

Optics at the Nanoscale: Light Emission in Plasmonic Nanocavities

Thesis by
Carrie Elizabeth Hofmann

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy



California Institute of Technology
Pasadena, California

2010

(Defended May 20, 2010)

© 2010
Carrie Elizabeth Hofmann
All Rights Reserved

For my parents, David and Judy Ross,
who taught me to embrace the pursuit of knowledge,
in memory of my grandmother, Patricia Ross,
whose laughter and smile have always been an inspiration,
and with love and gratitude to Doug
for his encouragement along the way.

Acknowledgements

The completion of this thesis would not have been possible without the assistance of a number of people. First and foremost, I'd like to thank my advisor, Professor Harry Atwater, for his support over the past six years. In choosing a graduate school and research group, I was interested in finding an advisor with exciting research and, more importantly, a genuine concern for and interest in his students. Harry has been an amazing mentor, constantly challenging me and simultaneously providing a nurturing environment to grow as a scientist. I will be forever grateful for what I have learned from him.

I have also been fortunate to have several additional mentors. Professor Albert Polman of the FOM Institute AMOLF hosted me as a visitor in his group twice, during the summers of 2005 and 2007. This collaboration has been very fruitful and is the basis of the cathodoluminescence work in Chapters 2 and 3. Albert has always provided excellent scientific insight, and I'm very thankful for the opportunity to work with his group. Professor Javier García de Abajo of the Institute of Optics, CSIC, has also been an invaluable resource. He is a wizard with electromagnetic theory, and I used his BEM code to perform calculations that are presented throughout this thesis. I am incredibly grateful for his advice. Dr. Henri Lezec was a visitor in the Atwater group during my first few years as a graduate student, and he was an excellent source of ideas. Henri was a master on the FIB, and he fabricated the structures presented in Chapter 3. A number of other Caltech faculty have been helpful during my graduate career. I would like to specifically thank my candidacy and thesis committee members, Professors Brent Fultz, Bill Johnson, and Axel Scherer. Their input helped me significantly in the early stages of my thesis research. My decision to pursue a graduate education was a result of a fabulous research experience at UF, and I would like to thank my undergraduate advisor Professor Kevin Jones for his guidance.

I have learned a ton from the graduate students and postdocs I've worked with while at Caltech. In particular, I'd like to acknowledge those who have joined me as

co-authors. I was fortunate to have Luke Sweatlock as an officemate, and he was an incredible teacher of EM theory when he saw me scratching my head in confusion. His work contributed to the theory presented in Chapter 3. In her two years as a postdoc in our group, Deirdre O’Carroll was an amazing help in the optics lab. She taught me everything I know about single nanostructure optical measurements such as those presented in Chapter 5, and was also a great sounding board for discussions about enhancing spontaneous emission, always with her great Irish wit. During my first trip to Amsterdam to work at AMOLF, I was introduced to CL by Timon van Wijngaarden. The results from experiments we performed together can be found in Chapter 2, and Ewold Verhagen performed some of the theoretical analysis. Ernst Jan Vesseur, also from AMOLF, performed CL measurements that are presented alongside my own in Chapter 3. I’m thankful for their contributions to this thesis, as well as for our insightful conversations at conferences over the years.

I’ve been honored to mentor two fantastic Caltech undergraduates. Stanley Burgos was a SURF student the summer of 2006, working incredibly independently on dispersion theory that became the source of his senior thesis. His work also laid the groundwork for fabrication techniques I continued after he joined the Atwater group as a graduate student. Anna Hiszpanski started as a SURF student in the summer of 2007, and continued research throughout the following two years. I was immediately impressed with her work ethic and attitude, and it was a pleasure to see her grow as a scientist. Her dedication produced the structures fabricated in Chapter 5.

The subset of students and postdocs in Harry’s group working on plasmonics have served as an excellent resource over the years. I’d like to specifically thank Jennifer Dionne (both roommate extraordinaire and plasmonics superstar), Eyal Feigenbaum (mode volume expert), Vivian Ferry (ladies’ night buddy and plasmon PV master), and Domenico Pacifici. Team spontaneous emission, formed at the 2009 Atwater group retreat, provided incredible insight into my own project. For this, I would like to thank Gerald Miller, Tim Taminiau, and Dennis Callahan. The group members working on Si nanowire growth both provided samples and trained me to grow my own. I’m amazed at what they have accomplished in pursuing Si nanowires for pho-

tovoltaics, and acknowledge Brendan Kayes, Mike Filler, Mike Kelzenberg, Morgan Putnam, Dan Turner-Evans, and Shannon Boettcher for their help. I've had a lot of assistance in the optics lab from Robb Walters with the PL setup and from Greg Kimball and Jim Fakonas with the lifetime system, and I'm very grateful for that. Several people have also worked with me on the Nanoprobe, and I thank Rene de Waele from AMOLF and Marine Leite for their patience with that system, and Eric Ostby for his assistance with fiber cleaving. I'm appreciative for help with the fabrication reported in Chapter 5 from Scherer group members David Henry, Mike Shearn, and Sameer Walavalkar. I also thank Professor Anna Fontcuberta i Morral and Carlo Colombo from EPFL for providing the GaAs nanowires included in Chapter 7.

My 244 officemates have been amazing in my time at Caltech. When I first joined the group, Julie Biteen, Christine Richardson, and Luke Sweatlock immediately made me feel welcome and were always available for a friendly chat or research advice. Kora Aydin (e-beaming buddy and powerpoint-drawing master), Ryan Briggs (hardest worker I know), and Imogen Pryce (fellow wine aficionado and early morning workout buddy) have made working on this thesis as enjoyable a process as possible, and I'm very thankful for their friendship and support.

I'd like to thank the other graduate students of the Atwater group for their support during my time at Caltech, including Melissa Archer, Jeff Bosco, Chris Chen, Naomi Coronel, Davis Darvish (always up for a good debate about SEC versus Pac10 football), Michael Deceglie, Matthew Dicken, Hal Emmer, Tao Feng, Seokmin Jeon (my 249 buddy), Emily Kosten, Krista Langeland (a great cat-sitter), Andrew Leenheer, Manav Malhotra, Keisuke Nakayama, Jennifer Ruglovsky, Katsu Tanabe, Emily Warmann (happy to drive you to the train station anyday!), and Samantha Wilson. The group postdocs have also been extremely helpful, and I would like to acknowledge Jonathan Grandidier, Sungjee Kim (quantum dot fab expert), Lise Lahourcade, Jeremy Munday, Young-Bae Park, and Adele Tamboli (always makes me laugh!).

A number of administrators have helped me over the past six years, including Pam Albertson, Lyra Haas, Irene Loera, Cierina Marks, Connie Rodriguez, Rosalie Rowe, Mary Sikora, and Eleonora Vorobieff. April Neidholdt was much more than

an assistant, she was the group “mom,” always lending an ear or offering advice, and most importantly a good laugh to cheer me up when I needed it most. The KNI and micro-nano lab staff have provided a lot of scientific support, including Nils Asplund, Bophan Chhim, Guy deRose, Carol Garland, Ali Ghaffari, and Melissa Melendes. I’m thankful for all of their support. I’d like to acknowledge funding sources that made my thesis research possible, including fellowship support from the National Science Foundation and the National Defense Science and Engineering Graduate Fellowship.

My first two years as a graduate student were dominated by coursework, and Mike Winterrose, Ken Diest, Jessie Rosenberg, Eve Stenson, and Glenn Garrett spent many late nights working through homework sets with me, with plenty of laughs along the way. “Girl time” with fellow graduate students Kakani Young and Emily McDowell was very important to me, and we always had a great time together. Outside of Caltech, I’d like to thank my church family for their encouragement and prayers during these last months, in particular my amazing couples’ small group and D-group girls.

Finally, and most importantly, I’d like to thank my family. Words cannot express my gratitude to them for their unconditional love and support. My parents, David and Judy, are both teachers and have encouraged my academic pursuits from day one. My sister and brother, Rachel and Joel, have always been there when I needed to talk. Here in California, I’m grateful to my in-laws Beth, Terry, Christy, Jen, and Nancy for all of the ways they have supported me over the past six years. Lastly, I’d like to thank my husband, Doug. Fate brought us to Caltech together, and our relationship blossomed over late nights of quantum homework and lab reports – I’m thankful to Caltech for their role in granting my ‘Mrs. degree.’ Doug, I’m so proud to be your wife, I love you, and I can’t wait to see what the future has in store. This thesis is dedicated, with love, to my family.

Carrie E. Hofmann

May 2010

Pasadena, CA

Abstract

Nanophotonics has greatly benefited from the unique ability of surface plasmons to confine optical modes to volumes well below the diffraction limit of light. Plasmonics is an emerging area of research that opens the path for controlling light–matter interactions on the subwavelength scale, enabling truly nanophotonic technologies that are unattainable with conventional diffraction-limited optical components. Novel surface plasmon devices exploit electromagnetic waves confined to the interface between a metal and a dielectric, and permit the researcher to shrink light to dimensions previously inaccessible with optics. The extremely high and localized fields in plasmonic nanocavities are finding applications in research areas such as single-molecule sensing, nano-lasers, and photothermal tumor ablation, among others.

This thesis explores, both experimentally and theoretically, light emission in a number of plasmonic nanostructures. We present cathodoluminescence imaging spectroscopy as a new method of characterizing surface plasmons on metal films and localized in nanocavity resonators, with experimental observations supported by analytical calculations and electromagnetic simulation. This technique enables extremely localized surface plasmon excitation, a feature we exploit in both planar metal geometries and plasmonic nanocavities. We also study a specific nanocavity geometry, the plasmonic core-shell nanowire resonator, investigating both passive and active semiconductor core materials. This geometry allows precise control of the local density of optical states (LDOS), exhibiting the highest LDOS and smallest mode volumes in structures with dimensions as small as $\lambda/50$. Moreover, we discuss the Purcell effect as it applies to plasmonic nanocavities, and calculate enhancements in the radiative decay rate of more than $3000\times$ in the smallest structures. These results demonstrate the promise of plasmonics to enable truly nanophotonic technologies and to manipulate light at the nanoscale.

Contents

List of Figures	xii
List of Tables	xv
List of Publications	xvi
1 Introduction	1
1.1 Optics at the Nanoscale	1
1.2 What are Surface Plasmons?	2
1.3 Single-Interface Surface Plasmons	4
1.4 Exciting Surface Plasmons	9
1.5 Scope of This Thesis	11
2 Cathodoluminescence Imaging Spectroscopy: A Tool for Investigating Metallic Films and Nanostructures	14
2.1 Introduction	14
2.2 Cathodoluminescence Imaging Spectroscopy	15
2.3 Measuring SPP Propagation Length Near Resonance	16
2.3.1 Grating Fabrication	20
2.3.2 CL Measurements	20
2.3.3 Comparison with Theory	22
2.4 Investigating Semiconductor-Metal Nanostructures Using Cathodoluminescence	24
2.4.1 Sample Fabrication	24

2.4.2	CL Spectroscopy and Imaging	26
2.5	Chapter Summary	30
3	Plasmonic Modes of Annular Nanoresonators Imaged by Spectrally Resolved Cathodoluminescence	32
3.1	Applications of Annular Nanoresonators	32
3.2	Fabrication and Experiment Setup	33
3.3	Determining Modes of Annular Nanoresonators	36
3.3.1	Finite Difference Time Domain (FDTD)	36
3.3.2	Boundary Element Method (BEM)	39
3.3.3	Resonant Modes	39
3.4	Imaging Modes Using Cathodoluminescence	43
3.4.1	Panchromatic CL Imaging	43
3.4.2	Imaging Modes of an Ag Nanoresonator	43
3.4.3	Imaging Modes of an Au Nanoresonator	45
3.5	Chapter Summary	48
4	Ultra-small mode volume Si-Ag core-shell nanowire resonators	50
4.1	Introduction	50
4.2	Resonant Modes of Si-Ag Core-Shell Nanowire Resonators	51
4.2.1	The Boundary Element Method	53
4.2.2	Longitudinal Modes of Core-Shell Nanowire Resonators	54
4.3	A Case Study: 3 Resonators, 3 Size Regimes	57
4.4	Enhancing Radiative Decay	63
4.5	Core-Shell Nanowire Resonators as Sensors	67
4.6	Chapter Summary	70
5	Fabrication and Characterization of Si-Ag Core-Shell Nanowire Resonators	72
5.1	Introduction	72
5.2	Fabrication of Si-Ag Core-Shell Nanowires	72

5.2.1	Bottom-Up Approach	72
5.2.2	Top-Down Approach	77
5.3	Optical Characterization	81
5.3.1	Dark-Field Spectroscopy of Bottom-Up Fabricated Si-Ag Core-Shell Nanowires	82
5.3.2	Dark-Field Spectroscopy of Top-Down Fabricated Si-Ag Core-Shell Nanowires	83
5.4	Chapter Summary	87
6	Enhancing the Rate of Spontaneous Emission in Active Core-Shell Nanowire Resonators	88
6.1	Introduction	88
6.2	Theoretical Methods	89
6.3	Modes of Active Core-Shell Nanowire Resonators	91
6.3.1	GaAs-In _{0.51} Ga _{0.49} P-Ag Resonator	92
6.3.2	Al _{0.42} Ga _{0.58} As-Al _{0.70} Ga _{0.30} As-Ag Resonator	95
6.3.3	In _{0.15} Ga _{0.85} N-GaN-Ag Resonator	98
6.4	Enhanced Radiative Decay	101
6.5	Chapter Summary	103
7	Summary and Outlook	105
A	Boundary Element Method Calculations of LDOS and Decay Rates	110
A.1	Decay Rates in Atomic Units	110
A.2	Example BEM Input File	112
A.3	Example BEM Material Data File	114
B	Optical Characterization in the Nanoprobe	116
	Bibliography	117

List of Figures

1.1	Lycurgus cup and Rose Window	2
1.2	Surface plasmons in nanoparticles and on planar films	3
1.3	Single-interface SPP dispersion	7
1.4	Metal-insular-metal waveguide	9
1.5	Methods of exciting surface plasmons	10
2.1	Schematic of cathodoluminescence imaging spectroscopy	17
2.2	Schematic of CL excitation and outcoupling of SPPs on metal gratings	18
2.3	Calculated propagation lengths of SPPs	19
2.4	CL intensity decay from Ag and Au gratings at several wavelengths .	21
2.5	Propagation lengths on Ag and Au films measured with cathodolumi- nescence	23
2.6	Schematic and SEM of a ZnO nanowire sandwiched between Ag films	25
2.7	Monte Carlo simulation of electron trajectories in Ag/ZnO/Ag/Si . .	26
2.8	CL spectra of Ag-coated ZnO nanowires at several incident beam energies	27
2.9	CL imaging of an Ag-coated ZnO nanowire	29
3.1	Schematic of a sensing device consisting of an annular nanoresonator	34
3.2	Monte Carlo simulation of electron trajectories in a thick Ag film . .	35
3.3	Method of determining resonant modes with FDTD	37
3.4	Schematic of modes of annular nanoresonators	40
3.5	Simulated spectral response from FDTD	41
3.6	Simulated CL of an Ag nanoresonator calculated by BEM	42

3.7	Panchromatic CL imaging of Ag nanoresonators	44
3.8	Imaging modes in an Ag nanoresonator with cathodoluminescence	46
3.9	Comparing CL experiment and theory	47
3.10	CL Imaging of an Au nanoresoantor	49
4.1	Si-Ag core-shell nanowire resonator schematic	52
4.2	Longitudinal modes of nanowire resonators	55
4.3	LDOS of Si-Ag core-shell nanoresonators as a function of core length and diameter	56
4.4	Modes of a Si-Ag core-shell nanowire resonator with $a = 50$ nm, $L =$ 500 nm, and $T = 100$ nm	58
4.5	Modes of a Si-Ag core-shell nanowire resonator with $a = 50$ nm, $L =$ 500 nm, and $T = 100$ nm	59
4.6	Modes of a Si-Ag core-shell nanowire resonator with $a = 25$ nm, $L =$ 150 nm, and $T = 100$ nm	61
4.7	LDOS and NF $ \mathbf{E} ^2$ cross sections for an Si-Ag resonator with $a =$ 25 nm and $L = 150$ nm	62
4.8	Modes of a Si-Ag core-shell nanowire resonator with $a = 5$ nm and $L = 25$ nm	64
4.9	Illustration of Purcell enhancement in a cavity resonator	66
4.10	Spontaneous emission enhancements and quantum efficiency in Si-Ag core-shell nanowire resonators	68
4.11	Si-Ag core-shell nanowire resonators as sensors	69
5.1	Si-Ag core-shell nanowire resonator schematic	73
5.2	Bottom-up fabrication procedure for Si-Ag core-shell nanowires	74
5.3	Oxidizing and etching CVD-grown Si NWs to achieve desired diameter	75
5.4	SEM Micrographs of Ag-coated Si NWs	76
5.5	Top-down fabrication method for Si-Ag core-shell nanowire resonators	78
5.6	Si nanowires and Ag-coated Si nanowires fabricated by electron beam lithography, reactive ion etching, and Ag sputtering	79

5.7	SEM images of fully fabricated Si-Ag core-shell nanowire resonators	80
5.8	Schematic of DF imaging and spectroscopy setup	81
5.9	SEM image of an Ag-coated Si NW and corresponding trenches used for normalization	82
5.10	Polarization dependent dark field scattering spectra from a FIB-cut Si-Ag NW	84
5.11	DF scattering image of Si-Ag core-shell NWs fabricated by EBL and RIE	85
5.12	DF scattering spectra of Si-Ag core-shell NWs fabricated by EBL and RIE	86
6.1	Schematic of an active plasmonic core-shell nanowire resonator	90
6.2	Modes of a GaAs-InGaP-Ag core-shell nanowire resonator	93
6.3	2D LDOS and NF $ \mathbf{E} ^2$ cross sections of a GaAs-InGaP-Ag core-shell nanowire resonator	94
6.4	Modes of an $\text{Al}_{0.42}\text{Ga}_{0.58}\text{As}-\text{Al}_{0.70}\text{Ga}_{0.30}\text{As}-\text{Ag}$ core-shell nanowire resonator	96
6.5	2D LDOS and NF $ \mathbf{E} ^2$ cross sections of an $\text{Al}_{0.42}\text{Ga}_{0.58}\text{As}-\text{Al}_{0.70}\text{Ga}_{0.30}\text{As}-\text{Ag}$ core-shell nanowire resonator	97
6.6	Modes of an $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}-\text{GaN}-\text{Ag}$ core-shell nanowire resonator	99
6.7	2D LDOS and NF $ \mathbf{E} ^2$ cross sections of an $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}-\text{GaN}-\text{Ag}$ core-shell nanowire resonator	100
6.8	Decay rate enhancement for III-V core-shell nanowire resonators	102
6.9	Far-field radiation polarization for III-V core-shell nanowire resonators	103
7.1	Schematic of single nanostructure PL and lifetime decay experimental setup	107
7.2	PL intensity and decay-rate enhancements in GaAs NWs on Ag films	108
B.1	Omicron Nanoprobe stage	117
B.2	Fiber-based CL of YAG:Ce in the nanoprobe	118

List of Tables

4.1	Summary of Q/V and decay rate enhancements in Si-Ag core-shell nanowire resonators	71
6.1	Summary of Q/V and decay rate enhancements in III-V semiconductor plasmonic core-shell nanowire resonators	104

List of Publications

Portions of this thesis have been drawn from the following publications:

“Enhancing the rate of spontaneous emission in III-V semiconductor plasmonic core-shell nanowire resonators.” C. E. Hofmann, F. J. García de Abajo, and H. A. Atwater, submitted.

“Conjugated polymer/metal nanowire heterostructure plasmonic antennas.” D. M. O’Carroll, C. E. Hofmann, and H. A. Atwater, *Advanced Materials* **22**, 1223-1227 (2010).

“A plasmonic ‘bull’s-eye’ nanoresonator.” C. E. Hofmann and H. A. Atwater, *SPIE Newsroom* 1088-2008-03-04 (2008).

“Plasmonic modes of annular nanoresonators imaged by spectrally resolved cathodoluminescence.” C. E. Hofmann, E. J. R. Vesseur, L. A. Sweatlock, H. J. Lezec, F. J. García de Abajo, A. Polman, and H. A. Atwater, *Nano Letters* **7**, 3612-3617 (2007).

“Direct imaging of propagation and damping of near-resonance surface plasmon polaritons using cathodoluminescence spectroscopy.” J. T. van Wijngaarden, E. Verhagen, A. Polman, C. E. Ross, H. J. Lezec, and H. A. Atwater, *Applied Physics Letters* **88**, 221111 (2006).