. As it's just a rectangular prism, the cladding also occupies the region where the v -SRR and coating are located, but it is, in effect, overwritten by the coating, whose inner portion is itself overwritten by the metallic v shape, due to the ordering in the object tree.

Figure 2.21–Screenshot of the Lumerical FDTD user interface with the object tree expanded on the left and the four views on the right.

Chapter 3 DEVELOPMENT OF ELECTRODEPOSITION

PROCESS

Strong plasmonic resonance in the visible spectrum requires high aspect ratio metallic resonators with deep subwavelength dimensions, which find applications as part of a cost-effective and practical optics-based sensing platform. Electrodeposition is a highly suitable method for fabricating such structures as it allows deposition of metals with much larger thickness and better morphology than that achieved by physical deposition. Herein, we present an in-depth study of pulsed electrodeposition of a gold film directly onto a transparent substrate without a seed layer and development of a reliable and efficient fabrication method for high aspect ratio metallic nanostructures with sub-10-nm features based on this approach. We demonstrate a low-cost fabrication of sub-100-nm metallic nanostructures based on a very high deposition rate (~ 7 nm/pulse) which nonetheless exhibit good surface morphology. Specifically, we realized high aspect ratio rotationally symmetric plasmonic nanostructures suitable for practical sensing platform, which exhibit strong resonances in the visible spectrum with Q factors as high as 10 under unpolarized excitation.

3.1 Introduction

The ability to fabricate patterned metallic nanostructures over a large area on a transparent substrate is of great scientific and engineering interest for applications in plasmonic nanolithography [95,96], imaging [97,98], bit patterned media [99,100], plasmon-enhanced fluorescence [37,101], solar energy conversion [102–104], and especially chemical and biological sensing based on surface enhanced Raman scattering (SERS) and localized surface plasmon resonance (LSPR) [35,58,105,106]. Traditional fabrication routes for achieving such subwavelength features ($\lambda_R/2n_{eff} \sim 100$ nm or less) include focused ion beam (FIB) milling [107] and physical deposition through template defined by electron beam lithography (EBL) [108] or nanosphere lithography (NSL) [109,110]. Owing to the redeposition of sputtered material, serial nature of pattern writing, and required slow writing time for high resolution features [111], FIB milling is not suitable for large area patterns. This makes the combination of lithography, physical deposition, and lift-off remain the preferable method for the best control of structure shape, size, and periodicity [112,113]. For a variety of applications, it is desirable to increase the interaction volume of incident radiation within the nanostructures [114]. Recently, electrochemical deposition of metal through nanometric templates has attracted much interest due to its advantages over physical deposition [21,110,115–117], such as lower material cost, better film morphology, and higher aspect ratio [117].

Typical plasmonic metals in the UV-VIS-NIR regions are silver, gold, aluminum and copper [118–120], all of which except aluminum can be electrodeposited using aqueous solutions. For plasmonic applications in the visible range, silver has the lowest loss. However, gold, having slightly higher loss, especially

below its interband transition at 539 nm, is often preferred due its inertness and biocompatibility [119,121]. It is for these reasons that gold is the metal of choice for biological and chemical sensing applications. In addition to intrinsic metal losses due to interband transitions and intraband damping, plasmonic structures can also exhibit loss due to extrinsic factors such as impurity and surface morphology. Increased surface roughness may be beneficial for SERS applications as it increases the number of local hotspots [122,123], but it proves detrimental to plasmonic sensing as it increases the surface resistivity and leads to mode broadening [77,124].

As a conductive surface is necessary for the electrodeposition process, the vast majority of electrodeposition carried out through a lithographically-defined template utilizes a metal seed layer and ends with template and seed layer removal [21,125–127]. In the context of LSPR applications where the discrete metal nanostructures are fabricated on a nonconductive (typically glass) substrate [127], the seed layer removal both adds steps to the fabrication process and risks impairing plasmonic performance due to degraded structure integrity. The wet etching process for nanoscale features is difficult to control and could entirely remove the nanostructures due to its isotropic nature. Meanwhile, dry etching of gold remains a challenge due to the low volatility and redeposition of etch byproducts [128]. Moreover, etching using various etchant gas recipes [129,130] is never completely anisotropic, even with a mask. We propose eliminating the need for these steps by depositing directly onto a glass substrate coated by a transparent conductive oxide, namely indium tin oxide (ITO). The surface conductivity of the ITO film is sufficient for electrodeposition, but not so high as to hinder plasmonic performance.

Electrodeposition is a complex electrochemical process. Factors affecting structure morphology and quality include anode and cathode geometry and materials,

type of electrolyte, bath additives, temperature, electrode number, agitation, and the choice of potentiostatic (fixed voltage) vs. galvanostatic (fixed current) deposition. It is known that pulsed deposition offers a higher degree of control of the nanocrystalline structure of the deposit over direct current deposition [131–134]. Such a characteristic is desirable for growing metallic nanostructures for plasmonic applications. Due to the numerous factors influencing growth, the establishment of a pulsed deposition process is often implemented as a parametric study [134–136], with the pulse parameters themselves being the simplest to manipulate. In this work, we present an in-depth study of the role of pulse parameters in the optical properties and morphology of the electrodeposited gold film. Furthermore, we demonstrate the fabrication of high-quality well-ordered polarization-invariant gold nanostructures directly onto ITO coated glass which are suitable for sensing applications in the visible range.

3.2 Results and Discussion

Schematics of the electroplating setup are shown in Figure 3.1. Owing to the negligible area occupied by the nanopatterns, the patterned sample is electroplated in parallel with a sacrificial bare ITO substrate for fixing the current density in the mA/cm² range. Platinized titanium mesh is used as an anode, while a total of four copper clips are used to secure the two samples (cathode). A pair of silicon o-rings (6 mm aperture diameter) is used to prevent leakage of the plating solution. The holder is shown schematically in Figure 3.1. All the electrodeposition in this work is done at 3 mA/cm² current density onto ITO-coated glass with a sheet resistance R_s of 20 $\Omega/\square$, unless stated otherwise.

Figure 3.1– Schematics of the dual-substrate electrodeposition holder: (a) top view, (b) side view, and (c) side view

Pulsed electrodeposition of nanostructures is highly dependent on two competing growth mechanisms: the nucleation rate and the growth of existing grains [135]. The extent to which one process dominates over the other is influenced by cathode (sample) and holder geometry, inclusion of growth inhibitors in the plating solution, and the characteristics of the interfacial double layer between the surface and the bulk solution. When the current is on (off), the double layer capacitance is charged (discharged), affecting the diffusion of gold species to the substrate. We vary the deposition characteristics by altering the pulse parameters, which consist of four quantities, only two of which are independent. These parameters are the pulse ON time T_{ON} , pulse OFF time T_{OFF} , pulse period $T = T_{ON} + T_{OFF}$, and duty cycle $D = T_{ON}/T$, which is usually expressed as a percentage. We used a square pulse shape, illustrated schematically in Figure 3.2(a). The various sets of pulse parameters and corresponding sample labels are shown below in Table 3.1, with two seconds of each pulse shape depicted in Figure 3.2(b).

Figure 3.2– (a) Illustration of current density pulse shape and parameters and (b) 2 seconds of each of the waveforms used in this work

Sample	T (s)	D	T_{ON} (s)	T_{OFF} (s)	T_{TOTAL} (s)	$T_{ON,TOT}$ (s)
S_1	DC	100%	n/a	n/a	60	60
S_2	1.0	50%	0.50	0.50	60	30
S_3	0.5	50%	0.25	0.25	60	30
S_4	1.0	75%	0.75	0.25	120	90
S_5	1.0	25%	0.25	0.50	120	30
S_6	1.0	10%	0.10	0.90	200	20
S_7	0.4	25%	0.10	0.30	120	30
S_8	0.5	20%	0.10	0.40	150	30

Table 3.1. Sample designations and pulse parameters. The total deposition times and current ON times are given in the last two columns. A current density of $j_{ON} = 3 \text{ mA/cm}^2$ was used for all samples.

To investigate how the pulse parameters affect the quality of gold grown directly onto ITO, with plasmonic applications in mind, we use first use optical spectroscopy and scanning electron microscopy (SEM) to respectively determine the spectral and morphological characteristics of bulk gold deposition. Representative reflection images, reflection spectra, and SEM micrographs are presented for the first three samples in Figure 3.3.

Figure 3.3– Reflection spectra at various positions on samples (a) S_1 , (d) S_2 , and (g) S_3 , with reflection images inset, and corresponding SEM images for (b)-(c) S_1 , (e)-(f) S_2 , and (h)-(i) S_3 . The thick line in the spectra represents the mean of the measurements, with the shaded blue area encompassing ± 1 std. dev. The dashed curve represents the ideal normalized reflectivity based on optical constant data. The inset images depict a square area of side $51.68 \mu\text{m}$.

Sample S_1 , grown using DC current, was the first experiment of depositing onto an unpatterned substrate. The optical quality of the electrodeposited gold is investigated by comparing the reflection spectra from 50 representative points across the sample with the ideal reflection of gold film (dashed curve). The range of reflection spectra within one standard deviation of the mean (indicated by the shaded blue area), which we denote here as the reflection band, gauges the uniformity of the electrodeposited gold film, while the difference of the average reflection (thick blue curves) from the ideal reflection of gold film gauges the quality of the gold film. As evident from Figure 3.3(a), the reflection band of S_1 is both large and spread out. Visually, the surface of sample S_1 appears opalescent in some areas and exhibits many

cracks in others. From the SEM inspection in Figure 3.3(b), some areas appear to be covered in gold (Figure 3.3(c)), while others are bare. This is far from the ideal deposition uniformity necessary for high quality structures. Sample S_2 was electrodeposited by pulsed current with a pulse period of 1 s and a duty cycle of 50%. As shown in Figure 3.3(d), the reflection spectra of S_2 , while still showing a large band, have smaller range (gray shaded area) compared to that of S_1 . Moreover, the average reflection spectrum is closer to the Fresnel reflectivity calculated using refractive index data [137]. While the surface visually appears much more uniform, SEM inspections indicate that the deposit quality varies from smooth (Figure 3.3(e)) to porous (Figure 3.3(f)). Next, S_3 was deposited at the same duty cycle of $D = 50\%$, but with half the period ($T = 0.5$ s). The reflection band for this sample is qualitatively similar to that of S_1 , however the average reflection is closer to the calculated ideal reflection. From the SEM images (Figure 3.3(h)-(i)), the surface topology varies among uniformly covered areas, areas with openings and loosely connected “islands” of gold growths, and areas with holes of various size. We further investigated the effect of duty cycle with a period fixed at $T = 1$ s, with representative spectra and images of S_4 ($D=75\%$), S_5 ($D=25\%$), and S_6 ($D=10\%$) presented in Figure 3.4.

Figure 3.4– Reflection spectra at various positions on samples (a) S_4 , (d) S_5 , and (g) S_6 with reflection images inset and , and corresponding SEM images for (b)-(c) S_4 , (e)-(f) S_5 , and (h)-(i) S_6 . The significance of the lines and shaded regions is the same as the previous figure. The inset images depict a square area of side 51.68 μm

As shown in Figure 3.4(a), sample S_4 ($T=1$ s, $D=75\%$), has a visual appearance akin to S_2 . The reflection spectra of S_4 are more concentrated toward the middle of the range, unlike those of S_2 , which are denser toward the top of the range. The SEM images reveal that the holes in S_4 are larger and more prevalent. The difference of hole size is likely attributed to more lateral diffusion of incoming gold ions during the OFF time, which decrease the hole size for a smaller duty cycle. Based on this reason, we decrease the duty cycle further to $D = 25\%$ (S_5), and observe much narrower reflection band as shown in Figure 3.4(d). The spectra all lie within a narrow range close to (and exceeding in some cases towards the near-infrared) the theoretical (ideal) value. Sample S_5 exhibits the best spectral results thus far. However, as indicated in the SEM images (Figure 3.4(e)-(f)), the electrodeposited gold appears to be porous in

some areas and sparsely populated below the surface in others. For completeness, we investigated the case of decreasing the duty cycle even further with S_6 ($T=1$ s, $D=10\%$). As shown in Figure 3.4(g), the reflection band of S_6 exhibits a large range, with the average reflection far below the ideal normalized reflection. The gold film appears to have bright and dark patches (Figure 3.4(g), inset), corresponding to highly uneven surface (Figure 3.4(h)) covered by nucleated gold grains (Figure 3.4(i)). It has been found for nickel that longer ON time, i.e. higher duty cycle, leads to more nucleation sites and smaller grain size in nickel deposits [138]; however what we see here is a lot of nucleated sites that have not grown when a low duty cycle is used. Indeed, a balance must be maintained between two competing growth mechanisms in pulse electrodeposition. The vertical growth and the lateral diffusion are mainly dependent on ON time and OFF time, respectively. Increasing ON time (increasing duty cycle) encourages more vertical growth, which often leave behind porous film. On the other hand, increasing the OFF time encourages more lateral diffusion, which could lead to discontinuous gold film and subsequently gold nanoparticles formations. Thus, the duty cycle and period must be carefully chosen to maintain the balance between the two competing processes. For this reason, we further fix the duty cycle to $D = 25\%$ while decreasing the period to $T = 0.4$ s with S_7 . This corresponds to T_{ON} of 0.1s and T_{OFF} of 0.3s. The reflection spectra and SEM images are presented in Figure 3.5(a).

Figure 3.5– Reflection spectra at various positions on samples (a) S_7 and (d) S_8 with reflection images inset, and corresponding SEM images for (b)-(c) S_7 , and (e)-(f) S_8 . The significance of the lines and shaded regions is the same as the previous figures. The inset images depict a square area of side $51.68 \mu\text{m}$

As evident from Figure 3.5(a), S_7 exhibits even better optical characteristics compared to S_5 . To see the effect of longer OFF time on the quality of electrodeposited film, we also conducted electrodeposition with T_{ON} of 0.1s and T_{OFF} of 0.4s for sample S_8 , where the OFF time is 100 ms longer than for the previous sample. Although the surface of S_8 has some areas that appear visibly smooth, there are also many areas that appear dark and patchy. The SEM inspections in Figure 3.5(e)-(f) reveal that the gold film of S_8 has many pores of dimension $\sim 1\text{-}2 \mu\text{m}$. This is also indicated by the reflection band in Figure 5(d), where the average reflection is leaning towards the theoretical reflection but with a large reflection band originating from patchy areas. This confirms that lateral diffusion during off-time plays important role in the morphology of the electrodeposited film, where 100ms longer OFF time is sufficient to severely degrade the film quality. Among all the pulse schemes presented in this work, S_7 is the best plating scheme in terms of the reflection spectra and visual appearance. The proximity towards the theoretical value and the narrow reflection

band indicates high uniformity of small grains with good surface coverage, as also confirmed by the SEM images in Figure 3.5(b)-(c). We conclude that for pulse electrodeposition of gold directly onto ITO-coated glass using our electrode and sample holder geometry, a pulse period of 0.4s with a duty cycle of 25% is optimal.

We proceeded to use this scheme for electrodeposition of various rotationally symmetric gold nanostructures, where nanopatterns with sub-20-nm features are defined by the cold sonicated development electron beam lithography process we developed previously[99]. Rotationally symmetric nanostructures are chosen in this study because they address the requirements of a practical sensing platform such as robust mode excitation and strong optical response under unpolarized light illumination. Here, we present nanopatterns grown using either or both (in the case of dimers) of two numbers of pulses. The growth of samples using $n=10$ and $n=21$ pulses corresponds to total ON times of 1 s and 2.1 s, respectively. The $n=10$ sample was deposited in parallel with a dummy substrate of ITO-coated glass, while the $n=21$ sample was deposited in parallel with a similar dummy substrate coated also with a layer of gold, as illustrated in Figure 3.6.

Figure 3.6– Schematic of the electrodeposition setups for the two nanostructure samples and their dummy substrates. Before depositing the nanostructures, the $n=10$ dummy sample surface was ITO, but the $n=21$ dummy sample surface had an additional layer of gold.

A selection of the fabricated nanostructures is shown in the oblique incidence SEM images in Figure 3.7, with normal incidence insets. Square dimers, having a design square side length s of 80 nm and a design gap g of 30 nm are shown in Figure 3.7(a) for $n=21$. Due to the nature of the gold growth and the compliance of the resist template, the resultant nanostructures have features that are wider than the defined patterns. The square dimers were measured to have average side lengths of ~ 99 nm and ~ 103 nm ($n=10$) and ~ 106 nm and ~ 111 nm ($n=21$) in the directions parallel and perpendicular to the gap, respectively. The increased dimer square size resulted in an average gap width of about ~ 9 nm in both cases, illustrating the achievable resolution of our electrodeposition method. From the oblique SEM images, using the scale bar and adjusting for the inclination angle, the average heights of the dimer structures are estimated to be 75 ± 5 nm ($n=10$) and 84 ± 7 nm ($n=21$).

Figure 3.7– SEM micrographs of various electrodeposited structures: (a) square dimers of side length $s = 80$ nm and nominal gap $g = 30$ nm, (b) six-fold rotationally symmetric stars ($s = 100$ nm), (c) four-fold internally rotationally symmetric gammadion crosses ($s = 100$ nm), and (d) four-fold externally rotationally symmetric ν -SRR ($s = 100$ nm, $\theta = 60^\circ$). All scale bars represent 400 nm.

We also fabricated internally C_6 -symmetric star shapes, as shown in Figure 3.7(b), with a design arm length of 100 nm, feature size of 20 nm and a periodicity of 300 nm in both lateral directions, grown using $n=21$ pulses. The central region of each star appears larger at the intersection of its individual arms due to EBL proximity effects originating from overlapping e-beam exposure lines. Additionally, Figure 3.7(c) shows gammadion cross structures ($n=21$) with a half-arm length of 100 nm and a periodicity of 350 nm. Finally, in Figure 3.7(d) we fabricated arrays of v -shaped split ring resonators ($n=10$) arranged to have four-fold rotational lattice symmetry (C_4 v -SRR), as shown in Figure 6(d). The v -SRRs were designed to have an arm length of 100 nm, feature size of 20 nm and an opening angle of 60° . It should be noted that v -SRRs with opening angles ranging from 40° to 90° , and arm lengths as small as 60 nm have been successfully grown using the current method, demonstrating good angular tunability (not shown here). With the estimation as above, the heights of the C_6 stars and gammadions are approximately 64 ± 5 nm, and that of the C_4 v -SRRs is 68 ± 8 nm.

These heights correspond to an average growth rate of 3-7 nm per pulse, or 30 – 70 nm per second of ON time. For a time rate including the pulse OFF time, this gives a growth rate of 7.5-17.5 nm/second, a much higher rate than other metallic nanostructure growth methods based on physical or chemical vapor deposition [125]. Several things should be noted about the growth rates. First, the height of structures grown on a given sample varies inversely with the lateral density or metal fill factor. Second, the reported growth rates are average values, and as can be inferred from the small marginal height gain achieved in the dimers by increasing from $n=10$ to $n=21$ pulses, the growth rate seems to decrease with increasing pulse number, as evidenced by the minima and maxima of the recorded voltage oscillations (see Appendix Figure A-1), which increase for the first several pulses, and then reach steady state values.

Additionally, the samples were deposited with pulses programmed with two different sampling times, causing the practical duty cycles and periods to differ slightly (Figure A-1). Finally, while the $n=10$ sample was deposited using a bare ITO substrate in parallel with the patterned one, the $n=21$ sacrificial substrate was covered in gold prior to nanopattern deposition. This may also account for the difference in deposition rates.

The resonance properties of the above plasmonic nanostructures in comparison with their planar counterparts are presented in Figure 3.8, where the resonance modes (λ_{LSPR}) are indicated by the transmission dips. Unpolarized light illumination and collection was used for all structures except for the dimers, which were measured under linear polarization (parallel to the dimer gap). The electrodeposited dimers exhibit a resonance mode at 680 nm (662 nm) with Q factor ($Q = \lambda_R/\Delta\lambda$) of $Q\sim 6.37$ ($Q\sim 6.27$) for fabrication with $n=10$ ($n=21$) pulses and higher spectral contrast than their planar counterpart (Figure 3.8(a)). This illustrates that the structural integrity of the sub-10-nm gap of the dimer is preserved during electrodeposition. The resonance of the electrodeposited dimer is also observably narrower, which is indicative of lower damping loss due to smoother gold surface.

Figure 3.8– Transmission spectra of (a) square dimer, (b) C_6 -symmetric star structure, (c) gammadion resonator, and (d) fourfold rotationally symmetric v-SRR array (C_4 v-SRR with $\theta = 45^\circ$ and $\theta = 60^\circ$) for planar ($h = 30$ nm) and electrodeposited ($h = 70 \pm 5$ nm) structures. The resonance modes are indicated by the solid, hollow, and double arrows.

The properties of polarization-invariant plasmonic nanostructures such as planar gammadion and star-shaped structures and their feasibility for biosensing have been studied previously [59]. While the present structures are not tall enough to exhibit longitudinal resonances associated with standing wave due to Fabry-Perot (FP) reflections, we note that many of these transverse resonances are blue-shifted from those of their planar counterparts. This blue shift with increasing height, which has been experimentally observed by other groups, may be attributed to an increase in the restoring force on electrons displaced by plasmon oscillations [139,140]. The transmission spectra of a planar and electrodeposited C_6 structures are presented in Figure 3.8(b), showing an observed blue shift from 962 nm to 856 nm as the thickness is increased 30 nm to 64 nm. The broad resonance of star-shaped nanostructures has been shown to originate from conductive coupling between their constituent nanorods

[59]. In our measurement, additional broadening may have originated from lower grating efficiency for wavelengths above 800 nm [58]. The effect of increased thickness in the star-shape structure is apparent in the observation of an additional resonance mode at 590 nm (hollow arrow), which was previously absent in the planar C_6 spectrum. This mode is associated with the surface plasmon oscillations along the longitudinal direction, which is likely the transition before the FP-like longitudinal mode emerges at increasing thickness.

Figure 3.8(c) presents the transmission spectra of planar and electrodeposited gammadions, where, of the two modes of the planar structure, only the higher order mode around 700 nm (denoted by a hollow arrow) is observed for the electrodeposited gammadion due to the spectral limit of our Cytoviva system to wavelengths below 1000 nm. The hybrid magnetic-electric resonance properties of the gammadion have been shown to emerge from the conductive coupling of its constituent nanorods [59]. For the planar gammadion with 30 nm thickness and 100 nm arm length, the fundamental mode (denoted by the solid arrow) and higher order mode (hollow arrow) are located at 1700 nm and 887 nm, respectively. We observe a blue shift from 887 nm to 700 nm for the higher order mode. Additionally, we clearly observe a mode (double arrow) at 545 nm associated with the height as in the case of C_6 structure. Furthermore, on the left side main dip in the tall gammadion spectrum, we observe what appears to be a resonance at around 625 nm whose own spectral dip is overshadowed by the main dip, due to its low prominence. The resonance mode of the electrodeposited gammadion exhibits more pronounced resonance, as evident from its higher resonance contrast, and a Q -factor of 11.1, compared to the 6.7 of its planar counterpart, a 65% increase. Finally, we present in Figure 3.8(d) the transmission spectra of planar and electrodeposited C_4 v -SRRs with 45° and 60° opening angles,

showing the expected blue shifts and higher spectral contrasts for the resonance modes of the electrodeposited v -SRRs. The polarization-dependent optical properties of planar v -SRRs of various angles and arm lengths arranged in a square lattice have been previously investigated in detail [58,141]. Here, the magnetic (solid arrows) and electric (hollow arrows) modes are observed at 820 nm and 637 nm (for 45° opening angle) and 770 nm and 649 nm (for 60° opening angle). The Q factors of the magnetic and electric modes are 6.8 and 7.9 (for 45° opening angle) and 10.1 and 9.4 (for 60° opening angle), respectively.

All of the above plasmonic structures demonstrate resonance modes in the visible spectrum with high spectral contrasts under unpolarized illumination. These characteristics are in line with the requirement for practical sensing platform such as simple and cost-effective implementation, robust mode excitation, and strong optical response. Moreover, realizing these structures by electrodeposition significantly reduces the cost of fabricating plasmonic nanostructures with desired optical characteristics. In terms of sensing performance, these polarization-invariant nanostructures are expected to exhibit higher bulk sensitivities in the same way as the electrodeposited dimers have been shown to exhibit 45% higher bulk sensitivity than that of the planar dimer [117], as will be demonstrated in the following Chapter.

3.3 Alternate Deposition Modalities

In addition to pulsed deposition through a positive-tone EBL resist template onto 20 $\Omega/\square$ ITO-coated glass, other electrodeposition methods were performed. These included deposition of gold using a negative resist template and deposition onto other

substrates, including onto glass coated with ITO of higher surface resistance and onto titanium. This section details some of them.

3.3.1 Deposition of Negative Patterns

The second technique presented in this report that allows us the use of larger areas and hence currents, without using a dummy sacrificial substrate, is that of electrodeposition with the negative technique, so called because it utilizes a negative tone EBL resist. To recap, when electroplating with the positive technique, all the nanopattern arrays are surrounded by resist immediately after the deposition, before resist removal. However, when electroplating with the negative technique, gold is also deposited onto the areas surrounding the nanopatterns. Therefore, using the negative technique allows for electrodeposition without using a sacrificial substrate in parallel. A comparison of the two techniques is shown in Figure 3.9.

Figure 3.9 Comparison of positive and negative techniques: (a) deposition using positive technique, with sacrificial area on the same sample, (b) deposition using the negative technique, and (c) final structure examples for a given EBL exposure pattern.

To the best of our knowledge, no one has attempted electrodeposition based on a negative-tone resist template. Because the negative technique is similar to deposition of an unpatterned gold film, it is possible that a higher current density may be used. As the patterns written using EBL eventually become grooves, slots, and holes in a metal film, this technique may serve as an alternative to FIB milling for the creation of such structures. These types of structures have important applications in, for example,

enhanced Surface Raman Spectroscopy and the study of the near field distribution of in-plane surface plasmons [142].

For the negative technique of EBL patterning, AZ5214E resist was used in image reversal mode. One advantage of this method is the lower required dose than that required by using AZ as a purely negative e-beam resist, as shown in the contrast curves of Figure 2.7(a). Electrodeposition using the negative technique was performed on several samples with ITO sheet resistance of $20 \Omega/\square$. Following electron beam patterning, bake, and flood exposure, the sample was developed using AZ developer. After electrodeposition, the remaining resist was removed by methanol and Technistrip P1316. The representative sample considered here is denoted as NS6. Electrodeposition was carried out with a DC current density of 3 mA/cm^2 for 60 seconds, resulting in a height of 62 nm, giving an average deposition rate of 1.03 nm/s. For NS6, the patterns attempted include hexagonal and square tessellations and arrays of annular cavities among others.

First, quality of the gold films deposited using the negative technique is investigated. This is shown in Figure 3.10. In the large film areas, there are some blemishes, observable in Figure 3.10(a); however, these may simply be resist residue. Moreover, the gold film quality is less important than that of the nanostructures. In Figure 3.10(b), a magnified in image of the film, we see that the grains composing the film are on the order of 50 to 100nm.

Figure 3.10 SEM images of the gold film electrodeposited onto NS6 at (a) lower and (b) higher magnification

Examples of the hexagonal and square patterns electroplated using the negative technique are shown in Figure 3.11. Accordingly, we can see an example of the metal deposited around the hexagonal pattern area, which renders the separate sacrificial area obsolete, in Figure 3.11(a). We observe that while the pattern shows good overall fidelity, the patterns exhibit some unevenness in the edges of the individual squares and hexagons. Some possible reasons for this are that the large metal area immediately surrounding the arrays may have some influence over the grain sizes with which the gold is deposited, or that the image reversal technique leaves the resist boundaries more jagged than the positive pattern that was originally written. Another reason may be post-deposition degradation due to the particular resist stripper used.

Figure 3.11 SEM images of (a) hexagonal and (b) square tessellation patterns, with higher magnifications inset

The last type of pattern that is presented for sample NS6 is the array of annular cavities, several examples of which are shown in Figure 3.12. In all these cases, the patterns exposed to the electron beam were arrays of circles. The pattern fidelity of the cavities, or how true they are to the original circular shape, is greatly influenced by the linewidth of the e-beam pattern, as evidenced by comparing Figure 3.12(a) to (b) and (c) to (d). This is attributed to the lateral pressure during electroplating process, where the atoms not only move upward but also laterally outward, discussed in further detail in Chapter 4. Moreover, the hardness of the image-reversed patterns depends on the exposure dose, reversal bake temperature and time. The more scissions occurring

in e-beam exposures, the more crosslinking is expected from the reversal bake step. Similarly, for the same exposure dose, more crosslinking is expected if the reversal bake temperature is increased. Thus, the higher exposure case is less jagged because the patterns are more resilient to the lateral pressure during electroplating. Additionally, it appears as though the higher dose leads to less jaggedness around the edges of the cavities, as can be seen by comparing Figure 3.12(b) to (c). Judging from Figure 3.12(e), it should be very easy to fabricate arrays of circular (or square) nanocavities. The only difference is that the pattern should be a disk instead of a circle of finite width. It is unclear why some of the patches of gold are darker than others, as this level of darkening is not likely due to electron beam exposure during SEM.

Figure 3.12 SEM images of the annular cavities, where the three numbers separated by dashes in each subfigure signify the relative EBL dose, the circle radius, and circle line width

3.3.2 Deposition onto other substrates

3.3.2.1 High sheet resistance ITO-coated glass

Fewer experiments were performed for electrodeposition onto the higher sheet resistance ITO, having $R_s=2\text{ k}\Omega/\square$, instead of the standard $20\text{ }\Omega/\square$ used in the previous results presented in this work. The representative sample that will be presented here is denoted S11. The deposition was carried out with a DC current density of 1.6 mA/cm^2 for 70 seconds. Patterns attempted for deposition onto S11 included tessellations of rectangles and hexagons, concentric square annuli, and arrays of nanopatterns like those shown previously. The most noticeable feature of electrodeposition onto the $2\text{ k}\Omega/\square$ ITO is that the larger area gold structures, such as the tessellations of rectangles and hexagons shown in Figure 3.13 and the concentric square annuli shown in Figure 3.14, no longer appear to be a continuous solid. They appear to consist of aggregations of gold nanoparticles which fail to grow vertically.

Figure 3.13 SEM images of the annular cavities, where the three numbers separated by dashes in each subfigure signify the relative EBL dose, the circle radius, and circle line width

Figure 3.14 Example of deposition of concentric square annuli onto high sheet resistance ITO substrate

Although vertical growth was not achieved on this higher resistivity ITO, the boundaries of nanoparticle-containing regions in the larger patterns still showed good fidelity with the EBL pattern. This is similar to the results of deposition of silver onto ITO [143]. However, as shown in Figure 3.15, attempts to deposit onto smaller patterns, such as the u-shapes and asterisks were unsuccessful. This may be because the average size of the nanoparticle deposited is on the order of the individual pattern widths or the necessary area for the particles to grow from the substrate.

Figure 3.15 –Results of deposition of nanostructure arrays onto 2 kΩ/□ ITO substrate. (a) *u*-shape SRRs and (b) C₅ star shapes

The quality of the gold deposited over larger areas varied based on the extent of the defined area and its surroundings. Figure 3.16(a) shows a sheet-like agglomeration

of nanoparticles covering the marker area used for height measurement. However, looking at the dummy area in Figure 3.16(b) and at higher magnification in (c) reveals an almost uniformly random deposition of nanoparticles. Figure 3.16(d) shows an oblique incidence view of a square pattern of nanoparticles at high magnification. From the mushroom-like morphology of the structures in this image we can speculate how the gold grows on the $2\text{ k}\Omega/\square$ ITO substrate. It appears that sparse thin cylindrical structures grow vertically first, and that these serve as nucleation centers for subsequent outward spherical growth. This is unlike deposition onto low sheet resistance ITO, the ITO area exposed to solution is seemingly uniformly covered by gold nucleation positions.

Figure 3.16 –Gold deposition onto the $2\text{ k}\Omega/\square$ ITO substrate: (a) the height marker, (b) the dummy area, (c) the dummy area at higher zoom, and (d) a square pattern at oblique incidence

As stated previously, this deposition was carried out using direct current. Varying the DC current density or instead using pulsed electrodeposition may change the conditions for growth so that the surface is more uniformly covered in sparse nanoparticles which themselves are more uniform in shape. This methodology

provides another method for growth of gold nanoparticles with diameters on the order of tens to hundreds of nanometers, with the nanoparticles likely to be smaller for shorter total current ON time.

3.3.2.2 Titanium

In addition to ITO, titanium was also used as a conductive surface upon which to perform electrodeposition through the negative technique. Although attempts to grow nanostructures were unsuccessful, deposition of gold nanoparticles and clusters of nanoparticles was observed over a large area. This is demonstrated in Figure 3.17(a) and (b) for areas with and without larger clusters, respectively. The latter image is resembles the results obtained from electrodeposition onto the $2\text{ k}\Omega/\square$ ITO substrate for large areas. Progressively magnified images of the nanoparticles are shown in Figure 3.17(c) and (d), and it can be seen from the measurements that individual nanoparticles are approximately 150-200nm in diameter. With further process refinement or the addition of bath additives to minimize aggregation into clusters, electrodeposition may be a suitable method for coating a titanium surface with nanoparticles of uniform size.

Figure 3.17 – SEM images of the large areas of titanium after electrodeposition

3.3.3 Concluding remarks on alternate deposition modalities

This Section has demonstrated the experimental results of electrodeposition performed using methods other than that used for the other works presented in this thesis. Specifically, results of deposition onto low sheet resistance ITO using EBL patterning with a negative resist were shown, followed by results of electrodeposition onto different substrates, namely high sheet resistance ITO and titanium. The negative process mentioned in Chapter 2, using AZ5214E photoresist as an image reversal e-beam resist, was used to deposit several types of gap structures. It was shown that the pattern fidelity is highly dependent on the e-beam exposure parameters, but that large area patterning of gaps and holes is feasible with this method. Similar to the motivation for electrodeposition using a positive-tone resist template, this process could be used to reduce the cost of fabricating arrays of nanoholes and nanogaps of various lattice configurations, which are typically fabricated by physical deposition followed by focused ion beam milling [12,144,145] or by using nanosphere

lithography or EBL, followed by liftoff [109,146]. Next, deposition onto other substrates was demonstrated. Using a high sheet resistance ITO as a substrate was shown to decrease the number of gold nucleation sites, leading effectively to a sparse pattern of nanoparticles with stems. The results are similar to those found with silver [143]. Deposition onto titanium also yielded particle growth, as opposed to vertical growth. After more experimentation and refinement of the process, these deposition modalities may be a useful alternative for deposition of nanoparticles onto a substrate.

3.4 Conclusion

We have investigated direct pulsed electrodeposition process for realizing high aspect ratio plasmonic nanostructures which find applications in cost-effective and practical sensing platform. The role of pulse time parameters in the optical properties and morphology of the electrodeposited film has been systematically studied, from which 25% duty cycle with 400ms pulse period have been found to be the parameters for the best film quality. Using these parameters, we have successfully electrodeposited metallic nanostructures with features in the sub-10-nm regime, with their plasmonic properties consistently better than those of their planar counterparts. Direct deposition onto ITO has been reported before [22], but never with such subwavelength features. Deposition onto ITO eliminates the need for a seed layer, either a conformal seed layer [21,147] which hinders plasmonic activity in the visible region for deep-subwavelength structures, a seed layer patterned using lithography and physical deposition [148] which adds time and material cost to the process. Specifically, we have demonstrated high aspect ratio rotationally symmetric plasmonic nanostructures that exhibit resonances in the visible spectrum and high spectral contrast under unpolarized light illumination. Coupled with the electrodeposition

process, which imparts much smaller cost than that based on physical deposition, these electrodeposited polarization-invariant nanostructures address the simplicity and cost-effective requirements of a practical optics-based sensing platform.

Chapter 4 HIGH ASPECT RATIO SUB-10-NM GAP GOLD

DIMERS

In this Chapter, we present some results of the proposed fabrication procedure, demonstrating robust gold square dimers with sub 10-nm gaps and gap aspect ratio of greater than eight. We show that smooth gold surfaces can be achieved by growing the gold film directly on transparent ITO substrate without a gold seed layer and demonstrate significant improvement of Q factors and resonance contrast in the electrodeposited dimers compared to the dimers fabricated by physical vapor deposition. We demonstrate that the electrodeposited dimers exhibit close to 50% higher bulk refractive index sensitivity than their planar counterparts.

4.1 Introduction

The ability to fabricate high density arrays of metallic nanostructures has enabled progress in diverse fields including high-density data storage [100,149], localized surface plasmon resonance (LSPR) [58,150,151], and surface enhanced Raman scattering (SERS) based chemical and bio-sensors [54,152]. It has also proven instrumental in more fundamental research areas such as subwavelength imaging [153] and metamaterials [154]. The strong interaction between surface plasmons and nanoscale objects has led to the development of highly sensitive biochemical sensing

at the wavelength bands covering from visible to mid-IR [12,55,58,155,156]. The sensitivity depends on the light-matter interaction, which is mostly determined by the surface area of the metal on which (bio-)molecules adhere. Therefore, the sensitivity can be improved by either increasing the lateral size or the height of the resonators. However, increasing resonator size is not effective due to the strong lateral size dependence of plasmonic resonance. In addition to having red shift in the plasmonic resonance, increasing size also decreases the pattern density which in turn negatively affects the spectral contrast. On the other hand, increasing the resonator height maintains the pattern density and does not significantly affect the resonance position. Moreover, increasing height also increases the spectral contrast due to enhanced light-matter interaction from larger surface area.

High aspect ratio metallic nanostructures are thus desired for the above applications. For both research and commercial applications of such structures, it is desirable to have a straightforward and cost-effective fabrication procedure. Several methodologies exist for fabricating 2D and quasi-3D arrays of metallic nanostructures, ranging from subtractive methods, such as focused ion beam (FIB) milling [107], to additive methods based on templates that can be fabricated either by means of self-assembly approaches [109] or lithographic patterning [21,141]. Each templated deposition approach has advantages and disadvantages. Self-assembled monolayers (SAM), of polystyrene nanospheres, for example, allow the formation of highly ordered lattices with high throughput, but at the expense of lack of control of the lattice (hexagonal) and structure shape (hole, ring, crescent) [109,146,157,158]. In addition, self-assembled monolayers often exhibit uncontrollable domain boundaries. The other more guided self-assembly approach utilizes anodized aluminum oxide (AAO), where a porous template can be defined by means of oxidation of aluminum

film. Although the lattice and pore shape can be directed to an extent by pre-anodization patterning using methods such as nanoindentation [159], FIB milling [160], or selective etching [161], AAO templates are constrained by the same lattice and domain issues as the SAM approach.

By contrast, direct template patterning using electron beam lithography (EBL) offers superb dimensional control at the expense of low throughput. While sub-10-nm resolution is required for realizing metallic resonators with strong light-matter interaction capabilities and resonances covering visible spectrum, these dimensions are normally achieved at the expense of decreased throughput due to the inherent resolution-throughput trade-off. Such a trade-off originates from the attempt to reduce proximity effects in a high contrast EBL process, where the exposed resist is more selectively removed by weak development schemes, such as using diluted developer and/or cold development [162–165]. The attempt to overcome this trade-off has been addressed by a cold sonicated development process [99,108,166], where sonication is introduced during development step to create interplay between gel-layer formation and removal in partially exposed resist. Using this method, we have achieved process contrast larger than $\gamma \sim 25$ at an exposure dose much lower than those in reported high contrast EBL processes, and demonstrated the fabrication of planar plasmonic nanostructures with sub-20-nm features [167]. However, the thickness of these planar resonators is constrained by the requirement of ensuring successful lift-off pattern transfer, thereby limiting the metal thickness to a few tens of nanometers. Increasing the aspect ratio is possible with thicker resist, but this is realized at the expense of decreased resolution.

We address this problem by combining high contrast EBL patterning of the sonicated cold development process with pulsed electrodeposition to realize arrays

metallic resonators with sub-10-nm features and aspect ratio of ~ 8 . We further demonstrate that these dimers exhibit strong resonances in the visible spectrum with their Q factors much higher compared to their planar counterparts. Such geometric and resonance characteristics makes them suitable candidates as chemical and bio-sensing substrates, among other applications.

4.2 Experiment

4.2.1 Nanopatterning

The EBL patterning was carried out by Raith e_LiNE system on 120 nm thick ZEP520A e-beam resist based on 20 keV energy and 30 pA beam current. For higher pattern fidelity, the square dimers were written as a series of single pixel lines as opposed to areal exposure. The line exposure was done at 300 pC/cm dose at 2 nm step size. The single pixel lines are separated by 10 nm, which is the intrinsic linewidth of a single dot exposure. Several iterations of square dimer arrays of footprint $10\mu\text{m}$ by $10\mu\text{m}$ were written. Each iteration was designed to have a square side length of 60nm or 80nm, and a gap distance of 20nm, 30nm, or 40nm, for a total of six arrays. In all cases, the periodicity was set to four times the square side length. The sample was then developed in a mixture of *n*-amyl acetate and isopropanol (2:1) using a sonicated cold development process with 5s pre-sonication time, 10s sonication time, and 20s post-sonication time. This process has been reported to exhibit high verticality (with $<5^\circ$ sidewall angle) [99] and aspect ratio of ~ 10 [108], making it suitable for growing square dimer with sub-10-nm gap. For planar square dimer fabrication, 30 nm thick gold is physically deposited by e-beam evaporator (Edwards 306) at 0.05 nm/s rate using 2 nm thick titanium as adhesion layer, followed

by lift-off process in N-methylpyrrolidine based solvent (Remover PG, MicroChem Corp) for 10 mins at room temperature.

4.2.2 Electrodeposition

For the growth of the gold dimer structure, the patterned sample and a bare ITO glass were placed in a holder exposing their conductive ITO surfaces to the electroplating solution. The purpose of using bare ITO glass as a dummy sample is to permit the control of current density which is independent of nanopattern area. It was previously found that good results could be achieved by providing a current density of 3 mA/cm² to the sample. Based on the areas of the patterns alone, the current needs to be in picoampere range to achieve the desired current density. However, by having bare ITO glass with 0.28 cm² opening area (i.e. the area of the 6 mm-diameter silicone O-ring used in the electroplating holder), and assuming the dummy area is much larger than that of the nanopatterns ($A_{dummy} \gg A_{nano}$), the required current is found as 0.85 mA. Based on this method, the plating current density has been varied to as low as 1 mA/cm² without much difficulty. The electroplating was done in a commercially available mixture based on potassium aurocyanide [KAu(CN)₂] at room temperature. The electroplating was done using both DC and pulsed current schemes. The latter is found to exhibit higher uniformity and smaller surface roughness. The pulsed plating was done with a Keithley 2400 SourceMeter at 0.85 mA current in square waveform of 400 ms period and 25% duty cycle. A total of 10 pulses were used in the plating, corresponding to a total “ON” time of 400 ms. The pulsed current waveform was programmed through the RS232 interface using SCPI and MATLAB. Following electrodeposition, the sample was rinsed in DI water. The resist template was then removed using N-methylpyrrolidine, followed by rinsing in isopropanol.

4.2.3 Characterization

SEM images were obtained using the EBL system at 10 keV. Measurements of the fabricated dimers were performed using Inkscape software. Lateral and vertical measurement bars on the SEM images, as well as the dimer height calculation method, can be found in the last section of this Chapter.

The square dimers were characterized by the Cytoviva hyperspectral imaging system. The halogen lamp was focused by a condenser into the sample and the transmission signals were collected by 10x objective lens (NA 0.3) under bright field geometry. The signals were directed to the transmission grating and CCD sensor, and the piezo stage was scanned in order to get the transmission image. The transmission for a particular dimer array was obtained from the pixels corresponding to the structure, followed by normalization with respect to the signals from the bare substrate.

4.3 Results and Discussion

4.3.1 Fabrication of square dimer with high aspect ratio gaps

In lift-off pattern transfer, metal is deposited anisotropically through resist with lithographic patterns, followed by resist removal that leaves behind metallic patterns. To ensure successful lift-off transfer, the as-deposited metal film needs to be discontinuous across the patterns. This empirically limits the metal thickness to $\sim 1/3$ that of the resist. This is qualitatively different from the electrodeposition process, which enables the growth of metal by filling the lithographic patterns with thickness only limited by the resist thickness. This would translate to $\sim 3\times$ higher aspect ratio

than that achievable in planar fabrication process. To ensure good quality metal film, a thin seed layer of the same metal is typically needed prior to electrodeposition. However, in this work the electrodeposition was performed directly onto indium tin oxide- (ITO-) coated glass with the following considerations: The sheet resistance of the ITO glass is chosen to be $20 \Omega/\square$, which is sufficient for electrodeposition without interfering too much with the plasmonic activity of the metal nanostructures. Such a direct electrodeposition also avoids the need to dry etch the gold seed layer, for which the low volatility of gold etch products has been found to be a problem [128]. Finally, in addition to simplifying the fabrication process, this method allows for direct spectral measurements of the nanostructures without the need for post-processing after template removal. DC electrodeposition through a lithographically defined template directly onto ITO has been demonstrated previously [22], but the resulting structures have large lateral features and rough metal surfaces.

In the following, we demonstrate the fabrication of high aspect ratio gold square dimers with gaps in the sub-10-nm regime by combining cold sonicated development and pulsed electrodeposition. The pulsed electrodeposition was based on square wave with 400 ms period and 25% duty cycle (see methods). Square dimers were chosen for their design simplicity and large local electric field across the dimer gaps. In addition, the plasmonic resonance of the square dimers is higher in Q factor compared to that of bowtie nanoantennas, making them suitable candidates for SERS and biosensing substrates [168]. As schematically shown in Figure 4.1, the dimer is generally characterized in terms of its side lengths (s_x, s_y), gap (g), and height (h). Note that although the dimer is designed as square ($s_x = s_y = s$), the actual dimer side lengths may differ due to nonidealities in electrodeposition and EBL proximity effects. In order to prevent strong coupling between adjacent dimers, the periodicity (p) of the

dimer array is normalized to $p = 4s$. This periodicity also provides a sufficient signal for measuring the transmission response.

Figure 4.1 (a) Schematic of the square dimer array on ITO substrate with the unit cell indicated by the dashed square. Top-view SEM micrograph of square dimers with sub-10-nm gaps fabricated by (b) physical vapor deposition and (c) electrodeposition method. The scale bars represent 100 nm.

The fabricated dimers with different side lengths and gaps are presented in Figure 4.2. The side lengths are designed as $s = 60$ nm and 80 nm, each of which is with gap variations of $g = 20$ nm, 30 nm, and 40 nm. All dimer structures generally have good pattern fidelity with smooth surface roughness, demonstrating the consistency of our fabrication process. We note an increasing rounding in the dimer at decreasing side length, and that the measured gap appears to be smaller than the designed gap. These are mainly attributed to the intra- and inter-proximity effects during EBL patterning. However, due to the high contrast EBL process based on sonicated cold development, the extent of such proximity effects is limited to a unit cell of the dimer array. This suggests that these proximity effects do not increase with the array footprint, as illustrated by the regularity of the fabricated dimers over a large area in Figure 3.

Figure 4.2 Oblique-incidence SEM images of the fabricated dimer arrays with normal-incidence SEM images inset. (a)-(c) Design square dimension of 80nm with gap decreasing from 40nm to 20nm and (d)-(f) the same as above but with square dimension of 60nm. The inclination angle for the oblique images is 25°. All scale bars are 400 nm.

Figure 4.3 (a) Zoomed out version of the array shown in Fig. 1 (e), with $s = 60\text{nm}$ and $g = 30\text{nm}$, showing the regularity of the fabricated array. The scale bar represents $2\text{ }\mu\text{m}$.

Note that some dimers in Figure 4.3 are shorter than the typical height, as indicated by the dashed yellow circles. This type of defect likely occurs during electrodeposition or resist removal step, particularly when the latter often requires sonication which may cause structural fracturing. Due to the nature of the growth mechanisms of the electrodeposition and the nanometric dimensions of the template,

the final structures exhibit larger lateral dimensions than defined by the template. We summarize the difference between the designed and the measured dimensions in Table 1, where the measurements of the lateral dimensions and height were carried out by normal and oblique incidences SEM micrographs, as shown in the last section of this Chapter.

The sub-10-nm gaps can be achieved for all the side lengths at $g = 20$ nm nominal gap, with the average heights larger than 70 nm. For both the s_{60} and s_{80} structures, the final maximum lateral dimensions of the squares were larger than the designed dimensions by slightly over 20 nm. This increase in size is due to the outward lateral pressure of the growing gold structures on the surrounding resist. Due to the pressure from the opposing dimer, the lateral growth in the x direction is less than that in the y direction by about 2%, 4-5%, and 7% for the dimers with design gaps of 40, 30, and 20 nm, respectively, based on the average measured values. This opposing dimer pressure also keeps the dimer faces straighter on the gap side, particularly for smaller gap size. Figure 4 illustrates the trends in fabricated lateral side length and gap size, normalized to the respective design parameters, with changing gap size, based on the mean data recorded in Table 4.1.

Structure		s_x	s_y	g	h	AR_{s_x}	AR_g
s_{60}	g_{20}	76.7	82.6	8.8	72.6	0.95	8.21
	g_{30}	79.3	83.3	14.4	82.0	1.03	5.68
	g_{40}	80.6	82.2	23.9	74.5	0.93	3.12
s_{80}	g_{20}	96.0	103.6	9.5	78.2	0.82	8.25
	g_{30}	98.5	102.8	16.2	75.3	0.76	4.64
	g_{40}	100.9	102.6	23.1	81.1	0.80	3.51

Table 4.1. Measured dimensions of dimers, in nm, and aspect ratios

Figure 4.4 Averages of the normalized measurements with error bars based on the standard deviations, plotted with respect to design gap size, for both the 60nm and 80nm iterations. Above, side length the measurements in the x (s_x) and y (s_y) and directions. Below, the normalized gap measurements. Jitter was added to the abscissa for clearer viewing.

Clearly, both the normalized gap widths and square side lengths in the x direction (s_x/s) increase with increasing design gap size, at roughly the same rates. The normalized side lengths s_y/s on the other hand exhibit slightly negative to no correlation with the gap size. This is because increasing the gap size allows more growth in the x direction, thus reducing growth in the y direction until the growth becomes laterally isotropic.

From the distribution of dimer heights in Figure 5, it can be seen the lower bounds are very close, with the exception of the $s_{80}g_{20}$ and $s_{80}g_{30}$ arrays, in which there were more defects. Additionally, excluding the largest measurement from the $s_{60}g_{30}$ structure, the upper bounds of the height measurements are all similar. The median heights of the arrays parallel the average values, however there doesn't seem to be any trend with respect to side or gap length. This is one intended outcome of the proposed fabrication process: that the final structure height is independent of lateral cross-sectional area.

Figure 4.5 Boxplots showing the distribution of measured dimer heights. Individual data points are also shown, with added jitter. Whiskers are extended to the measured extrema.

We define the aspect ratio as the ratio of height to smallest lateral dimension. The aspect ratios of the side length (AR_{s_x}) and the gap (AR_g) are listed in Table 1. Despite the aspect ratios of the square structures themselves being unremarkable, ranging from 0.76 to 1.03, the aspect ratios of the gaps reached as high as 8.21 and 8.25 for the $s_{60}g_{20}$ and $s_{80}g_{20}$ structures, respectively. The upper limit for the achievable aspect ratio based on sonicated cold development process is ~ 10 [108], suggesting that further optimization is still possible.

4.3.2 Plasmonic characteristics of gold square dimers

We used a broadband source and hyperspectral imaging system to measure the transmission spectra of the planar and high aspect ratio dimers. As illustrated in Figure 6, which depicts the transmission responses under x and y polarizations, the plasmonic resonances for the taller dimers exhibit higher Q factor and spectral contrast than those of the planar dimers. This is attributed to lower damping loss due to smoother metal surface in the electrodeposited dimers. We also observed a blue shift of the transverse mode resonance resulting from the increase in dimer height, where the resonance shift

from 701 nm (682 nm) to 679 nm (623 nm) for resonances under x polarization (y polarization).

Figure 4.6 Transmission responses of high aspect ratio (on $20 \Omega/\square$ ITO) and planar (on $50 \Omega/\square$ ITO) square dimer structures ($s = 80$ nm, $g = 30$ nm) under x and y polarizations.

Figure 7 shows the transmission characteristics of electrodeposited square dimers with varying nominal side lengths and gaps. As expected from the optical properties of dimers, as the incident light is polarized along dimer long axis (x -polarization), the resonance progressively red shifts at decreasing gap separation as a result from longitudinal dipolar coupling. The coupling strength increases dramatically at decreasing gap due to $1/g^3$ dependence in dipolar coupling [169]. This can clearly be seen in the gap is in sub-10-nm regime (corresponding to the nominal $g = 20$ nm), where the resonance becomes wider and less pronounced due to the increase in coupling loss. The corresponding x -polarized resonance positions at nominal gaps of $g = 40$ nm, 30 nm, 20 nm are 633.4 nm, 642.4 nm, and 660 nm (for s_{60} structures) and 678.5 nm, 680.4 nm, and 693.7 nm (for s_{80} structures). The resonances along the y polarization are invariably shorter than the x -polarized resonances and their resonance positions have little dependence on the gap separation. This is attributed to the absence

of capacitive interaction between the two gold squares because their dipole oscillations are orthogonal to the dimer gap.

Figure 4.7 Transmission response of the square dimer structures under x and y polarizations. Here, the parameters s and g refer to the nominal square side length and gap, respectively, as illustrated schematically in Figure 4.1.

Table 2 summarizes the Q factors of all the dimers considered in this work. As expected from smoother metal surface, the Q factor for the electrodeposited dimers is higher than their planar counterparts for all combination of sizes and gaps. The Q factors for the y -polarized resonances are noticeably higher than those for the x -polarized resonance, which is attributed to the absence of coupling loss associated with longitudinal dipolar coupling under y polarization. The Q factors for the electrodeposited dimers with sub-10-nm gaps are $Q_x \sim 7.62$ ($s = 60$ nm) and $Q_x \sim 6.27$ ($s = 80$ nm) under x polarizations. This is suitable for light-matter interaction at the nanoscale where both high Q factor and high intensity enhancement are simultaneously achieved. More importantly, such pronounced resonances and their strong field enhancements occur within the visible spectrum, which is of practical importance for realizing robust sensing platform based on inexpensive light sources and detectors.

Structure		Electrodeposited		Planar	
		Q_x	Q_y	Q_x	Q_y
s_{60}	g_{20}	7.62	8.85	4.28	6.97
	g_{30}	7.60	9.41	6.07	7.02
	g_{40}	8.19	9.23	5.89	6.99
s_{80}	g_{20}	6.27	8.05	2.75	5.09
	g_{30}	6.34	8.82	4.87	5.86
	g_{40}	6.05	8.82	5.03	5.86

Table 4.2 Summary of Q factors.

4.3.3 Bulk Sensing Performance

To compare the plasmonic sensing performance of the electrodeposited structures with that of their planar counterparts, we measured the respective transmission spectra of the dimer arrays after spin-coating with two resists with two different refractive indexes, namely poly(methyl methacrylate) (PMMA) and AZ5214E. Prior to the bulk sensitivity measurements the structures were first cleaned by piranha solution to remove residual organics. We found that this cleaning affects the spectral characteristics of our dimer, where the spectral contrasts after piranha cleaning are observably lower than those of the as-fabricated dimers. The transmission spectra of the electrodeposited and planar $s_{80}g_{40}$ and $s_{80}g_{30}$ arrays are shown in Figure 8 for the three cladding situations.

Figure 4.8 Comparison of electrodeposited deposited and planar dimer transmission spectra in air and in two resists: (a) $s_{80}g_{40}$ electrodeposited array, (b) $s_{80}g_{40}$ planar array, (c) $s_{80}g_{30}$ electrodeposited array, and (d) $s_{80}g_{30}$ planar array. In all spectra, the resonance wavelength is denoted with a circle.

We use the transmission dip wavelengths, denoted by the circles in Figure 8, along with the refractive indexes of air, PMMA, and AZ5214E to plot the wavelength as a function of cladding index for each of the two dimer arrays in Figure 9. The refractive indexes of PMMA and AZ5214E are taken from reference 33 and found using the Cauchy equation with parameters given on the manufacturer's data sheet, respectively (see Appendix Section A.2). Assuming $\lambda = 600$ nm, representative of the operation wavelength of interest for visible sensing characterization, the refractive indexes are $n_{PMMA} = 1.4901$ and $n_{AZ} = 1.6370$.

The resonance wavelengths follow the linear relationships represented by the dashed lines of best fit. The refractive index sensitivities (S) are given by the slopes of the lines, in nanometers per refractive index unit (nm/RIU). The sensitivities for the $s_{80}g_{40}$ dimers are 115.6 nm/RIU (planar) and 167.2 nm/RIU (electrodeposited), while those for the $s_{80}g_{30}$ are 116.6 nm/RIU (planar) and 169.6 nm/RIU (electrodeposited).

These represent increases in the sensitivities of the electrodeposited ($h \sim 75\text{--}80\text{ nm}$) over the planar ($h \sim 30\text{ nm}$) arrays of about 45% in both cases. These sensitivities are close to those of colloiddally-prepared gold nanorods for the same resonance wavelength range, which have the best surface morphology owing to their crystallinity [68,76]. The figure of merit (FOM) for refractometric sensors is defined as $FoM = S/FWHM$, where FWHM is the full-width at half-maximum linewidth of the resonance in air. Using $Q = \lambda_R/FWHM$ and the $S \propto \lambda_R$ dependence of sensitivity on resonance wavelength [171], we can arrive at the following conclusion $FoM \propto Q$ [59]. Taking Q factors for $s_{80}g_{40}$ and $s_{80}g_{30}$ from Table 4.2 Summary of Q factors.

, it can be concluded that the FoMs increase by factors of 1.3 and 1.2, respectively, in addition to having higher sensitivity with lower starting λ_R . Since $Q \propto \lambda_R$, we can infer that the increase in Q for the electrodeposited structures is due to the higher quality of the gold.

Figure 4.9 Transmission dip minima plotted against cladding refractive index for the two dimer arrays. The regression lines for the points are also shown.

To investigate what happens as the height grows further, we measure the refractive index sensitivity of the LSPR mode as the height of the dimer structures is increased to $\sim 140\text{ nm}$. By measuring the transmission spectrum with x -polarized light

in air and in refractive index liquids with indexes of 1.30 to 1.38 in steps of 0.02, we found that the sensitivity reaches as high as 281.5 nm/RIU, a drastic increase over the both the planar and shorter electrodeposited dimers presented thus far. These results are shown below in Figure 4.10.

Figure 4.10 (a) Transmission spectra of dimers with side length $s=80$ nm, gap $g=30$ nm, and height $h\sim 140$ nm in air and various refractive index liquids, and (b), a plot of the dip location versus refractive index, indicating the sensitivity with the slope of the line of best fit

4.4 Conclusions

We have demonstrated a novel process for fabricating metallic nanostructures on an ITO-coated substrate by combining electron beam lithography using a sonicated cold development process with pulsed electrodeposition. EBL allows for precise control of template size, shape, and position, while sonicated cold development ensures near vertical sidewalls at a lower exposure dose. Due to the nature of the templated electrodeposition growth in a soft resist, the metal structures have more rounded features and are laterally larger than the lithographically defined template. Locating structures in close proximity, as is the case with the fabricated dimers, enables the consistent fabrication sub-10-nm gaps. Among dimer arrays presented in this paper, at average heights of 72.6 and 78.2 nm, respectively, the $s_{60}g_{20}$ and $s_{80}g_{20}$ dimer arrays achieved average gap aspect ratios of over 8. Because the height

attainable with electrodeposition is dependent only on the height of the resist template, it is possible to use the demonstrated technique to grow much taller structures and achieve higher aspect ratios. Compared to more planar dimers with gold deposited via e-beam evaporation and lift-off, the SEM images of the electrodeposited structures indicate smoother gold film. Though increased height is also a factor, this is also evidenced by the comparatively higher Q factors of the resonance dips in the transmission spectra. The sensitivity obtained for the electrodeposited dimers of height ~ 80 nm, while not as good as the structures, represented in Figure 2.4, none of which are dimers, is about twice as much as that from the transverse mode reported in [172] and about 37% higher than that reported in [173] in the visible region. The taller dimers performed even better with a measured sensitivity of 281.5 nm/RIU, which is both higher than the sensitivity of the shorter electrodeposited dimers and well above the theoretical limit shown in Figure 2.4, which will be visually compared later. These considerations make the electrodeposited structures more suitable for applications in biological and chemical sensing, among others. Furthermore, because of the direct deposition onto the ITO, the need to both deposit and subsequently remove a metal seed layer, at the possible expense of adversely affecting structural integrity, are eliminated.

Chapter 5 EVOLUTION OF THE LONGITUDINAL MODE AND SENSING CHARACTERISTICS AS A FUNCTION OF HEIGHT

Previously, in Chapter 4, it was shown in the case of square dimers that by increasing the dimer height from $h = 30\text{nm}$ to $h = 70\text{nm}$, we were able to increase the bulk refractive index sensitivity of the dimer arrays by almost 50%. As nanostructures are grown in height from the typical planar lift-off regardless of nanostructure shape, a trend of decreasing LSPR resonance wavelength of the transverse mode(s) as the structure height increases is observed, both in simulations and experiments. Despite the fact that the resonance wavelength in air decreases, the transverse mode resonances of moderately tall (not tall enough to support longitudinal resonances) structures seemingly exhibit larger analyte refractive index sensitivity than their planar counterparts, despite the well-known phenomenon that refractive index sensitivity $S = \Delta\lambda/\Delta n$ generally increases linearly with increasing resonance wavelength in air, λ_{R0} , as has been shown analytically, through simulations, and in a meta-analysis [68].

This Chapter contains investigation into the evolution of modes, both transverse and longitudinal, as nanostructure height is increased from the planar case to be on the order of the wavelength, or more. We also investigate under what conditions an increased structure height translates into higher refractive index sensitivity, whether bulk or analyte.

5.1 Effect of height on nanostructure resonance properties

As shown previously, planar ($h=30\text{-}40$ nm) nanostructures may be capable of supporting one or more localized plasmonic resonances, particularly for structures lacking rotational symmetry, whose resonance properties may change depending on incident light polarization. The situation becomes more complicated as the height is increased from the planar case. With moderate height increase, the LSPR wavelength λ_R experiences a moderate blue shift. This is shown in the transmission spectra below in Figure 5.1, both in simulations and from experiments, for various arrays of nanostructures, including square dimers of designed side length $s=80$ nm and gap $g=30$ nm ($s_{80}g_{30}$ from Chapter 4) C_6 rotationally symmetric star-shaped structures with arm length $s=100$ nm in a square lattice, and gammadion cross structures with a half-arm length of $s=60$ nm. Unpolarized light was used to obtain the transmission spectra for all structures except the dimers, for which incident light was linearly polarized in the direction parallel to the gap.

Figure 5.1 Spectral effects from a moderate increase in height. (a) Simulation and (b) experimental transmission spectra for square dimers with a design side length of 80 nm and gap of 30 nm ($s_{80}g_{30}$). The simulated dimers have dimensions matching the experimental measurements presented in Chapter 4. (c) Simulation and (d) experimental transmission spectra for C_6 star shaped structures with design arm length of $s=100$ nm. (e) Simulation and (f) experimental transmission spectra for gammadion cross structures is arm section length of $s=60$ nm. Heights of structures in nm are displayed adjacent to their corresponding curves. Arrows show shift of relevant transmission minima.

In the case of the dimer simulations, main resonance wavelength decreases from 826 nm at a height of $h=20$ nm to a minimum of 710 nm when $h=90$ nm. For the experimental measurements we find that λ_R decreases from 701 nm ($h=30$ nm) to 659.4 nm ($h=84$ nm) to 652.9 nm ($h=104$ nm). Similarly, simulated C_6 stars blueshift from a dip at 1036 nm ($h=30$ nm) to a dip at 842 nm ($h=110$ nm), while experimentally the resonance was found to decrease from 951 nm ($h=30$ nm) to 859

nm ($h=65$ nm) to 820 nm ($h=80$ nm). In the case of the gammadion crosses, the planar structures exhibit a fundamental resonance at a long wavelength, and a higher order resonance at a shorter wavelength, as discussed previously [59]. For half arm lengths greater than $s=60$ nm, the fundamental mode is in the infrared (IR) range. The shorter arm length is chosen here because the fundamental resonance is measureable on the Cytoviva hyperspectral imaging system. In the simulations, as the height is increased from 30 nm to 110 nm, the fundamental mode blueshifts from 1080 nm to 884 nm, while the higher order mode undergoes a significantly less shift from 654 nm to 632 nm. Meanwhile, experimental data show that as the height is increased from 30 nm to 45 nm to 63 nm, the fundamental mode resonance wavelength shifts from 974.4 nm to 901.4 nm to 879.1 nm, and the higher order mode, shifting from 654.2 nm to 582.3 nm to 591.1 nm, shifts more than the simulations show. It should be noted that both in simulations and experiments, the higher order mode wavelength starts to redshift slightly after initially blue shifting, for increasing height. The simulation and experimental resonance wavelengths listed above are plotted in Figure 5.2.

Figure 5.2 Graphical representation of the blue shifts shown in the spectra of the previous figure

The blue shift of plasmonic resonance from an increase of resonator height is not comprehensively studied in the literature [174]. For example, the scattering properties of spheroidal nanoparticles have been theoretically studied [27,30], where the scattering efficiency peak of a prolate spheroid particle blue shifts as its aspect ratio is increased. This finding is experimentally confirmed by Henson et al. [139], who studied the effect of nanoparticle disk height in arrays of varying periodicities and heights. However, as shown in Figure 5.1, this phenomenon is not unique to a single nanostructure geometry. Although the geometries in the current study are not quite the same, we accept this as one plausible reason for the observed blueshift. One interpretation given by Henson et al. [139] uses the harmonic oscillator model. Alternatively, we also provide another interpretation, as follows:

Intuitively, the blue shift can be understood from the perspective of a localized plasmonic resonance as surface plasmon oscillation that is confined within the metallic nanostructure. This assumption is also the same premise for the “LC model” that explains the resonance behavior of split ring resonator [174]. As most plasmonic resonators can be understood as LC resonators, the LC model also holds for other resonator geometries [59]. By assuming that the damping loss to be dominated by ohmic loss of the plasmonic “wire”, increasing the resonator thickness can be understood as decreasing the “resistance” for the oscillating surface plasmons due to the larger cross-sectional area of the “plasmonic wire”. From the perspective of LC model, in the presence of loss the LC circuit is modified into the RLC parallel circuit with resistance in series with the inductor, which has resonance frequency of

$$\omega_0 = \sqrt{\frac{1}{LC} - \left(\frac{R}{L}\right)^2}. \quad (5.1)$$

Thus, we can see that smaller resistance, resulting from thicker resonator, give rise to a blue shift in the resonance frequency.

As the height is increased even more, on the order of the wavelength of visible light, the nanostructures may become cable of supporting so-called longitudinal modes. These modes may be considered as Fabry-Perot resonances, satisfying the condition

$$2k_0 n_{eff} h + \phi_1 + \phi_2 = 2\pi m, \quad (5.2)$$

where $k_0 = 2\pi/\lambda_0$ is the free space wavenumber of incident light, n_{eff} is the real part of the wavelength-dependent effective refractive index of a particular mode, h is the structure height, ϕ_1 and ϕ_2 are the wavelength-dependent reflection phases at the ends of the structure, and m is an integer. We may infer from this equation that, assuming the reflection don't suddenly decrease very rapidly, for a given m , increasing the structure height should increase the wavelength that satisfies the longitudinal resonance condition.

5.1.1 Square dimer simulations

We performed simulations for arrays of square dimers having side lengths s of 80 nm and 100 nm, and gaps g of 20 nm, 30 nm, and 40 nm, with period $p = 4s$ in both directions, varying the heights from 20 nm to 1000 nm in steps of 10 nm, with incident light polarized in either the x direction (parallel to gap separation) or the y direction (perpendicular to the gap). Transmission spectra for $s_{80}g_{20}$ (x -pol) for some heights between 20 nm and 140 nm are shown in Figure 5.3(a). It is clear that a longitudinal

mode develops with increasing height, as indicated by the arrows for $h=120$ nm and $h=140$ nm. We note that unlike the normal LSPR modes which blueshift with a moderate height increase, the longitudinal modes redshift with increasing height.

Figure 5.3 (a) Transmission spectra for periodic dimers $s_{80}g_{20}$, with heights from 20 nm to 140 nm in increments of 10 nm, and (b) Differences in transmission for dimers whose heights differ by 10 nm, where the subscripts indicate height in nm

In fact, this mode is present for heights even below 120 nm, as evidenced by asymmetry and bulges on either side of the LSPR peak for heights between 60 nm and 100 nm, which are due to the low-contrast longitudinal mode. In order to get a clearer idea of the height at which the longitudinal mode begins to be supported, we plot the differential transmission between dimers of heights differing by 10 nm in Figure 5.3(b). The curves are labeled such that $T_{40} - T_{30}$ indicates the transmission of dimers of height 40 nm minus that of dimers of height 30 nm. From the differential transmission, the blueshift of the LSPR mode is again clearly visible, as verified by the large shift in oscillation between $T_{30} - T_{20}$ and $T_{40} - T_{30}$. However, what can be seen in the differential transmission that is not as clear in the absolute transmission is the gradual redshift of the longitudinal mode, clearly visible in the progression from $T_{90} - T_{80}$ to $T_{100} - T_{90}$ and beyond. To investigate the behavior as the dimers are

grown even taller, we plot the transmission of the periodic dimer arrays with several heights ranging from 20 nm to 1000 nm below in Figure 5.5.

Figure 5.4 (a) Transmission spectra for periodic dimers $s_{80}g_{20}$, with heights from 20 nm to 140 nm in increments of 10 nm, and (b) Differences in transmission for dimers whose heights differ by 10 nm, where the subscripts indicate height in nm

The transmission through bare ITO is included in this figure to show that the gradual decrease in transmission for increasing wavelength is not due to the structures themselves, but due to the substrate. Though they are excited even at lower wavelengths, longitudinal modes can be seen clearly for wavelengths above 800 nm. They are easy to distinguish for heights above 100, as they lie at wavelengths longer than that of the LSPR resonance. For very tall structures, the transmission in the range of wavelengths less than about 550 nm becomes almost nil. We can gain a better understanding of what is happening to the longitudinal modes in the case of the dimers by looking at the data as heatmaps, where the x and y axes represent dimer height and transmission is represented by color. This is shown below in Figure 5.5, for all six combinations of dimer size and gap size, for dimers without rounded corners and with sizes equal to their nominal values.

Figure 5.5 Heatmaps of the transmission under x -polarization of square dimers with various side lengths s and gaps g , with heights from 20 nm to 1000 nm. (a) $s_{80}g_{20}$, (b) $s_{80}g_{30}$, (c) $s_{80}g_{40}$, (d) $s_{100}g_{20}$, (e) $s_{100}g_{30}$, and (f) $s_{100}g_{40}$. White lines have been added to trace the evolution of the longitudinal modes with height.

For all six of the dimers, we see the blue shift of the main resonance dip at $\lambda_R=750\text{-}800$ nm in the planar case ($h=20$ nm) to $\lambda_R=700\text{-}750$ nm for the moderately tall case. As the dimers increase in height above 100 nm, there appears to be no change in the location of this mode. For both the s_{80} and s_{100} dimers, we see the transmission dip at $\lambda=600$ nm, beginning when $h=60$ nm and becoming more prominent as the dimers get taller, eventually becoming indistinguishable from the broadband absorption occurring at all wavelengths below $\lambda=600$ nm. To verify that is indeed absorption occurring in that range, we plot the absorption and reflection heatmaps (and the transmission heatmap as in Figure 5.5(a) for reference) below in Figure 5.6.

Figure 5.6 Heatmaps for absorption, reflection and transmission for $s_{80}g_{20}$ under x -polarization, with heights from 20 nm to 1000 nm

Interestingly, the longitudinal resonances, marked with thin white lines in the Figure 5.5, appear to be very linear over a large range. In fact, each heatmap, only one linear slope ($d\lambda_R/dh$ - unitless) was determined independently. The remaining slopes were determined by multiplying the independent slope by simple rational numbers. If we denote the slope of the first mode to appear with increasing height as m_1 (also the highest slope), the slope of the next mode as m_2 , and so on, then we find that

$$m_j = \frac{m_1}{j}, j = 2, 3, 4, 5, \quad (5.3)$$

except in the case of $s_{100}g_{40}$ (Figure 5.5(f)), where the existence $j = 5$ mode cannot be seen within the height range simulated. The slopes of the white lines corresponding to the longitudinal resonances in the figure are tabulated below in Table 5.1.

Structure	$j = 1$	$j = 2$	$j = 3$	$j = 4$	$j = 5$
s_{80}	g_{20}	2.961	1.480	0.987	0.740
	g_{30}	2.755	1.377	0.918	0.689
	g_{40}	2.618	1.309	0.873	0.654
s_{100}	g_{20}	2.941	1.470	0.980	0.735
	g_{30}	2.709	1.354	0.903	0.677
	g_{40}	2.600	1.300	0.867	0.650

Table 5.1. Slopes $d\lambda_R/dh$ of white lines in Figure 5.5, denoting the slope of the j^{th} longitudinal resonance

We may infer from Equations (5.2) and (5.3) that after the first ($j = 1$) longitudinal mode, the subsequent modes are just “harmonics” of the fundamental mode. In other words, disregarding the phases from the reflections at the ends of the structure, whereas the fundamental longitudinal mode ($j = 1$) corresponds to a wavelength such that $h \cong \lambda_{R1}/2n_{eff}$, the second longitudinal mode ($j = 2$) corresponds to $h \cong 2 \lambda_{R1}/2n_{eff}$, and so on.

Though the above results are valid for a large range of wavelengths and structure heights, the slopes ($d\lambda_R/dh$) of the of the modes shown in the previous figures are not constant. Looking closely at the origins of the modes, we can see that their slopes are small following their becoming above cutoff (i.e. as the structure becomes tall enough to support it). After the height increases a bit more, the slope increases more quickly, eventually becoming constant. Perhaps most evident in the fundamental longitudinal modes, the slope does not remain constant indefinitely. Rather, it begins to decrease as structure height is increased further. The behavior resembles the dispersion relation of other types of waveguides, such as the LP_{01} mode of a single mode fiber [175] or the TM modes of a grounded slab waveguide [176].

From the heatmaps presented so far, we see that with increasing structure height there is quite a bit of modal interplay in the spectral region between the transmission dip existing in the planar case (and later blueshifting) and the transmission dip below $\lambda=600$ nm. Many of the longitudinal modes begin to appear at around a wavelength of 600 nm, above the region of broadband absorption, and then continue to increase in wavelength, moving through the “planar” dimer resonance, sometimes in a complex fashion. For example, in the case of the $s_{80}g_{20}$ dimer transmission (Figure 5.5(a) and Figure 5.6(c)), we can see the transmission dip of the fundamental longitudinal mode beginning (with low dip prominence) at around $\lambda=625$ nm for $h=70$ nm and continuing

fairly linearly through the transverse mode resonance with increasing height. The second through fourth longitudinal harmonics exhibit similar behavior. However, the $j=5$ resonance has no clear origin at wavelengths below those of the main transverse resonance. It is unclear whether the transmission dip evolving from $\lambda=625$ nm at $h=550$ nm to $\lambda=675$ nm at $h=875$ nm is related to the $j=5$ mode, in which case it resembles Rabi splitting between two coupled modes, or to a higher order ($j=6$ or other) mode.

Thus far, the results presented for the modal characteristics of arrays of tall square dimers have only considered x -polarized (parallel to the gap) light. For completeness, we also briefly look at the orthogonal polarization. In this case, incident light is not affected by the size of the gap, and so it is expected that the spectra will be the same for different gap sizes. To verify this, we plot below in Figure 5.7 the y -polarized transmission spectra for all six dimers at three various heights. As can be seen, an increasing gap size makes very little difference, resulting only in slightly lower transmission, particularly below $\lambda=600$ nm, and a slight redshift of 2 nm.

Figure 5.7 Simulation results of y -polarization transmission spectra for low ($h=30$ nm), moderately tall ($h=120$ nm), and tall ($h=1000$ nm), square dimers with gaps of 20, 30, and 40 nm. (a) square dimension $s=80$ nm dimers and (b) square dimension $s=100$ nm dimers

Because the transmission spectra for dimers of a given side length s but differing gap length g are so similar, for each s we examine all three types of spectra

(absorption, reflection, and transmission) for one value of g , namely $g=30$ nm. These spectra are shown below in Figure 5.8.

Figure 5.8 Heatmaps of y -polarization spectra for dimers with heights from $h=20$ nm to $h=1000$ nm (a)-(c) $s_{80}g_{30}$ and (d)-(f) $s_{100}g_{30}$

From the y -polarized transmission spectra (Figure 5.8(c) and (f)), we can see the transverse mode blue shift fairly quickly with increasing height and remain at the same wavelength for further increase in height. This resonance is particularly narrow for the $s=100$ nm dimers. It is easiest to see the existence of multiple longitudinal modes, or possibly the fundamental longitudinal mode and harmonics by looking at the reflection spectra in Figure 5.8 parts (b) and (e). The behavior of the $s=80$ nm and $s=100$ nm dimers is similar, so we will comment on the $s=80$ nm case. Here, it seems that there are three spectral regions where we see several modes exhibiting distinct positive values of $d\lambda_R/dh$, namely for $\lambda < 550$ nm, for $550 \text{ nm} < \lambda < 725$ nm, and for $\lambda > 725$

nm. The modes in the different spectral regions seem to be contiguous, but the interaction is complex, and as in the x -polarization case, there appears to be some mode interaction resembling Rabi splitting. Notably the y -polarization longitudinal modes have much lower contrast than those using x -polarization. This is also evident in the structures for $h=1000$ nm in Figure 5.7.

5.1.2 Rotationally symmetric structure simulations

As shown above, the spectral response of the dimer arrays is heavily dependent on the polarization of incident light. Because we are interested in making a plasmonic sensing platform that is inexpensive, we also focus on rotationally symmetric structures that exhibit more invariance to the incident polarization, such as C_6 rotationally symmetric stars and gammadion cross structures (see Figure 5.1), whose refractive index sensitivities and other spectral characteristics we have studied previously for the planar case [59]. We simulated the C_6 structure with arm length $s=80$ nm, for heights ranging from 30 nm to 1000 nm, with incident light polarized parallel to an opposing pair of arms. The absorption, reflection, and transmission spectra are presented below in Figure 5.9.

Figure 5.9 Heatmaps of spectra for C_6 stars with $s=80$ nm and period $p=240$ nm in the x and y directions, for heights from $h=30$ nm to $h=1000$ nm

The absorption, reflection, and transmission heatmaps of the C_6S_{80} structures in Figure 5.9, like those of the dimers, show a single transverse mode in the planar case which blueshifts upon height increase. Likewise, they also exhibit three spectral regions for taller structures: The first, below $\lambda=600$ nm, entails broadband absorption. The second, between 600 nm and the dip of the shifted transverse mode (between 700-750 nm), shows some existence of longitudinal modes interacting with the transverse mode. The third, for $\lambda>750$ nm, shows purely longitudinal modes with approximately linear slope $d\lambda_R/dh$. The final type of structure whose simulated spectral heatmaps are studied is the gammadion cross structure, with half-arm length of $s=60$ nm and periodicity $p=350$ nm, in both the x and y directions.

Figure 5.10 Heatmaps of spectra for gammadion cross structures with half arm length $s=60$ nm, for heights from $h=30$ nm to $h=1000$ nm

The spectra of gammadion cross structures presented in Figure 5.10 illustrate more complex mode evolutions than those seen for the previous structures. This is correlated to the existence of both a fundamental mode and a higher order mode, at 1080 nm and 654 nm, respectively, for a height of 30 nm. The fundamental mode undergoes a large blueshift between $h=30$ nm and $h=150$ nm, whereas the higher order mode only blueshifts slightly, remaining stationary for heights above 50 nm. Not only

is the spectral evolution with height very complex between these two modes, but there also appears to be more modes than for the other structures in the reflection for lower wavelengths. As before, longitudinal modes for longer wavelengths are visible; however, they are low contrast like those of the C_6 structure or the dimers under y -polarization.

5.2 Growth of nanostructures of various heights and comparison of sensitivities

In order to compare the refractive index sensitivities of structures of increasing height, the proposed seedless pulsed electrodeposition process was utilized with many different numbers of pulses, with the pulse parameters as follows: current density $j_{ON}=3 \text{ mA/cm}^2$, pulse period $T=0.4 \text{ s}$, and duty cycle $D=25\%$, the same as those used for electrodeposition of the nanostructures in **Error! Reference source not found.**Chapter 3 and dimers in Chapter 4. The types of structures fabricated include arrays of the following:

- C_n star shapes for $n=3,4,5,6$, and 8, with $s=80$ and 100 nm;
- u -shaped SRRs (u -SRRs) with side lengths $s=60, 80, 100, 120, 150, 180$, and 200 nm;
- Hybrid u -SRR-dimer shapes of various side lengths and gaps;
- Square dimers of side lengths $s=80$ and 100 nm, with gaps $g=20$ nm and 30 nm, and various connections;
- v -shaped SRRs (v -SRRs) of side various side lengths $s=60, 80$, and 100 nm, and opening angles $\theta=90^\circ, 60^\circ$, and 40° ; and
- Gammadion crosses with half-arm lengths of $s=60, 80, 100$, and 120 nm.

The EBL layout of these structures is shown in Figure 5.11.

Figure 5.11 Layout of the EBL pattern for deposition of structures using various numbers of pulses

The designations of various samples, along with the numbers of pulses and the surface material of the sacrificial dummy substrate, are shown in Table 5.2. Additionally, screenshots of many of the samples that were scanned using the Cytoviva hyperspectral imaging system are shown in Figure 5.12.

Sample	n_{pulse}	substrate	Sample	n_{pulse}	substrate
T12	3	ITO	T22	27	ITO
T13	6	Au	T23	30	Au
T14	9	Au	T24	33	Au
T15	12	Au	T25	21	Au
T16	15	Au	T26	24	Au
T17	15	ITO	T27	33	ITO
T18	18	Au	T28	36	Au
T19	21	Au	T29	42	Au
T20	24	Au	T30	48	Au
T21	27	Au	T31	54	Au

Table 5.2. Sample names, number of pulses, and surface material of dummy substrate

Figure 5.12 Compilation of screenshots of various scans from Cytoviva and ENVI software, with one dose from T21 enlarged for clarity.

As seen in the table, some of the samples were deposited in parallel with a bare ITO substrate, while others were deposited in parallel with an ITO substrate coated with gold. The effect on the growth rate has been previously discussed in Chapter 3, along with non-uniformity of the heights of different types of nanostructures on a given sample, which depend on the structure size and planar density. As there are many structures, heights were measured from oblique SEM micrographs as described in Chapter 4 for some of the structures, enough that heights can be approximated if necessary. For sample deposition when the dummy substrate is ITO (samples T17, T22, and T27 for the results shown here), the structures show a monotonic increase in height with increasing pulse number, as expected. However, a sample deposited in parallel with a dummy substrate coated with gold may have shorter structures than a sample deposited with fewer pulses in parallel with a bare ITO coated substrate. This is attributed to the lower resistivity of the gold, leading to a larger proportion of ions going to the gold rather than the templated ITO. Regardless, the samples used in the following experimental discussion, generally in order of increasing height, are T17, T21, T19, T24, T22, and T27. Examples from T27, the sample exhibiting tallest, and hence highest aspect ratio, structures achieved in this work, are shown in the figures.

Figure 5.13 SEMs of T27square dimers with EBL pattern having side length $s=100$ nm, $g=20$ nm, and periods $p=4s$, at 65% dose at (a) normal and (b) oblique incidence. The scale bars represent 500 nm.

Figure 5.14 SEMs of C_3 stars with EBL pattern arm length $s=100$ nm and periods $p=3s$: (a) 75% dose pattern at normal incidence, and periods (b) 65% dose at oblique incidence. The scale bars represent 500 nm.

From length measurements performed on the dimers shown in Figure 5.13, it was found that the average height is 142 ± 10 nm, and the average gap separation is 4.8 ± 1.5 nm. This represents a gap aspect ratio of 29.6, which is much higher than what was reported in the work of Chapter 4. The narrower gap in this case is likely due to the larger square patterns surrounding the resist, introducing more lateral pressure during the growth. The C_3 star structures with 65% full e-beam dose were measured to have an average height of 150.2 ± 9.9 nm, representing the tallest structures measured using the seedless pulsed electrodeposition method presented in this work. With a measured arm width of ~ 30 nm for the structures at 75% dose, these star shape components have aspect ratios of at least 5, as higher dose leads to laterally larger features. We note that, in order to avoid minimize the effects of overexposure at the center of the star patterns,

the writing patterns for the arms for the stars do not start from the center, but from a few nanometers off-center. Hence, for almost all the low-dose stars and some of the high-dose ones, there are gaps at the centers of the structures.

In Figure 5.15, we plot smoothed transmission spectra of the $C_{60}S_{80}$ arrays for several of these samples, showing the effect of increasing height. The directly measured and estimated heights of the structures are shown in the legend.

Figure 5.15 Measured transmission spectra for $C_{60}S_{80}$ structures from various samples. The measured and estimated heights (in nm) are shown in the legend

Except for the first two spectra, the trend of LSPR blueshift is observed as height is increased. It should be noted that that a higher e-beam dose was used in the patterning of the spectra shown for T17, leading to features of a slightly different lateral size. This is the likely explanation for an inherent blueshift of this “short” structure. Also noteworthy is the evolution of the longitudinal mode, as it noticeably redshifts from the $h \sim 80$ nm case to the $h \sim 140$ nm case. Next, the spectral change with an increase in bulk refractive index is examined. The structures were spin-coated with

PMMA, which has a refractive index of about $n=1.49$. The transmission spectra with air cladding (as in Figure 5.15) and with PMMA cladding (offset by 0.8) are shown in Figure 5.16, along with dashed and dotted lines tracing the redshift of the modes with increasing bulk refractive index n_B .

Figure 5.16 Measured transmission spectra for C_6S_{80} with air cladding and PMMA cladding (offset), with dashed and dotted lines connecting distinguishable modes

Figure 5.16 clearly demonstrates the redshifts that occur for the structures of different heights when the refractive index of the cladding is increased. It appears that for the blueshifted transverse modes, the shift is lower as height is increased above $h=60$ nm, as evidenced by the slopes of the dashed lines connecting the corresponding resonances. For T27, since the measurement with PMMA yields a broad peak whose origin (corresponding peak in the air cladding case) is unclear, there are no lines connecting the two spectra. However, for T24 and T22, despite the clear visibility of the longitudinal modes for the $n=1$ case, when the cladding index is increased to $n=1.49$, the larger-shifting dips caused by these modes do not lead to a clearly defined

dip (i.e. where $dT/d\lambda = 0$), as they shift to be too close to the respective transverse modes. Their location however can be estimated based on the lowest value calculated for $dT/d\lambda$ near their disturbance. Using this method, we tabulate the resonance wavelengths plotted in Figure 5.16 below in Table 5.3, along with estimates for the bulk sensitivity $S = \Delta\lambda/\Delta n$ based on the two points.

Sample	λ_{R0} (nm)	λ_{R1} (nm)	$\Delta\lambda$ (nm)	S (nm/RIU)
T17	746.8	847.7	100.9	205.9184
T21	748.9	837.7	88.8	181.2245
T24	567.2	675.8	108.6	221.6327
	715.7	802.6	86.9	177.3469
T22	595.6	713.7	118.1	241.0204
	701	768.7	67.7	138.1633
T27	609.6	-	-	-
	663.3	-	-	-

Table 5.3. Measured resonances in air (λ_{R0}) and in PMMA (λ_{R1}), the gray cells correspond to resonance locations that did not have obvious dips with zero derivative.

From the estimated sensitivities in the table, longitudinal modes clearly exhibit higher sensitivity than the transverse modes. However, using peak (dip) detection as a basis for sensitivity, it is important that the dips be distinguishable. With this information, two directions may be investigated: (1) using other types of nanostructures or nanostructures of different size to guaranty minimal overlap of the transverse and longitudinal modes in the refractive index range of interest, and (2) using a different sensitivity metric than simple peak/dip detection, such as the maximum normalized intensity derivative $FOM_B^* = \left(\frac{dI/dn}{I}\right)_{max}$ discussed in 2.2. Next, we show how through simulations how analyte sensitivity can be increased by using high aspect ratio dimers.

As shown previously, the tall nanostructures support longitudinal which shown an increased sensitivity to the surrounding refractive index over their planar counterparts. To demonstrate this, we performed FDTD simulations of arrays of

square dimers of side length $s = 100\text{nm}$, gap $g = 50\text{nm}$, and period $p = 400\text{nm}$ in the x and y directions, shown in Fig. 3(a), while varying the height and thickness of a coating of dielectric with refractive index 1.4. Light was polarized in the x direction, and periodic boundary conditions in the x and y directions were used.

Figure 5.17 Simulation of square dimer array. (a) On the top, a schematic representation of the array, and on the bottom, of one unit cell, and (b) transmission spectra for structure heights of 40nm, 120nm, and 400nm, offset vertically, with dielectric coating thickness of 0nm (none) to 20nm, from [177].

The transmission spectra for the various heights (offset) and coating thicknesses of the array of periodic square dimers are shown in Figure 5.17(b). For the short array, the resonance dip starts at 758 nm and shifts by only 44nm as the coating thickness is varied from 0nm (none) to 20 nm. However, the spectral characteristic changes as we increase the height to 120 nm, and we observe two sets of dips whose peak shift is greater than for the shorter structure, one which starts at 564 nm and increases by 50 nm, and another which goes from 756 nm to 828 nm, a shift of 72 nm. Finally, as the structures are grown even taller, to a height of 400nm, we see a set of resonance dips which start at 796 nm and increase to 940 nm as coating thickness is increased, meaning a shift of 144 nm, over 3 times higher than for the quasi-planar structures.

In order to verify the increased sensitivity of the longitudinal modes over their localized counterparts, we used a series of refractive index liquids to perform bulk

sensing experiments for some of the structures fabricated on sample T27. The spectra shown below in the figure are from the non-rotationally symmetric v -SRR array with an interior angle of 40° , a design arm length of $s=100$ nm, and a period of $p=3s$, written at 65% of full EBL dose. Similar structures on this sample were found to have a height around 130 nm. The refractive index liquids ranged from $n=1.30$ to $n=1.38$ in steps of 0.02.

Figure 5.18 Spectral measurements of the non-rotationally symmetric array of v -SRRs with arm length $s=100$ nm, opening angle of 40° , and period of $p=3s$ measured in air and in different refractive index solutions. (a) x-polarized and (b) y-polarized spectra, and dip position and best fit lines for (c) x-pol and (d) y-pol spectra.

Looking at the x -polarized spectra, it is difficult to distinguish the longitudinal mode from the magnetic mode present in the planar case [58], yet we see an increase in the sensitivity over similar ($\theta = 40^\circ$) planar structures with arm lengths ranging from 50 nm to 80 nm which have respectively monotonically increasing measured sensitivities of 50.8 nm/RIU to 96.4 nm/RIU [58]. In this tall ($h \sim 130$ nm) case, the sensitivity reaches 399 nm/RIU. For the y -polarized spectra, it is clear that the

longitudinal mode is separate from the mode which localized in the planar case. Tracking this mode, we find that the sensitivity is 387 nm/RIU. These numbers are higher than the theoretical maximum predicted for LSPR sensitivity by Zalyubovskiy [68], as shown in the figure below, which has been modified further from Figure 2.4. Also shown in the figure is the data from the tall ($h \sim 140$ nm) dimers in Chapter 4. The data points clearly lie above the curve representing the theoretical maximum sensitivity for LSPR, with the ν -SRRs having much higher sensitivity points with similar resonant wavelength, excluding the shell structure.

Figure 5.19 An extension of Figure 2.4. Scatter plot of the LSPR sensitivity data in other works (from Table 2.1) in yellow, along with the theoretical maximum in Equation (2.25) in blue. The orange squares with black outline represent the ν -SRR data from T27 as shown above in Figure 5.18. Adapted from [68].

5.3 Conclusions

This Chapter demonstrated the complexity of mode evolution for increasing structure height for several types of nanostructures, including square dimers, C_6 star structures, and gammadion crosses. Several samples with several types of

nanostructures were grown, and comparison of estimated bulk sensitivity was shown for the C_6 structures. It was shown that tall structures supporting longitudinal modes indeed offer the opportunity of higher bulk sensitivity than transverse modes of their planar counterparts, however, either structure type and height must be chosen carefully for a given refractive index range, or alternate means of detection may need to be considered, such as that based on the normalized intensity derivative. Moreover, simulations of dimers showed a large increase in analyte sensitivity over their planar counterparts, even for moderate heights of $h=120\text{nm}$. We also showed experimentally, that the tall ($h\sim 130\text{ nm}$) $v\text{-SRR}$ structures are capable of supporting longitudinal modes which enable a drastic increase in sensitivity over the theoretical maximum for LSPR-based sensing, almost 400 nm/RIU . Furthermore, the sensitivity results for the tall ($h\sim 140\text{ nm}$) dimer, with a $\sim 540\text{ nm}$ resonance in air and 281.5 nm/RIU sensitivity using the “localized” mode, deserve further study for determining the principle behind such high sensitivity. For LSPR sensors fabricated using lithography and physical deposition, this work represents a method that, while originally implemented with the goal of cost reduction, is also capable of delivering higher performance, in terms of sensitivity.

Chapter 6 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

In this thesis, we have demonstrated several processes involving seedless electrodeposition onto low-resistivity ITO-coated glass. This process was developed to be a more cost-effective alternative to the typical top-down method of nanostructure fabrication, e-beam evaporation, with the aim of lowering the cost of substrates to be used for biosensing applications.

In the first part of thesis we showed the development of a process for seedless pulsed electrodeposition with optimal pulse parameters and successful electrodeposition of gold on conductive substrates to create several types of structures, including high aspect ratio arrays of metallic nanostructures. To the best of our knowledge, this is the first experimental demonstration of seedless pulsed electrodeposition of high aspect ratio metallic nanostructures onto a substrate.

This work also showed electrodeposition of gold onto ITO using other modalities, such as using a negative resist pattern, the first such demonstration, and deposition onto high-resistivity ITO-coated glasses and titanium. With the negative technique, the pattern exposed on the substrate corresponds to the areas upon which gold is not deposited. This method has been thus far used to make tessellations of geometric

shapes and annular slits. It has higher potential than the positive technique for creating arrays of nanocavities in a metal matrix.

Different behavior was observed for the other substrates, for which the positive technique was used exclusively. On the high-resistivity ITO, in contrast to vertical growth seen in the low-resistivity case, we saw the deposition of gold nanoparticles on the surface. Attempts to deposit onto defined arrays of various metamaterial shapes were unsuccessful in faithfully reproducing the shapes. However large- and medium-area patterns were satisfactorily filled with nanoparticles of uniform size and spatial distribution, similar to what was previously shown using silver [143]. Applying the process to large areas of titanium also resulted in deposition of clearly visible nanoparticles, along with some clusters.

Almost all the structures were characterized with air cladding, while some also been characterized with other claddings, such as spin-coated resist, to quantify and compare the refractive index sensitivities of structures of different heights. It was found that the taller dimer structures presented in Chapter 4, while having lower refractive index sensitivity ($S \sim 168 \text{ nm/RIU}$) than other types of structures with visible resonance as tabulated and plotted in Chapter 2, represents a significant improvement over the 87 nm/RIU [172] and 123 nm/RIU [173] reported by others for similar structures.

As this process is capable of growing arrays of nanostructures taller than other fabrication methods, we wanted to investigate the nanostructure height effects on modes and sensitivity. Hence, this thesis shows the results of numerous simulations showing the complex mode evolution with an increase of nanostructure height. We used the established seedless pulsed electrodeposition process to grow many types of structures on several samples, varying the pulse number to achieve different heights,

began investigation into the effect of height on the transmission spectra and the sensitivity, and showed that taller structures, exhibiting longitudinal resonances, are capable of achieving higher refractive index sensitivity under certain conditions, as evidenced by the measured sensitivities of almost 400 nm/RIU at a resonant wavelength of 667 nm for ν -SRRs and 281 nm/RIU at a resonant wavelength of 541 nm for the dimers, well into the visible range and significantly above the theoretical limit for LSPR sensitivity for the given resonant wavelengths. This represents a step forward for LSPR-based sensors in terms of both cost reduction and performance enhancement.

6.2 Recommendations

1. The experimental fabrication described in Chapter 5 has yielded a plethora of structures of different heights. The spectra of these structures have all been analyzed for the case where the refractive index cladding is air. Many have also been analyzed with resist spin-coated on to provide a different cladding environment. However, for better bulk sensitivity characterization, more bulk index environments are needed, such as water and ethanol, at least for the subset of samples (T17, T21, etc.)
2. The fabricated structures should be characterized for their analyte sensitivity, preferably using self-assembled monolayers of thiols. These may be used in the context of comparing spectra with different chain lengths for characterizing the sensitivity or used for a specific binding experiment to determine how the limit of detection changes with structure height for a particular biological target.

3. For better understanding the modal interactions as structure height and cladding refractive index is changed in a simulation context, software such as MODE Solutions from Lumerical should be used to calculate modal indexes of refraction and dispersion properties.
4. The proposed processes may be used for fabricating structures for use in collaboration with other researchers with more biological and functionalization expertise. These processes may include both high aspect ratio structures and arrays of patches of nanoparticles. For the latter, this would entail the determination of the process parameters affecting the deposition properties of nanoparticles onto a low conductivity ITO substrate. These parameters, including deposition time, temperature, pulse duty cycle, bath additives, and pattern sizes, among others, should be varied for a comparison of the results. The properties compared consist mainly of nanoparticle size, density, and morphology.
5. It may be prudent to investigate the feasibility and possible applications of creating such high aspect ratio structures of other metals. These may include another noble metal such as silver, or ferromagnetic materials such as the commonly used nickel and the seldom deposited iron.

AUTHOR'S PUBLICATIONS

Journals

1. **Mueller AD**, Tobing LYM, Zhang DH. Combining sonicated cold development and pulsed electrodeposition for high aspect ratio sub-10 nm gap gold dimers for sensing applications in the visible spectrum. *Nanoscale*. 2018;5221–8. (**First Author**)
2. Soehartono AM*, **Mueller AD***, Tobing LYM, Chan KK, Zhang DH, Yong K-T. Ultra-small v-shaped gold split ring resonators for biosensing using fundamental magnetic resonance in the visible spectrum. *Nanotechnology*. 2017;28:405305. (**Co-First Author**)
3. **Mueller AD**, Tobing LYM, Zhang DH. Reliable Fabrication of High Aspect Ratio Plasmonic Nanostructures Based on Seedless Pulsed Electrodeposition. *Adv. Mater. Technol.* 2019;1800364:1–9 (**First Author**)
4. **Mueller AD**, Tobing LYM, Zhang DH. Effect of nanostructure height on plasmonic modes and sensitivity. In preparation. (**First Author**)
5. Tobing LYM, Goh GY, **Mueller AD**, Ke L, Luo Y, Zhang DH. Polarization invariant plasmonic nanostructures for sensing applications. *Sci Rep*. 2017;7(1):1–14.

Conference Proceedings

1. **Mueller AD**, Tobing LYM, Luo Y, Zhang DH. Vertical growth of plasmonic nanostructures via electrodeposition on a conductive oxide. *ICMAT 2017. Procedia Engineering* **215**, 60-65. **(First Author)**

REFERENCES

- [1] CDC. National Health Report Highlights. 2012.
- [2] Quesada-González D, Merkoçi A. Nanomaterial-based devices for point-of-care diagnostic applications. *Chem Soc Rev*. 2018;47:4697–709.
- [3] Howick J, Cals JWL, Jones C, Price CP, Plüddemann A, Heneghan C, et al. Current and future use of point-of-care tests in primary care: an international survey in Australia, Belgium, The Netherlands, the UK and the USA. *BMJ Open*. 2014;4:e005611.
- [4] Dey D, Goswami T. Optical Biosensors: A Revolution Towards Quantum Nanoscale Electronics Device Fabrication. *J Biomed Biotechnol*. 2011;2011:348218.
- [5] Damborsky P, Vitel J, Katrlík J. Optical biosensors. *Essays Biochem*. 2016;60(1):91–100.
- [6] Long F, Zhu A, Shi H. Recent Advances in Optical Biosensors for Environmental Monitoring and Early Warning. *Sensors*. 2013;13(10):13928–48.
- [7] St John A, Price CP. Existing and Emerging Technologies for Point-of-Care Testing. *Clin Biochem Rev*. 2014;35(3):155–67.
- [8] Homola J. Present and future of surface plasmon resonance biosensors. *Anal Bioanal Chem*. 2003;377:528–39.
- [9] Homola J. Surface Plasmon Resonance Sensors for Detection of Chemical and Biological Species. *Chem Rev*. 2008;108(2):462–93.
- [10] Li M, Cushing SK, Wu N. Plasmon-enhanced optical sensors: a review. *Analyst*. 2014;140:386–406.
- [11] Masson J-F. Surface Plasmon Resonance Clinical Biosensors for Medical Diagnostics. *ACS Sensors*. 2017;2:16–30.
- [12] Cetin AE, Etezadi D, Galarreta BC, Busson MP, Eksioğlu Y, Altug H. Plasmonic Nanohole Arrays on a Robust Hybrid Substrate for Highly Sensitive Label-Free Biosensing. *ACS Photonics*. 2015 Aug;2(8):1167–74.
- [13] Choi S, Chae J. Methods of reducing non-specific adsorption in microfluidic biosensors. *J Micromechanics Microengineering*. 2010;20(7).
- [14] Wu J, Gu M. Microfluidic sensing: state of the art fabrication and detection techniques. *J Biomed Opt*. 2011;16(8):080901.
- [15] Yu C, Irudayaraj J. Quantitative Evaluation of Sensitivity and

Selectivity of Multiplex NanoSPR Biosensor Assays. *Biophyscial J.* 2007;93(November):3684–92.

[16] Couture M, Ray KK, Crofton A, Masson J. 96-Well Plasmonic Sensing with Nanohole Arrays. *ACS Sensors.* 2016;1:287–94.

[17] Svedendahl M, Chen S, Dmitriev A, Käll M. Refractometric Sensing Using Propagating versus Localized Surface Plasmons: A Direct Comparison. *Nano Lett.* 2009;9(12):4428–33.

[18] Marquart JA. SPR Instruments [Internet]. SPR-Pages. [cited 2018 Jul 16]. Available from: <https://www.sprpages.nl/instruments>

[19] OpenSPR - Nicoya Lifesciences, Inc. [Internet]. Available from: <https://nicoyalife.com/products/openspr/>

[20] Anker JN, Hall WP, Lyandres O, Shah NC, Zhao J, Van Duyne RP. Biosensing with plasmonic nanosensors. *Nat Mater.* 2008;7(6):442–53.

[21] Päivänranta B, Merbold H, Giannini R, Büchi L, Gorelick S, David C, et al. High aspect ratio plasmonic nanostructures for sensing applications. *ACS Nano.* 2011;5(8):6374–82.

[22] Giorgis V, Zilio P, Massari M, Ruffato G, Zacco G, Romanato F. Fabrication of multiple large arrays of split ring resonators by X-ray lithographic process for sensing purposes. *Microelectron Eng.* 2014;127:68–71.

[23] Gorelick S, Guzenko V a, Vila-Comamala J, David C. Direct e-beam writing of dense and high aspect ratio nanostructures in thick layers of PMMA for electroplating. *Nanotechnology.* 2010;21:295303.

[24] Hanson GW. *NanoElectromagnetics.* 2011.

[25] Maier SA. *PLASMONICS: FUNDAMENTALS AND APPLICATIONS.* Springer Science+Business Media; 2007.

[26] Fan X, Zheng W, Singh DJ. Light scattering and surface plasmons on small spherical particles. *Light Sci Appl.* 2014;(March):1–14.

[27] Bohren CF, Huffman DR. *Absorption and Scattering of Light by Small Particles.* John Wiley & Sons, Inc.; 1998.

[28] Mie G. Contributions on the Optics of Turbid Media, Particularly Colloidal Metal Solutions. Vol. 25, *Annalen der Physik, Series IV.* 1908. p. 377–445.

[29] Stratton JA. *ELECTROMAGNETIC THEORY BY.* IEEE Press; 2007.

[30] Asano S. Light scattering properties of spheroidal particles. *Appl Opt.* 1979;18(5):712–23.

[31] Voshchinnikov N V., Farafonov VG. Optical properties of spheroidal particles. *Astrophys Space Sci.* 1993;204(1):19–86.

[32] Taflove A, Hagness SC. *Computational Electrodynamics: The Finite-Difference Time-Domain Method, Third Edition.* 3rd ed. Artech House; 2005. 1038 p.

[33] Jin J-M. *The Finite Element Method in Electromagnetics.*

Wiley-IEEE Press; 2014. 876 p.

[34] Draine BT, Flatau PJ. Discrete-Dipole Approximation For Scattering Calculations. *J Opt Soc Am A*. 1994;11(4):1491.

[35] Špačková B, Wrobel P, Bocková M, Homola J. Optical Biosensors Based on Plasmonic Nanostructures: A Review. *Proc IEEE*. 2016;104(12):2380–408.

[36] Krupin O, Wang C, Berini P. Detection of leukemia markers using long-range surface plasmon waveguides functionalized with Protein G. *Lab Chip*. 2015;15(21):4156–65.

[37] Lakowicz JR, Ray K, Chowdhury M, Szymanski H, Fu Y, Zhang J, et al. Plasmon-controlled fluorescence: a new paradigm in fluorescence spectroscopy. *Analyst*. 2008;133(10):1308.

[38] Chung T, Lee SY, Song EY, Chun H, Lee B. Plasmonic nanostructures for nano-scale bio-sensing. *Sensors*. 2011;11(11):10907–29.

[39] Yang JJ, Huang M, Tang H, Zeng J, Dong L. Metamaterial Sensors. *Int J Antennas Propag*. 2013;2013:1–16.

[40] Scarano S, Mascini M, Turner APF, Minunni M. Surface plasmon resonance imaging for affinity-based biosensors. *Biosens Bioelectron*. 2010;25(5):957–66.

[41] Lieberman RA, Blyler LL, Cohen LG. A Distributed Fiber Optic Sensor Based on Cladding Fluorescence. *J Light Technol*. 1990;8(2):212–20.

[42] Yuan J, El-sherif MA. Fiber-Optic Chemical Sensor Using Polyaniline as Modified Cladding Material. *IEEE Sens J*. 2003;3(1):5–12.

[43] Wang P, Brambilla G, Ding M, Semenova Y, Wu Q, Farrell G. High-sensitivity , evanescent field refractometric sensor based on a tapered , multimode fiber interference. *Opt Lett*. 2011;36(12):2233–5.

[44] Ding J, Zhang AP, Shao L, Yan J, He S. Fiber-Taper Seeded Long-Period Grating Pair as a Highly Sensitive Refractive-Index Sensor. *IEEE Photonics Technol Lett*. 2005;17(6):1247–9.

[45] Jensen JB, Pedersen LH, Hoiby PE, Nielsen LB, Hansen TP, Folkenberg JR, et al. Photonic crystal fiber based evanescent-wave sensor for detection of biomolecules in aqueous solutions. *Opt Lett*. 2004;29(17):1974–6.

[46] Rindorf L, Jensen JB, Dufva M, Pedersen LH, Høiby PE, Bang O. Photonic crystal fiber long-period gratings for biochemical sensing. *Opt Express*. 2006;14(18):358–62.

[47] Wu DKC, Kuhlmeier BT, Eggleton BJ. Ultrasensitive photonic crystal fiber refractive index sensor. *Opt Lett*. 2009;34(3):322–4.

[48] Li J, Zhu J-J. Quantum dots for fluorescent biosensing and bio-imaging applications. *Analyst*. 2013;138:2506–15.

[49] Ao L, Gao F, Pan B, He R, Cui D. Fluoroimmunoassay for Antigen Based on Fluorescence Quenching Signal of Gold Nanoparticles. *Anal Chem*. 2006;78(4):1104–6.

- [50] Hong W, Li W, Hu X, Zhao B, Zhang F, Zhang D. Highly sensitive colorimetric sensing for heavy metal ions by strong polyelectrolyte photonic hydrogels. *J Mater Chem*. 2011;21:17193–201.
- [51] S AP V, Joseph P, G KDSC, Lakshmanan S, Kinoshita T, Muthusamy S. Colorimetric sensors for rapid detection of various analytes. *Mater Sci Eng C*. 2017;78:1231–45.
- [52] Stiles PL, Dieringer JA, Shah NC, Duyne RP Van. Surface-Enhanced Raman Spectroscopy. *Annu Rev Anal Chem*. 2008;1:601–26.
- [53] Orendorff CJ, Gearheart L, Jana NR, Murphy CJ. Aspect ratio dependence on surface enhanced Raman scattering using silver and gold nanorod substrates. *Phys Chem Chem Phys*. 2006;8(1):165–70.
- [54] Yu Q, Braswell S, Christin B, Xu J, Wallace PM, Gong H, et al. Surface-enhanced Raman scattering on gold quasi-3D nanostructure and 2D nanohole arrays. *Nanotechnology*. 2010;21:355301.
- [55] Chen Y, Ming H. Review of surface plasmon resonance and localized surface plasmon resonance sensor. *Photonic Sensors*. 2012 Mar;2(1):37–49.
- [56] Homola J. Surface plasmon resonance sensors for detection of chemical and biological species. *Chem Rev*. 2008;108(2):462–93.
- [57] Liu H, Wang B, Leong ESP, Yang P, Zong Y, Si G, et al. Enhanced Surface Plasmon Resonance on a Smooth Silver Film with a Seed Growth Layer. *ACS Nano*. 2010;4(6):3139–46.
- [58] Soehartono AM, Mueller AD, Tobing LYM, Chan KK, Zhang DH, Yong K-T. Ultra-small v-shaped gold split ring resonators for biosensing using fundamental magnetic resonance in the visible spectrum. *Nanotechnology*. 2017;28:405305.
- [59] Tobing LYM, Goh GY, Mueller AD, Ke L, Luo Y, Zhang DH. Polarization invariant plasmonic nanostructures for sensing applications. *Sci Rep*. 2017;7(1):1–14.
- [60] Špringer T, Ermini ML, Špačková B, Jabloňkú J, Homola J. Enhancing sensitivity of surface plasmon resonance biosensors by functionalized gold nanoparticles: Size matters. *Anal Chem*. 2014;86(20):10350–6.
- [61] Verellen N, Dorpe P Van, Huang C, Lodewijks K, Vandenbosch GAE, Lagae L, et al. Plasmon Line Shaping Using Nanocrosses for High Sensitivity Localized Surface Plasmon Resonance Sensing. *Nano Lett*. 2011;11:391–7.
- [62] Gutha RR, Sadeghi SM, Hatef A, Sharp C, Lin Y. Ultrahigh refractive index sensitivity via lattice-induced meta-dipole modes in flat metallic nanoantenna arrays. *Appl Phys Lett*. 2018;112(22).
- [63] Homola J. Surface Plasmon Resonance Based Sensors. Berlin, Germany: Springer; 2006.
- [64] Miller MM, Lazarides AA. Sensitivity of Metal Nanoparticle Surface Plasmon Resonance to the Dielectric Environment. *J Phys Chem B*.

2005;109:21556–65.

[65] Khalavka Y, Becker J, Sönnichsen C. Synthesis of Rod-Shaped Gold Nanorattles with Improved Plasmon Sensitivity and Catalytic Activity. *J Am Chem Soc.* 2009;131:1871–5.

[66] Lee KS, El-Sayed MA. Gold and Silver Nanoparticles in Sensing and Imaging : Sensitivity of Plasmon Response to Size , Shape , and Metal Composition. *J Phys Chem B.* 2006;110:19220–5.

[67] Chen H, Kou X, Yang Z, Ni W, Wang J. Shape-and Size-Dependent Refractive Index Sensitivity of Gold Nanoparticles. *Langmuir.* 2008;24:5233–7.

[68] Zalyubovskiy SJ, Bogdanova M, Deinega A, Lozovik Y, Pris AD, An KH, et al. Theoretical limit of localized surface plasmon resonance sensitivity to local refractive index change and its comparison to conventional surface plasmon resonance sensor. *J Opt Soc Am A.* 2012;29(6):994–1002.

[69] Sherry LJ, Jin R, Mirkin CA, Schatz GC, Duyne RP Van. Localized Surface Plasmon Resonance Spectroscopy of Single Silver Triangular Nanoprisms. *Nano Lett.* 2006;6(9):2060–5.

[70] Sonnefraud Y, Verellen N, Sobhani H, Vandenbosch GAE, Moshchalkov V V, Van Dorpe P, et al. Experimental Realization of Subradiant, Superradiant, and Fano Resonances in Ring/Disk Plasmonic Nanocavities. *ACS Nano.* 2010;4(3):1664–70.

[71] Sun Y, Xia Y. Increased Sensitivity of Surface Plasmon Resonance of Gold Nanoshells Compared to That of Gold Solid Colloids in Response to Environmental Changes. *Anal Chem.* 2002;74(20):5297–305.

[72] Coronado EA, Schatz GC. Surface plasmon broadening for arbitrary shape nanoparticles : A geometrical probability approach. *J Chem Phys.* 2003;119(7):3926–34.

[73] Nehl CL, Liao H, Hafner JH. Optical Properties of Star-Shaped Gold Nanoparticles. *Nano Lett.* 2006;6(4):683–8.

[74] Wang H, Brandl DW, Le F, Nordlander P. Nanorice : A Hybrid Plasmonic Nanostructure. *Nano Lett.* 2006;6(4):827–32.

[75] McPhillips J, Murphy A, Jonsson MP, Hendren WR, Atkinson R, Höök F, et al. High-performance biosensing using arrays of plasmonic nanotubes. *ACS Nano.* 2010;4(4):2210–6.

[76] Mayer KM, Lee S, Liao H, Rostro BC, Fuentes A, Scully PT, et al. A label-free immunoassay based upon localized surface plasmon resonance of gold nanorods. *ACS Nano.* 2008;2(4):687–92.

[77] Lyvers DP, Moon JM, Kildishev A V., Shalaev VM, Wei A. Gold nanorod arrays as plasmonic cavity resonators. *ACS Nano.* 2008;2(12):2569–76.

[78] Bukasov R, Shumaker-Parry JS. Highly Tunable Infrared Extinction Properties of Gold Nanocrescents. *Nano Lett.* 2007;7(5):1113–8.

[79] Larsson EM, Alegret J, Käll M, Sutherland DS. Sensing Characteristics of NIR Localized Surface Plasmon Resonances in Gold

Nanorings for Application as Ultrasensitive Biosensors. *Nano Lett.* 2007;7(5):1256–63.

[80] Nusz GJ, Curry AC, Marinakos SM, Wax A, Chilkoti A. Rational Selection of Gold Nanorod Geometry for Label-Free Plasmonic Biosensors. *ACS Nano.* 2009;3(4):795–806.

[81] Estevez MC, Otte MA, Sepulveda B, Lechuga LM. Trends and challenges of refractometric nanoplasmonic biosensors: A review. *Anal Chim Acta.* 2014;806(January):55–73.

[82] Becker J, Trügler A, Jakab A, Hohenester U, Sönnichsen C. The Optimal Aspect Ratio of Gold Nanorods for Plasmonic Bio-sensing. *Plasmonics.* 2010;5:161–7.

[83] Li J, Ye J, Chen C, Li Y, Verellen N, Moshchalkov V V, et al. Revisiting the Surface Sensitivity of Nanoplasmonic Biosensors. *ACS Photonics.* 2015;2:425–31.

[84] Dubois L, Nuzzo RG. SYNTHESIS, STRUCTURE, AND PROPERTIES OF MODEL ORGANIC SURFACES. *Annu Rev Phys Chem.* 1992;43:437–63.

[85] Chieh C. Bond Lengths and Energies [Internet]. Personal Page of Chung Chieh, Professor Emeritus of Chemistry University of Waterloo. Available from: <http://www.science.uwaterloo.ca/~cchieh/cact/c120/bondel.html>

[86] Boeckl M, Graham D. Molecular Self-Assembly. *Mater Matters.* 2006;1(2).

[87] MicroChemicals. Resists, Developers and Removers. 2013.

[88] Liu H yu, Liu ED. Diffusion in AZ-5214 image reversal process and its application to e-beam proximity effect correction. *Microelectron Eng.* 1987;6(1–4):439–46.

[89] Dunbobbin DR, Faguet J, Lin BJ. Single-Step, Positive-Tone, Lift-Off Process Using AZ 5214-E Resist. In: *Proceedings of SPIE - The International Society for Optical Engineering. International Society for Optics and Photonics*; 1988. p. 247–55.

[90] Bard AJ, Faulkner LR. *ELECTROCHEMICAL METHODS Fundamentals and Applications. Electrochemistry. I.* Faulkner, Larry R. John Wiley & Sons, Inc.; 2001. 833 p.

[91] Paunovic M, Schlesinger M. *Fundamentals of Electrochemical Deposition.* 2nd ed. Wiley-Interscience; 2006.

[92] Abys JA, Brankovic SR, Dini JW, Bari GA Di, Tacconi NR de, Dimitrov N, et al. *Modern Electroplating.* 5th ed. Schlesinger M, Paunovic M, editors. 2010. 737 p.

[93] Reid J. Damascene Copper Electroplating. In: *Handbook of semiconductor manufacturing technology.* Taylor & Francis Group, LLC; 2007. p. 1–48.

[94] Lumerical Solutions, Inc. [Internet]. Available from: <https://www.lumerical.com/tcad-products/fdtd/>

- [95] Srituravanich W, Fang N, Sun C, Luo Q, Zhang X. Plasmonic nanolithography. *Nano Lett.* 2004;4(6):1085–8.
- [96] Xie Z, Yu W, Wang T, Zhang H, Fu Y, Liu H, et al. Plasmonic Nanolithography: A Review. *Plasmonics.* 2011;6(3):565–80.
- [97] Wang S, Wu PC, Su VC, Lai YC, Hung Chu C, Chen JW, et al. Broadband achromatic optical metasurface devices. *Nat Commun.* 2017;8(1):1–9.
- [98] Khorasaninejad M, Capasso F. Metalenses: Versatile multifunctional photonic components. *Science* (80-). 2017 Dec 1;358(6367):eaam8100.
- [99] Tobing LYM, Tjahjana L, Zhang DH. Sub-10-nm Size and Sub-40-nm Pitch Metal Dot Patterning for Low-Cost Bit Patterned Media Application. *IEEE Trans Nanotechnol.* 2014;13(3):496–501.
- [100] Albrecht TR, Bedau D, Dobisz E, Gao H, Grobis M, Hellwig O, et al. Bit Patterned Media at 1 Tdot/in² and Beyond. *IEEE Trans Magn.* 2013;49(2):773–8.
- [101] Fort E, Grésillon S. Surface enhanced fluorescence. *J Phys D Appl Phys.* 2008;41(1).
- [102] Zhan Z, Grote F, Wang Z, Xu R, Lei Y. Degenerating Plasmonic Modes to Enhance the Performance of Surface Plasmon Resonance for Application in Solar Energy Conversion. *Adv Energy Mater.* 2015;5(24):1–7.
- [103] Mubeen S, Lee J, Singh N, Krämer S, Stucky GD, Moskovits M. An autonomous photosynthetic device in which all charge carriers derive from surface plasmons. *Nat Nanotechnol.* 2013;8(4):247–51.
- [104] Linic S, Christopher P, Ingram DB. Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. *Nat Mater.* 2011;10(12):911–21.
- [105] Mosier-Boss P. Review of SERS Substrates for Chemical Sensing. *Nanomaterials.* 2017;7(6):142.
- [106] Zhan Z, Lei Y. Sub-100-nm nanoparticle arrays with perfect ordering and tunable and uniform dimensions fabricated by combining nanoimprinting with ultrathin alumina membrane technique. *ACS Nano.* 2014;8(4):3862–8.
- [107] Luches P, di Bona A, Contri SF, Gazzadi GC, Vavassori P, Albertini F, et al. Arrays of Metal Nanostructures Produced by Focussed Ion Beam. *Acta Phys Pol A.* 2007;112(6):1297–312.
- [108] Tobing LYM, Tjahjana L, Zhang DH. Direct patterning of high density sub-15 nm gold dot arrays using ultrahigh contrast electron beam lithography process on positive tone resist. *Nanotechnology.* 2013;24(7):075303.
- [109] Barcelo SJ, Lam S, Gibson GA, Sheng X, Henze D. Nanosphere lithography based technique for fabrication of large area well ordered metal particle arrays. In: *Proc SPIE 8323, Alternative Lithographic Technologies IV.*

2012. p. 83232L.

[110] Halpern AR, Corn RM. Lithographically Patterned Electrodeposition of Gold, Silver, and Resonances. *ACS Nano*. 2013;7(2):1755–62.

[111] Lindquist NC, Nagpal P, McPeak KM, Norris DJ, Oh S. Engineering metallic nanostructures for plasmonics and nanophotonics. *Reports Prog Phys*. 2012;75:036501.

[112] Chen Y. Nanofabrication by electron beam lithography and its applications: A review. *Microelectron Eng*. 2015;135:57–72.

[113] Lindquist NC, Nagpal P, McPeak KM, Norris DJ, Oh S-H. Engineering metallic nanostructures for plasmonics and nanophotonics. *Reports Prog Phys*. 2012;75(3):036501.

[114] Yan Y, Rashad MI, Teo EJ, Tanoto H, Teng J, Bettiol AA. Selective electroless silver plating of three dimensional SU-8 microstructures on silicon for metamaterials applications. *Opt Mater Express*. 2011;1(8):1548.

[115] Chen YT, Lo TN, Chiu CW, Wang JY, Wang CL, Liu CJ, et al. Fabrication of high-aspect-ratio Fresnel zone plates by e-beam lithography and electroplating. *J Synchrotron Radiat*. 2008;15(2):170–5.

[116] Kim MR, Lee DK, Jang D-J. Template-Based Electrochemically Controlled Growth of Segmented Multimetal Nanorods. *J Nanomater*. 2010;(203756):1–7.

[117] Mueller AD, Tobing LYM, Zhang DH. Combining sonicated cold development and pulsed electrodeposition for high aspect ratio sub-10 nm gap gold dimers for sensing applications in the visible spectrum. *Nanoscale*. 2018;5221–8.

[118] Blaber MG, Arnold MD, Ford MJ. A review of the optical properties of alloys and intermetallics for plasmonics. *J Phys Condens Matter*. 2010;22(14):143201.

[119] West PR, Ishii S, Naik G V., Emani NK, Shalaev VM, Boltasseva A. Searching for better plasmonic materials. *Laser Photonics Rev*. 2010;4(6):795–808.

[120] Tobing LYM, Zhang DH. New processes associated with electron beam lithography for ultra- small resonators. In: *Proc SPIE 10146, Advances in Patterning Materials and Processes XXXIV*. 2017. p. 101461Q–1.

[121] Etchegoin PG, Le Ru EC, Meyer M. An analytic model for the optical properties of gold. *J Chem Phys*. 2006;125:164705.

[122] Rupp R, Field E, Near E, Bump a S, Rupp R. Electric field enhancement near a surface bump. *Solid State Commun*. 1981;39(4):903–6.

[123] Koenderink AF, Alu A, Polman A. Nanophotonics: Shrinking light-based technology. *Science (80-)*. 2015;348(6234):516–21.

[124] Cao G. *Nanostructures & Nanomaterials: Synthesis, Properties & Applications*. Imperial College Press; 2004.

[125] Cui Z. *Nanofabrication Principles, Capabilities, and Limits*.

Springer; 2008. 343 p.

[126] Chiam SY, Singh R, Gu J, Han J, Zhang W, Bettiol AA. Increased frequency shifts in high aspect ratio terahertz split ring resonators. *Appl Phys Lett*. 2009;94(6):92–5.

[127] Du K, Wathuthanthri I, Mao W, Xu W, Choi CH. Large-area pattern transfer of metallic nanostructures on glass substrates via interference lithography. *Nanotechnology*. 2011;22(28):285306.

[128] Green TA. Gold etching for microfabrication. *Gold Bull*. 2014;47(3):205–16.

[129] Ranade RM, Ang SS, Brown WD. Reactive Ion Etching of Thin Gold Films. *J Electrochem Soc*. 1993;140(12):3676.

[130] Kang TY, Kim G, Cho IH, Seo D, Hong SJ. Process optimization of CF₄/Ar plasma etching of Au using I-optimal design. *Thin Solid Films*. 2009;517(14):3919–22.

[131] Qu NS, Zhu D, Chan KC, Lei WN. Pulse electrodeposition of nanocrystalline nickel using ultra narrow pulse width and high peak current density. *Surf Coatings Technol*. 2003;168(2–3):123–8.

[132] El-Sherik AM, Erb U, Page J. Microstructural evolution in pulse plated nickel electrodeposits. *Surf Coatings Technol*. 1996;88:70–8.

[133] Ibl N, Puippe JC, Angerer H. Electrocrystallization in pulse electrolysis. *Surf Technol*. 1978;6(4):287–300.

[134] Chen CJ, Wan CC. A Study of the Current Efficiency Decrease Accompanying Short Pulse Time for Pulse Plating. *J Electrochem Soc*. 1989;136(10):2850–5.

[135] Karami H, Babaei H. Electroplating Nanostructured Hard Gold through the Pulse Galvanostatic Method. *Int J Electrochem Sci*. 2012;7:601–14.

[136] Alfantazi AM, Page J, Erb U. Pulse plating of Zn-Ni alloy coatings. *J Appl Electrochem*. 1996;26(12):1225–34.

[137] Johnson PB, Christy RW. Optical Constants of the Noble Metals. *Phys Rev B*. 1972;6(12):4370–9.

[138] Melciu D, Maidee N. Pulse-Electroplating : Process Parameters and Their Influence on the Formed Microstructure Pulse-Electroplating : Process Parameters and Their Influence on the Formed Microstructure. Chalmers University; 2015.

[139] Henson J, Dimaria J, Paiella R. Influence of nanoparticle height on plasmonic resonance wavelength and electromagnetic field enhancement in two-dimensional arrays. *J Appl Phys*. 2009;106(9):1–6.

[140] Zhan Z, Xu R, Mi Y, Zhao H, Lei Y. Highly Controllable Surface Plasmon Resonance Property by Heights of Ordered Nanoparticle Arrays Fabricated via a Nonlithographic Route. *ACS Nano*. 2015;9(4):4583–90.

[141] Tobing LYM, Luo Y, Low KS, Zhang D, Zhang DH. Observation of the Kinetic Inductance Limitation for the Fundamental Magnetic Resonance in Ultrasmall Gold v-Shape Split Ring Resonators. *Adv Opt Mater*.

2016;4(7):1047–52.

[142] Xu Z, Li T, Zhang D, Yan C, Li D, Tobing LYM, et al. Groove-structured metasurfaces for modulation of surface plasmon propagation. *Appl Phys Express*. 2014;7(052001):1–4.

[143] Yang B, Lu N, Huang C, Qi D, Shi G, Xu H, et al. Electrochemical Deposition of Silver Nanoparticle Arrays with Tunable Density. 2009;(24):55–8.

[144] Garcia-Vidal FJ, Lezec HJ, Ebbesen TW, Martin-Moreno L. Multiple Paths to Enhance Optical Transmission through a Single Subwavelength Slit. *Phys Rev Lett*. 2003;90(21):213901.

[145] Yin L, Vlasko-vlasov VK, Pearson J, Hiller JM, Hua J, Welp U, et al. Subwavelength Focusing and Guiding of Surface Plasmons. *Nano Lett*. 2005;5(7):1399–402.

[146] Cho K, Loget G, Corn RM. Lithographically patterned nanoscale electrodeposition of plasmonic, bimetallic, semiconductor, magnetic, and polymer nanoring arrays. *J Phys Chem C*. 2014;118(50):28993–9000.

[147] Liu J, Ma Y, Shao J, Zhang S, Chen Y. Ultra-tall sub-wavelength gold nano pillars for high sensitive LSPR sensors. *Microelectron Eng*. 2018;196(March):7–12.

[148] Hili K, Fan D, Guzenko V a., Ekinci Y. Nickel electroplating for high-resolution nanostructures. *Microelectron Eng*. 2015;141:122–8.

[149] Wi J, Lee H, Lim K, Nam S, Kim H, Park S, et al. Fabrication of Silicon Nanopillar Teradot Arrays by Electron-Beam Patterning for Nanoimprint Molds. *Small*. 2008;4(12):2118–22.

[150] Huang X, Neretina S, El-Sayed M a. Gold nanorods: From synthesis and properties to biological and biomedical applications. *Adv Mater*. 2009;21:4880–910.

[151] Kabashin A V., Evans P, Pastkovsky S, Hendren W, Wurtz GA, Atkinson R, et al. Plasmonic nanorod metamaterials for biosensing. *Nat Mater*. 2009 Nov;8(11):867–71.

[152] Caldwell JD, Glembocki O, Bezares FJ, Bassim ND, Rendell RW, Feygelson M, et al. Plasmonic Nanopillar Arrays for Large-Area, High-Enhancement Surface-Enhanced Raman Scattering Sensors. *ACS Nano*. 2011;5(5):4046–55.

[153] Ono A, Kato J, Kawata S. Subwavelength Optical Imaging through a Metallic Nanorod Array. *Phys Rev Lett*. 2005 Dec;95(26):267407.

[154] Elser J, Wangberg R, Podolskiy V a., Narimanov EE. Nanowire metamaterials with extreme optical anisotropy. *Appl Phys Lett*. 2006;89(26):261102.

[155] Cetin AE, Etezadi D, Altug H. Accessible Nearfields by Nanoantennas on Nanopedestals for Ultrasensitive Vibrational Spectroscopy. *Adv Opt Mater*. 2014 Sep;2(9):866–72.

[156] Clark AW, Glidle A, Cumming DRS, Cooper JM. Plasmonic split-ring resonators as dichroic nanophotonic DNA biosensors. *J Am Chem*

Soc. 2009;131(48):17615–9.

[157] Hulteen JC, Duyne RP Van. Nanosphere lithography: A materials general fabrication process for periodic particle array surfaces. *J Vac Sci Technol A Vacuum, Surfaces, Film*. 1995;13(3):1553–7.

[158] Hulteen JC, Treichel DA, Smith MT, Duval ML, Jensen TR, Duyne RP Van. Nanosphere Lithography: Size-Tunable Silver Nanoparticle and Surface Cluster Arrays. *J Phys Chem B*. 1999;103:3854–63.

[159] Masuda H, Yasui K, Sakamoto Y, Nakao M, Tamamura T, Nishio K. Ideally Ordered Anodic Porous Alumina Mask Prepared by Imprinting of Vacuum-Evaporated Al on Si. *Jpn J Appl Phys*. 2001;40:L1267–9.

[160] Chen B, Lu K, Tian Z. Novel Patterns by Focused Ion Beam Guided Anodization. *Langmuir*. 2010;27(2):800–8.

[161] Smith JT, Hang Q, Franklin AD, Janes DB, Sands TD. Highly ordered diamond and hybrid triangle-diamond patterns in porous anodic alumina thin films. *Appl Phys Lett*. 2008;93:043108.

[162] Ocola LE, Stein A. Effect of cold development on improvement in electron-beam nanopatterning resolution and line roughness. *J Vac Sci Technol B Microelectron Nanom Struct*. 2006;24(6):3061.

[163] Hu W, Sarveswaran K, Lieberman M, Bernstein GH. Sub-10 nm electron beam lithography using cold development of poly(methylmethacrylate). *J Vac Sci Technol B Microelectron Nanom Struct*. 2004;22(4):1711–6.

[164] Yan M, Choi S, Subramanian KR V., Adesida I. The effects of molecular weight on the exposure characteristics of poly(methylmethacrylate) developed at low temperatures. *J Vac Sci Technol B Microelectron Nanom Struct*. 2008;26(6):2306.

[165] Cord B, Lutkenhaus J, Berggren KK. Optimal temperature for development of poly(methylmethacrylate). *J Vac Sci Technol B Microelectron Nanom Struct*. 2007;25(6):2013.

[166] Tobing LYM, Tjahjana L, Zhang DH. Large contrast enhancement by sonication assisted cold development process for low dose and ultrahigh resolution patterning on ZEP520A positive tone resist. *J Vac Sci Technol B Microelectron Nanom Struct*. 2012;30(5):051601.

[167] Tobing LYM, Zhang DH. New processes associated with electron-beam lithography for ultra-small resonators. In: Hohle CK, Gronheid R, editors. *International Society for Optics and Photonics*; 2017. p. 101461Q.

[168] Hao E, Schatz GC. Electromagnetic fields around silver nanoparticles and dimers. *J Chem Phys*. 2004;120(1):357–66.

[169] Liu N, Giessen H. Coupling Effects in Optical Metamaterials. *Angew Chemie Int Ed*. 2010 Dec;49(51):9838–52.

[170] Polyanskiy MN. Refractive index database.

- [171] Tobing LYM, Tjahjana L, Zhang DH, Zhang Q, Xiong Q. Deep subwavelength fourfold rotationally symmetric split-ring-resonator metamaterials for highly sensitive and robust biosensing platform. *Sci Rep*. 2013;3:2437.
- [172] Cheng Y, Wang M, Borghs G, Chen H. Gold Nanoparticle Dimers for Plasmon Sensing. *Langmuir*. 2011;27:7884–91.
- [173] Takei H, Bessho N, Ishii A, Okamoto T, Vieker H, Götzhäuser A. Enhanced Infrared LSPR Sensitivity of Cap-Shaped Gold Nanoparticles Coupled to a Metallic Film. *Langmuir*. 2014;30:2297–305.
- [174] Rockstuhl C, Zentgraf T, Guo H, Liu N, Etrich C, Loa I, et al. Resonances of split-ring resonator metamaterials in the near infrared. *Appl Phys B Lasers Opt*. 2006;84(1–2):219–27.
- [175] Saleh BEA, Teich MC. *Fundamentals of Photonics*. John Wiley & Sons, Inc.; 2001.
- [176] Pozar D. *Microwave Engineering* Fourth Edition. 2005. 1-756 p.
- [177] Mueller AD, Tobing LY, Luo Y, Zhang D-H. Vertical growth of plasmonic nanostructures via electrodeposition on a conductive oxide. *Procedia Eng*. 2017;215:60–5.

Appendix A SUPPORTING INFORMATION FOR

FABRICATION AND MEASUREMENTS

A.1 Pulse Waveforms for Nanostructures in Chapter 3

Figure A-1 shows the voltage and current waveforms for the two different samples. The sample with $n=10$ pulses had a signal sampling time of 0.1 s (one on sample per period), whereas the $n=21$ sample had a sampling time of 0.02 s (five ON samples per period). The total time of the first signal agrees with 10 cycles of the nominal period (0.4 s), for a total of 4 s. However, we found that there were slight delays when we decreased the signal sampling time, so that the $n=21$ waveform was about a second longer than the nominal 8.4 s. We note that there is an exponentially decaying voltage recorded for each single pulse when the current is off; this is due the discharging of the capacitive double layer. Also from the figure, with the help of the voltage envelopes added, we can see that the maxima and minima of the $n=10$ sample are respectively higher and lower than those of the $n=21$ sample after the first few pulses, from which we can infer faster charging and discharging of the capacitive double layer. This may or may not be influenced by the original surface of the sacrificial substrate.

Figure A-1—Current (lower) and voltage (upper) waveforms used for pulsed electrodeposition for the samples with $n=10$ (solid lines) and $n=21$ (dashed lines) pulses, corresponding voltage envelopes (black solid and dashed lines) added for clarity.

A.2 Supporting Information for Dimer Measurements in

Chapter 4

This section contains information that supplementary to the main text of Chapter 4. This includes images of the lateral and vertical dimensions of the dimers, a short explanation of the observed blueshift with increased height, and information on how the refractive indices of materials were determined for bulk refractive index sensitivity determination.

A.2.1 Detailed Measurement of Lateral Dimensions

The data for the dimer side lengths, s_x and s_y , and gaps g were obtained by overlaying bars in respective locations on the SEM images, followed by converting the bar length to a distance based on the scalebar length. Figure A-2 through Figure A-7 show the images and bar overlays used for these measurements. In Figure A-2, the data from the dimers in red boxes were excluded due to the joining of the two

individual dimers. In all these figures, the brown bars represent s_x , the cyan bars represent s_y , and the red bars represent g .

Figure A-2–Lateral measurements for the $s_{60}g_{20}$ structures. The dimers in red boxes were excluded from the measurements due to the joining of the individual dimer squares.

Figure A-3–Lateral measurements for the $s_{60}g_{30}$ structures.

Figure A-4—Lateral measurements for the $s_{60}g_{40}$ structures.

Figure A-5—Lateral measurements for the $s_{80}g_{20}$ structures. The dimer in red box was excluded from the measurements due to the joining of the individual dimer squares.

Figure A-6–Lateral measurements for the $s_{80}g_{30}$ structures.

Figure A-6–Lateral measurements for the $s_{80}g_{40}$ structures.

A.2.2 Dimer Height Measurements

For calculation of the heights based on the line segments shown in the oblique-incidence SEM pictures, the following procedure was used. Suppose that before sample rotation, the sample is lying flat in the xy plane. The sample is rotated by an

angle of $-\alpha$ about the z axis and then by an angle of θ (for inclination) about the x axis. This is illustrated schematically in Figure A-7.

Figure A-7–Schematic of sample tilting for height measurements.

Using a product of appropriate rotation matrices, it can be shown that the new directions of the sample axes are given by

$$\hat{x}' = \begin{pmatrix} \cos \alpha \\ -\sin \alpha \cos \theta \\ -\sin \alpha \sin \theta \end{pmatrix}, \quad \hat{y}' = \begin{pmatrix} \sin \alpha \\ -\cos \alpha \cos \theta \\ -\cos \alpha \sin \theta \end{pmatrix}, \quad \hat{z}' = \begin{pmatrix} 0 \\ -\sin \theta \\ \cos \theta \end{pmatrix}.$$

Thus, when viewed from the $+\hat{z}$ direction, a structure of height h_0 will appear to have a height, based on the $\hat{x}$ and $\hat{y}$ components of $\hat{z}'$, of $|h_{SEM}| = h_0 \sin \theta$. Therefore, we find that the height of the structure is simply given by $h_0 = |h_{SEM}| / \sin \theta$. For our system, the inclination angle was $\theta = 25^\circ$. This corresponds to multiplying the scalebar-normalized heights by a factor of $1/\sin \theta \cong 2.366$. The oblique SEM images with overlaid scalebars are shown below in Figure A-8 through Figure A-13.

Figure A-8–Height measurements for the $s_{60}g_{20}$ structures.

Figure A-9–Height measurements for the $s_{60}g_{30}$ structures.

Figure A-10–Height measurements for the $s_{60}g_{40}$ structures.

Figure A-11–Height measurements for the $s_{80}g_{20}$ structures.

Figure A-12–Height measurements for the $s_{80}g_{30}$ structures.

Figure A-13–Height measurements for the $s_{80}g_{40}$ structures.

A.2.3 Calculation of the Refractive Index of AZ5214E

For calculation of the refractive indexes of AZ5214E, we used the Cauchy equation $n(\lambda) = N_1 + N_2\lambda^{-2} + N_3\lambda^{-4}$, with parameters given in the manufacturer's data sheet for unbleached resist: $N_1 = 1.6035$, $N_2 = 0.0055741 \mu\text{m}^2$, and $N_3 = 0.00234 \mu\text{m}^4$.