Plasmonic Gallium Nanoparticles – Attributes and Applications

by

Pae C Wu

Department of Electrical and Computer Engineering
Duke University

Date: _______________________

Approved:

___________________________

April S. Brown, Supervisor

____________________________

Henry O. Everitt

____________________________

Jeffrey Glass

____________________________

Thomas Katsouleas

____________________________

Anne Lazarides

____________________________

David R. Smith

Dissertation submitted in partial fulfillment of
the requirements for the degree of Doctor
of Philosophy in the Department of
Electrical and Computer Engineering in the Graduate School
of Duke University

2009
ABSTRACT

Plasmonic Gallium Nanoparticles – Attributes and Applications

by

Pae C Wu

Department of Electrical and Computer Engineering
Duke University

Date:_______________________

Approved:

___________________________
April S. Brown, Supervisor

___________________________
Henry O. Everitt

___________________________
Jeffrey Glass

___________________________
Thomas Katsouleas

___________________________
Anne Lazarides

___________________________
David R. Smith

An abstract of a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Electrical and Computer Engineering in the Graduate School of Duke University

2009
Abstract

Expanding the role of plasmonics in tomorrow’s technology requires a broader knowledge base from which to develop such applications today. Several limitations to the current plasmonics field limit progress to incremental advances within a narrow set of materials and techniques rather than developing non-traditional metals and flexible growth and characterization methods. The work described herein will provide an introduction to the burgeoning field of spectroscopic ellipsometry for plasmonic characterization; in particular, the power of its real-time monitoring capabilities and flexibility will be demonstrated. More importantly, a novel plasmonic metal, gallium, is investigated in detail. Critical characteristics of gallium for an array of applications include its tunability over a wide spectral range, phase stability across a wide temperature range, plasmon stability even after air exposure, and an ultra high vacuum evaporation growth process enabling simple, alloyed nanostructure development. Deeper scientific investigation of the underlying ripening mechanisms driving gallium nanoparticle formation and in concert with in situ alloying paves the way for future work contributing to the development of advanced nanostructured alloys. Finally, this work demonstrates the first example of gallium nanoparticle-enhanced Raman spectroscopy – an area craving materials innovation. While the specific application of gallium for SERS detection is interesting, the far-reaching implication lies in the demonstrated potential for plasmonic gallium nanoparticles’ ultimate use in a wider variety of applications enhanced by nanoscale materials.
## Contents

Abstract ........................................................................................................................................ iv

List of Tables ................................................................................................................................... viii

List of Figures ................................................................................................................................... ix

Acknowledgements .......................................................................................................................... xv

Chapter 1 Introduction ....................................................................................................................... 1

1.1 Plasmonics and nanoparticles: The state of the art ................................................................. 1

1.2 Plasmonic applications .............................................................................................................. 3

1.3 Motivation ................................................................................................................................... 4

1.4 Summary of this work ............................................................................................................... 6

Chapter 2 Theoretical background ................................................................................................... 8

2.1 Volume plasmons – 3D bulk metals .......................................................................................... 8

2.2 Surface plasmons – 2D metal films .......................................................................................... 10

2.3 Localized surface plasmons – 0D metal sphere ....................................................................... 12

2.4 Anisotropy and plasmon mode splitting ................................................................................ 15

2.5 Spectroscopic ellipsometry .................................................................................................... 21

2.7 Molecular beam epitaxy and nanoparticle ripening ............................................................... 25

Chapter 3 Demonstration of real-time spectroscopic ellipsometry for plasmon monitoring during nanoparticle growth .............................................................................................. 29

3.1 The pseudo-optical constants and optical modeling .............................................................. 30

3.2 Plasmonic interpretation of the pseudoextinction function ..................................................... 33

3.3 Extracting the absorption spectrum from the pseudoextinction function ............................ 38

Chapter 4 Characterization of plasmonic group-III metals ............................................................ 42
4.1 Metal nanostructure and evolution revealed by plasmonic ellipsometry .......... 43
4.2 Ga nanoparticle plasmon mode splitting .................................................. 47
4.2 Thermal annealing the plasmon resonance ................................................. 53
  4.2.1 Annealed Indium nanoparticles ............................................................ 53
  4.2.2 Annealed Ga nanoparticles ................................................................. 55
4.3 Metal oxidation and the plasmon resonance ............................................ 57
4.4 Conclusions ................................................................................................. 59

Chapter 5 Bimetallic Ga-Mg plasmonic nanoparticles ......................................... 61
  5.1 Limitations to geometry-based plasmon tuning ........................................... 61
  5.2 The Ga-Mg system for plasmonic alloys .................................................... 63
  5.3 Composition-based bimetallic plasmon tuning ............................................ 68
    5.3.1 Ga-seeded Ga-Mg bimetal epitaxy ....................................................... 69
    5.3.2 Mg-seeded Ga-Mg bimetal epitaxy ...................................................... 77
    5.3.3 Simultaneous Ga-Mg bimetal epitaxy .................................................. 79
    5.3.4 Room temperature Ga-Mg epitaxy ...................................................... 81
  5.3 Temperature-controlled alloy stabilization ............................................... 81
  5.4 Chemical and structural analysis of Ga-Mg alloys ....................................... 89

Chapter 6 Ga nanoparticle-polar semiconductor interface charge and metal nanoparticle assembly ................................................................. 98
  6.1 Polar semiconductors .................................................................................. 99
  6.2 Ga nanoparticle assembly dynamics on polar semiconductor supports ......... 102
  6.3 Electrowetting and the intrinsic interface potential ..................................... 108

Chapter 7 Applications of Ga plasmonic nanoparticles ..................................... 113
  7.2 Surface-enhanced Raman scattering ......................................................... 113
7.3 SERS proof of concept

7.4 Demonstration of SERS with MEH-PPV

7.6 Ga plasmon coupling with III-N quantum well emitters

7.5 Discussion

Chapter 8 Final thoughts and the future

8.1 Conclusions

8.2 Future directions

Appendix

Appendix A Characterization methods

Atomic Force Microscopy

Raman spectroscopy

Scanning Electron Microscopy

Transmission Electron Microscopy

X-ray Photoelectron Spectroscopy

Appendix B Abbreviations

References

Biography
List of Tables

Table I Bulk plasma frequencies and reported 2D surface plasmon resonances of the MBE metals. .......................................................................................................................................... 42

Table II Room temperature Ga-Mg bimetallic nanoparticle growth parameters .......... 69

Table III Elevated temperature Ga-seeded bimetallic epitaxy conditions ..................... 85

Table IV Properties of wurtzite ZnO, GaN, and 4H-SiC along (0001). Ref. a) [133], b) [134], c) [135], d) [136]. ........................................................................................................................................ 101

Table V Schottky potentials at the Ga/semiconductor interface determined from X-ray photoelectron spectroscopy core-level measurements, and the sign of the polarization-induced surface charge for each polar surface .................................................................................. 110
List of Figures

Figure 1 A semi-infinite metal/dielectric two layer system.......................................................... 10

Figure 2 Surface plasmons at a metal-dielectric interface evanesce in the z-direction while propagating along the interface (x-direction). The fields concentrate at the metal surface.......................................................... 11

Figure 3 Surface plasmon (2D) dispersion relation and the light line. .................................. 11

Figure 4 Dipole and multipole excitation depends on the nanoparticle size with respect to the excitation wavelength, \( \lambda \).......................................................... 15

Figure 5 Geometric anisotropy affects s- and p-polarized components of the incident field.......................................................... 17

Figure 6 Two particle interactions where the polarization along the long axis redshifts and vice versa.......................................................... 18

Figure 7 Dielectric anisotropy due to image charge in the substrate. The electric fields include NP dipole and image charge dipole causing mode splitting................................................. 20

Figure 8 Comparison of the reflection of s- and p-polarized incident fields.......................... 22

Figure 9 Schematic representation of in situ phase-modulated spectroscopic ellipsometer .................................................................................. 24

Figure 10 Nanoparticle coalescence by Ostwald ripening and sintering.................................. 27

Figure 11 The standard substrate/layer system described by the pseudodielectric function \( \langle \epsilon \rangle \).......................................................... 30

Figure 12 Thin film layer model for increasing thickness (left) compared to measured Ga on SiC real-time ellipsometric spectra (right).......................................................... 35

Figure 13 The Ga bulk dielectric function measured by spectroscopic ellipsometry............. 36

Figure 14 Ga plasmon resonance redshifts with increasing nanoparticle diameter.............. 37

Figure 15 The plasmon resonance measured by SE is insensitive to azimuthal rotations (left) and variable angle of incidence (VAOI) measurements (right). .............................. 38

Figure 16 The multilayer system to model the substrate/Ga nanoparticles/air samples. 39
Figure 17 Extracted extinction spectrum for Ga nanoparticles on sapphire compared to the experimental pseudoextinction spectrum. ................................................................. 40

Figure 18 Extinction spectrum of bare Si (100) (left). Extracted plasmon resonance extinction spectrum of Ga nanoparticles on Si (100) compared to the experimental pseudoextinction spectrum (right). ................................................................. 40

Figure 19 The group III metal bulk dielectric functions are Drude-like. Ga and In were measured by SE (0.1-0.2nm Ga on glass, 1-2 µm In on Si) while Al is the Aspnes reference dielectric function. .................................................................................. 42

Figure 20 Real-time SE spectra during Al deposition on GaN proceeds from a 3D morphology with an observable plasmon resonance to a Drude-like thin film. SEM imagery confirms the nearly coalesced surface morphology (inset). ......................... 43

Figure 21 Ga nanoparticles deposited on sapphire with effective thicknesses of (a) 650ML, (b) 482ML, and (c) 325ML.................................................................................. 45

Figure 22 The In nanoparticle on GaN plasmon resonance redshifts with increasing metal dosage. The nanoparticle size increases with dosage while the areal density decreases ........................................................................................................ 46

Figure 23 Tilted (45°) SEM image of the Ga nanoparticles deposited on sapphire illustrate Ga’s truncated spheroid shape. .................................................................................. 48

Figure 24 The transverse plasmon resonance amplitude is sensitive to angle of incidence, whereas the longitudinal mode is stable ........................................................................ 49

Figure 25 In plasmon resonance as a function of mean nanoparticle diameter. Lines are drawn to guide the eyes ........................................................................................................ 51

Figure 26 The Ga nanoparticle plasmon resonance as a function of mean nanoparticle diameter. Ga nanoparticles were grown on (a) Si, (b) GaN, and (c) sapphire. Both the longitudinal and transverse modes are shown along side work from [30]. ......................... 52

Figure 27 In nanoparticles exhibit remarkable plasmon stability (energy and amplitude) up to 300°C, above which the plasmon redshifts slightly and decreases in amplitude. 53

Figure 28 Comparison of oxidized In nanoparticles before and after annealing up to 350°C. ................................................................................................................................. 54

Figure 29 The Ga plasmon resonance is stable at temperatures ranging from -80°C to 600°C. ................................................................................................................................. 56
Figure 30 The Ga nanoparticle transverse plasmon mode slight redshifts upon oxidation. The longitudinal mode is largely unaffected.

Figure 31 High resolution Ga 3d core level measurement of Ga nanoparticles on sapphire by XPS reveals both metal and oxide components.

Figure 32 Ga-Mg phase diagram from [109].

Figure 33 Two extreme geometries of bimetallic nanoparticles – core-shell vs. homogenous alloy.

Figure 34 Real-time SE of pure Mg (black) deposited onto pure Ga nanoparticles (blue). Spectra are measured once per second and the Mg deposition clearly redshifts the Ga nanoparticle plasmon resonance for an effective Mg dose of 1.4Å.

Figure 35 Mean nanoparticle diameter measured by AFM as a function of effective Mg composition.

Figure 36 Ga nanoparticle longitudinal plasmon resonance as a function of average nanoparticle diameter on Si (A), glass (B), GaN (C), and sapphire (D) substrates (from Wu, et al, APL, 90, 103119 (2007) [30,54]).

Figure 37 The extinction spectrum for Ga-Mg bimetallic nanoparticles as a function of effective % Mg. The pseudoextinction spectra (inset) are included to show the Si substrate effect.

Figure 38 Total effective bimetallic dosage of 12nm extends the plasmon resonance range the UV (3.6eV) to the near IR (1.75eV).

Figure 39 Comparison of the plasmon resonance sensitivity to effective %Mg and pure Ga nanoparticle mean diameter. The red and black curves correspond to 95nm and 50nm mean nanoparticle diameter, respectively.

Figure 40 Ga deposited on Mg seeds blueshifts the plasmon resonance.

Figure 41 Phase AFM and plasmon resonance of pure Mg (0% Ga, left), 57% Ga (middle), and 73% Ga (right) Mg seeded epitaxy of Ga. Phase images are used to highlight surface texture.

Figure 42 Kinetic SE of simultaneous Ga and Mg deposition with the final spectrum (black) and no evidence of a plasmon resonance. Accompanying phase AFM is provided to highlight the surface’s texture.

Figure 43 Amplitude AFM image of room temperature (25°C) grown Ga-seeded bimetallic nanostructures of Ga-Mg (a). An incomplete, rough Mg layer covers the...
underlying 3D nanostructure. SEM exhibits inhomogeneous metal coverage by image brightness (b). The plasmon resonance oxidizes overtime and eventually becomes quenched (c).

Figure 44 Amplitude AFM (a) and SEM (b) of high temperature Ga-seeded deposition (300°C). The plasmon resonance is slightly redshifted after oxidation and is remarkably stable over a long period (c).

Figure 45 AFM and line profiles for D764 and D766 along with their respective in situ and post-oxidation plasmon resonance spectra.

Figure 46 Pre-anneal and post-anneal spectra show the plasmon resonance stability.

Figure 47 Nanoparticle size distributions as a function of nanoparticle diameter for D764 (left) and D766 (right).

Figure 48 EF-TEM images of the Ga jump ratio (left) and Mg jump ratio (right) for D766. The jump ratio maps reveal uniform composition within the nanoparticles.

Figure 49 Comparison of alloy survey spectra between the Mg 2p and Ga 3d core levels. The binding energy difference between Mg 2p and Ga 3d are marked to show the charge transfer-induced core level shifting.

Figure 50 High-resolution Ga 3d core level spectra of D764 (upper) and D766 (lower) reveal alloy component(s) at binding energies <18eV.

Figure 51 High-resolution O 1s core level spectra of D764 (upper) and D766 (lower).

Figure 52 High-resolution C 1s core level spectra of D764 (upper) and D766 (lower).

Figure 53 HAADF-STEM image of D766 showing occasional bright spots corresponding to higher mean atomic number regions.

Figure 54 The extinction spectra of D764 (MgxGay) and D766 (MgGa).

Figure 55 Bonding structures and polarity schematics for wurtzite GaN, ZnO, and 4H-SiC. Ga-polar, Zn-polar and Si-polar (0001) faces and N-polar, O-polar and C-polar (000-1) faces for GaN, ZnO and SiC are shown. The corresponding polarization and sign of fixed polarization charge is also reported, pointing out the inversion of polarization for SiC with respect to GaN and ZnO.

Figure 56 Real-time evolution of ellipsometric spectra of the pseudoextinction coefficient, $<k>$, recorded during Ga nanoparticle formation on (a) C-polar and (b) Si-polar SiC (140s total deposition time corresponding to 96ML of Ga): spectra are shown every 20s (corresponding to 14ML); only the longitudinal plasmon mode is visible in the
investigated photon energy range; (c) C-polar and (d) Si-polar SiC (475s total deposition time corresponding to 325ML of Ga): spectra are shown every 50s (corresponding to 34ML); both the longitudinal and the transverse mode (at higher energy) are visible.

Figure 57 The plasmon resonance extracted from kinetic measurements as a function of Ga dosage (ML) for (a) SiC, (b) GaN, and (c) ZnO. Associated nanoparticle density and mean diameter as a function of Ga dosage are included.

Figure 58 Ga nanoparticles deposited on Ga-polar and N-polar GaN substrates. The bare N-polar GaN is more defective than the Ga-polar surface.

Figure 59 The contact angle varies with $U_{pzc}$ (interface potential) strength. Representative 3D AFM images Ga nanoparticles (325ML) on GaN reveal variation in Ga nanoparticle wetting on the two polar surfaces.

Figure 60 Energy diagram depicting the Raman scattering shifts.

Figure 61 The chemical enhancement (charge-transfer) mechanism partially enables SERS [158].

Figure 62 The electromagnetic mechanism governing SERS.

Figure 63 Absorption spectra corresponding to a) 3.1eV (442nm), b) 1.96eV (633nm), and c) 1.58eV (785nm) Ga nanoparticle on sapphire plasmon resonances with corresponding SEM images and accompanying nanoparticle diameter distribution. The decrease in the nanoparticle density as a function of increasing mean nanoparticle diameter is evident from the SEM imagery. FWHM of the size distributions, derived from Gaussian fit, are 23nm, 84nm, and 33nm/81nm from smallest to largest mean nanoparticle diameter, respectively.

Figure 64 (a) Full spectrum of surface-enhanced CFV Raman on sapphire. Sapphire only contributes the Raman features between 1350-1450cm$^{-1}$. (b) High resolution SERS spectra for the strongest CFV mode at 590cm$^{-1}$ for Ga nanoparticles with plasmon resonance at (i) 3.1eV (442nm), (ii) 1.58eV (785nm), (iii) 1.96eV (633nm) and (iv) bare sapphire without Ga nanoparticles.

Figure 65 Calibration of CFV SERS on Ga nanoparticles. Calibration measurement error bars range from 4-20% (mean = 12%), quite small even at the largest concentrations, implying reproducibility. The Raman mode at 590cm$^{-1}$ CFV is shown for each concentration solution (inset).

Figure 66 Raman spectra of MEH-PPV thin films spin cast onto (a) Ga nanoparticles on sapphire compared to identical MEH-PPV on (b) bare sapphire. Sapphire modes are removed between 1300-1400cm$^{-1}$ for clarity. Characteristic features (966cm$^{-1}$, 1112cm$^{-1}$, 1207cm$^{-1}$).
1283cm\(^{-1}\), and 1583cm\(^{-1}\) are observed only in the presence of the Ga nanoparticles. All other features are sapphire background.
Acknowledgements

This time of sustained reflection on my work over the last six years has reaffirmed my belief that no science can be done without also considering the giants on whose shoulders we stand. These are not the giants who informed the theory underlying our vision, but rather those, without whom none of this work, literally, could have been possible. The countless days I spent in the frigid MBE lab with Dr. Tong-Ho Kim were at once informative and entertaining. Any conversation with him involved equal parts imparting scientific knowledge and wisdom, probing to help a student develop her research direction, and discussing the joys of a simple life replete with good food and drink. Our appreciation of good food and drink was complemented by our close collaboration with Dr. Maria Losurdo. Arguments over our latest data sprang up with Maria in every possible locale – across the lab, across the Internet, across a stretch of beach, and across the dinner table – and her ethic has been a great motivator. The final element of the Italian arm of this project, Dr. Giovanni Bruno, welcomed me to his lab and his home on numerous occasions and taught me that crazy water fish is a gift best savored amongst friends. Growing up in a small, freshly started lab meant the relationship built with my senior labmate, Soojeong Choi, was critical to developing my knowledge base and her readiness to answer any and every physics or math question under the sun made me a better thinker. Prof. Henry Everitt, with whom conversation often revolved around Duke Basketball and true Barbecue, enthusiastically provided me with sometimes painfully honest assessment of my work that helped me develop a sense of scientific gravitas. A Ph.D. is in some ways a team effort, and I have had the
best teammates and coach. Daily conversations and mutual jab-taking amongst Mike M., Inho, and Andy kept me laughing and in many ways, I think my labmates know me better than anyone else and could be counted on when launching ‘verbal attacks’. Dr. Brown’s guidance extended far beyond the science and our student-boss relationship has evolved into true friendship. By her mentoring, I have experienced much outside the lab and developed a self-awareness that will have an immeasurable affect on my future. The rich, fruitful collaborations borne out of the Brown lab are testament to April’s tireless work to promote and engage our work beyond our lab walls.

Becoming a human requires relationships beyond your work life. Amongst my network of friends who have all improved my life, it is unfair to identify individuals, but life is unfair. Those with whom I have worked on the Basketball Committee have informed my life so much – you can never get the full measure of how a beer-can-to-the-head will bring people together until it happens. Dr. Audrey Ellerbee has been the sort of positive influence in my life that your mother hopes you find at some point. She was not just my roommate, but also a friend, confidant, role model, and practically a sister. My adopted, middle sister – Miriam Krieger – probably does not realize how instrumental her friendship and home have been both in the production of this document and in my mental state. My real sister, Mae, has on some days been a minute-by-minute witness to my life and she has been wholly supportive of me throughout my life and she has always been the measuring stick against which I have judged myself. And finally my parents who, without reservation, have provided me with the best education and life allowing me to try to become my best self. To each of these giants, I thank you.
Chapter 1 Introduction

1.1 Plasmonics and nanoparticles: The state of the art

Through the late 20th C and early part of this century, nanotechnology has been the catchall phrase encompassing a vast sea of work ranging from fuel cells to cosmetics. In truth, nanotechnology has upheld Richard Feynman’s assertion that “there’s plenty of room at the bottom” in particular because the behavior of materials changes drastically at the nanoscale compared to their bulk properties. Quantum well solid-state lasers, antibacterial socks, and plasmonic nanoparticles all owe their remarkable (and profitable) characteristics to nanoscale manipulation of the active materials.

The optical properties of metallic nanostructures have an illustrious history dating to the 4th C when the Lycurgus cup, which transmits in red, but reflects in green, was designed [1]. Metal inclusions embedded in glass matrices, better known as stained glass, yield brilliantly colored windows seen the world over. Since Mie published the full scattering solution for small spherical objects in 1908, particle size manipulation for tuning the color has been well studied, exploited, and ceases to have any novelty – in particular for Ag or Au metal nanoparticles [2]. We are now at a stage of incremental contributions to the body of knowledge for optically active noble metal nanoparticles. The surface plasmon resonance of nanoscale metal structures has been calculated, studied, and manipulated, but a vast plain of potential applications yearning for a solution still exists. Cancer therapy, chemical detection, light emission enhancement, and subwavelength optical circuits are just a few of the world changing directions that
plasmon resonant metal nanoparticles are taking today [3,13]. In order for plasmonics to move forward, technologically relevant processing techniques along with new plasmonic metals require careful investigation to uncover their useful properties that cannot be replicated by Ag or Au. Traditional Ag and Au nanoparticle processing is well understood with controllable wet chemistry and lithography established as the standards [14,15], but plasmonic metal integration with solid-state optoelectronic devices is an intriguing new direction that requires controllable interfaces between the nanoparticles and the active materials. To ensure the pristine quality between the plasmonic structures and the active device regions (e.g. in the well region of a quantum well emitter) direct growth of the metallic nanostructures on the active material is desirable, but is unattainable by the traditional Ag and Au growth techniques. Furthermore, little effort has been devoted to finding and characterizing novel alternative plasmonic metals. Even mixtures of Ag and Au or metals with dielectric structures to add a secondary tuning variable (relative composition) has remained loyal to traditional plasmonic metals, without clearly describing the exact correlation between composition and plasmon resonance [16,17]. Given the maturity of Ag and Au plasmonics, much can still be done to characterize unstudied, new plasmonic metals. Along with growth/control and metal selection, another limitation to the current state of the field is the reliance on post-growth optical characterization that requires prior knowledge of the conditions necessary to exactly tune nanoparticles to desired specifications. Addressing each of these limitations simultaneously would be a boon to advancing discovery in the plasmonics field.
Simple, integrated growth, real-time tuning, and especially nontraditional metals are areas ripe for change and novelty – areas to which the Brown group is strategically primed for significant contributions.

1.2 Plasmonic applications

Much interest in surface plasmon resonance of metal nanoparticles focuses on local field enhancement or enhanced optical absorption [18,19]. The collective oscillations of the free electrons at the nanoparticle surface resonate at frequencies corresponding to the dipole and higher order modes, thereby enhancing optical absorption and local field strength. Increasing the local fields of the plasmon resonant nanoparticles can be exploited for surface enhanced Raman scattering (SERS) and plasmonic waveguiding [5,20,21]. Near-field coupling from the nanoparticles to neighboring molecules or other plasmon resonant nanoparticles requires a sufficiently small separation to ensure evanescent waves can couple. The diffraction limit of light poses a significant challenge to the miniaturization and high-density integration of optical nanocircuits in optical, imaging, and sensing devices [3,22]. Exploitation of metal nanoparticles and their localised surface plasmon resonance [23,24] enables plasmonic devices that can overcome the dimensional limitation currently preventing present optical systems from including sub-wavelength features (d << λ). Of particular importance and utility is that the plasmonic properties of metal NPs are influenced by the particle dielectric function, size, and shape along with the chemical and physical (e.g. refractive index) properties of the materials surrounding the particles [15,25]. Thus, electronic and chemical interactions between the particles and the surrounding media can strongly
affect the optical properties of the localised surface plasmon resonance (SPR) when compared to the free particles.

Plasmonic and photonic device coupling is also of great interest. The resonant behavior of the metal nanoparticles lends themselves for integration with photonic devices to enhancement optical performance. Optical emission of LEDs and optical absorption of photodetectors are sources of constant work to increase the efficiency of the respective optical process. As incident light couples to these surface plasmon modes of a metal nanoparticle, the scattered signal exhibits an extinction cross section resonance corresponding to the photon energy of the surface plasmon mode, which has been shown to be sensitive to particle geometry and material as well as the local dielectric environment [26,27]. Si-based photodetectors employing Au nanoparticles for increased optical absorption have already been demonstrated [1,19]. Coupling emission from photonic devices to surface plasmon modes also provides a means for emission enhancement by increasing the photon density of states [8]. Most demonstrations of optical enhancement, however, have been confined to the visible-IR range limitations of the well-studied metals such as Ag and Au. Thus, plasmonic applications yearn for the discovery of new plasmonic metals resonant across a wider tunable range, especially into the UV.

1.3 Motivation

Three major limitations to the state of plasmonics were described earlier – metal variety, nanostructure growth and tunability, and plasmon characterization. Molecular beam epitaxy, however, can address all of these current constraints. An ultra-high
vacuum growth technique, molecular beam epitaxy can couple high quality (crystalline, optical, and electrical) semiconductor device growth with plasmonic nanostructure control, which we can optically monitor and tune in real-time by \textit{in situ} spectroscopic ellipsometry.

Plasmonic research focuses almost exclusively on two metals – Ag and Au. While they exhibit many useful properties, they are still limited by several key, intrinsic problems – limited range of tunability (visible to IR) and, in the case of Ag, excessive corrosion when exposed to air that entirely dampens the plasmon resonance \cite{28,29}. Even mixtures of these two metals with each other or dielectric cores cannot overcome the limited optical range for these metals.

To effectively tune plasmonic metal nanoparticles (NPs) \textit{via} dry chemistry requires improving characterization methods and synthesis-controllability. Plasmonic integration with solid-state devices grown by molecular beam epitaxy (MBE) will broaden the utility of plasmonic NPs since they can be grown on semiconductor supports for direct integration during device layer epitaxy. The combination of our interest in nanoscale material development by MBE and \textit{in situ} characterization catalyzed the Brown group’s foray into plasmonics, the initiation of which is detailed in this dissertation. First we will evaluate \textit{in situ} spectroscopic ellipsometry for real-time monitoring of plasmon evolution during MBE metal deposition. Recent demonstrations of the viability of spectroscopic ellipsometry for plasmon resonance characterization dovetail with our III-nitride MBE system’s capabilities. One previous study of the gallium surface plasmon resonance only confirmed the plasmon’s existence in the visible range \cite{30,31}, but given
its grouping with aluminum and indium, we believe it is a logical candidate for UV surface plasmon applications. The significant and impactful contributions of this work, however, involve detailed studies characterizing the plasmonic properties and applications of metals available for MBE growth. We will unveil novel properties heretofore not well studied of the plasmon/semiconductor interface, metal alloying, and nontraditional plasmonic metals, namely Mg and the group-III metals aluminum, indium, and most importantly, gallium. The most far-reaching and high impact quality of this work, however, derives from our generalizable techniques and these results should not be regarded as specific to the materials systems studied herein.

1.4 Summary of this work

In this work, we develop a fundamental understanding of the optical and material properties of a new plasmonic metal – gallium, while examining the efficacy of a new plasmon resonance measurement technique, spectroscopic ellipsometry. The applicability of plasmonic Ga nanoparticles in technology is foreshadowed by the nanoparticle characteristics discovered throughout this work. Chapter 2 introduces the theoretical background of surface plasmons and spectroscopic ellipsometry providing a framework within which the experimental work in this dissertation lies. In Chapter 3 we will examine the efficacy of a new plasmon resonance measurement technique, UV-visible spectroscopic ellipsometry (SE) for real-time monitoring and tuning of plasmonic nanoparticle growth by molecular beam epitaxy (MBE). Through this demonstration of in situ ‘plasmonic’ ellipsometry, peculiar properties of the gallium (Ga) nanoparticle behavior as evidenced by its plasmon resonance(s) emerge, including the phase stability
over a wide temperature range, oxidation stability over a large time-scale, and the nanoparticle shape during metal evaporation. We extend the real-time tuning of metal nanoparticles grown by MBE in Chapter 4 by studying the group-III metals (Al, Ga, and In) and Mg. These four metals common to MBE demonstrate the power of spectroscopic ellipsometry for characterizing different metals’ morphological evolution during deposition. The evolution of the plasmon resonance measured in real-time allows us to infer the variation in the different metals’ growth process, which are characteristic of their wetting on solid surfaces. Beyond plasmon tuning by manipulating nanoparticle size, we exploit the real-time monitoring of spectroscopic ellipsometry to grow tunable, plasmonic, bimetallic and alloyed nanoparticles in Chapter 5. Inspecting the temporal information available from in situ spectroscopic ellipsometry, we can discern nanoparticle assembly kinetics. While the interaction of plasmonic nanoparticles with various dielectric environments is understood from a theoretical and optical perspective, the electronic properties of semiconductor substrates and their influence on the plasmon evolution, and nanoparticle growth macroscale kinetics, is examined in Chapter 6. Specifically, we uncover the impact of semiconductor polarity on nanoparticle coalescence and wetting by monitoring the real-time plasmon resonance evolution by in situ spectroscopic ellipsometry. Finally, an application specific proof of principle is revealed in Chapter 7 where we demonstrate the first instance of surface-enhanced Raman scattering (SERS) by Ga nanoparticles. Chapter 8 highlights major conclusions and future directions for this body of work.
Chapter 2 Theoretical background

2.1 Volume plasmons – 3D bulk metals

Critical physical, chemical, and electronic properties of nanoscale metal particles are manifested as perturbations to the plasmon resonance. To understand these extrinsic influences on the metal’s intrinsic electron density behavior, a physical intuition of the plasmon’s origins provides context. Most simply, metals can be described as a sea of free electrons. These unbound electrons oscillate in response to an incident, harmonic, electric field \( \tilde{E} = E e^{i \omega t} \). For a neutral, bulk metal, the net charge is zero and no fields exist within the metal. Writing the equation of motion for the unbound electrons (K=0) of mass, \( m \), due to the incident electric field, \( E \), by the Drude approximation we get

\[
F = ma = m \frac{d^2 x}{dt^2} + \gamma_d \frac{dx}{dt} = qEe^{i \omega t}
\]  

[2.1]

where \( \gamma_d \) is a damping factor accounting for the finite mean free path of the electrons within the lattice and the solution is

\[
x = \frac{-qEe^{i \omega t}}{m(\omega^2 + i \gamma_d \omega)}.
\]  

[2.2]

Accounting for the induced dipole moment per oscillator and extrapolating to the volume density of oscillators (\( n_e \)), we can show that the net polarization is,

\[
P = \frac{\omega_p^2}{\omega^2 + i \gamma_d \omega} e_n E,
\]  

[2.3]

where the plasma frequency is defined as
Within this neutral metal bulk, the net polarization describes the net charge separation of the electron cloud with respect to the ionic core, where the displacement, \( x \), is known from equation [2.2]. Therefore, an electromagnetic field incident on a metal bulk causes the unbound electrons to oscillate coherently. The resonant frequency of the plasma, \( i.e. \) the “natural” frequency of the plasma, is defined as the bulk plasma frequency, \( \omega_p \); the volume plasmon is therefore the quantum entity defined by the collective oscillation of the free electron density. From the constitutive relation of the polarization and electric field, the complex dielectric function of a bulk metal in the Drude model is

\[
\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma_d\omega} \tag{2.5}
\]

where

\[
\epsilon(\omega) = \epsilon_r + i\epsilon_i = (n + ik)^2 \tag{2.6}
\]

Physically, a material’s dielectric function is a measure of the optical response of that material. The complex dielectric function and complex refractive index are wavelength dependent quantities and in the case where \( \omega = \omega_p \), \( \epsilon_r \) vanishes and the electric field in the bulk is longitudinal ( \( \nabla \times E = 0 \)). Thus, at the bulk plasma frequency, the quantized, coherent, free electron oscillations, the volume plasmon, can only support a longitudinal plane wave. This is especially relevant when launching plasmons, as the incident, exciting field must then be \( p \)-polarized for volume and surface (2D) plasmons.
2.2 Surface plasmons – 2D metal films

Introduction of a boundary condition in one dimension yields a semi-infinite, two-layer metal/dielectric plane.

![Figure 1 A semi-infinite metal/dielectric two layer system](image)

At the interface, $p$-polarized fields exist.

\[
\begin{aligned}
E_{\text{metal}} &= (E_{x,m} \hat{i} + E_{z,m} \hat{k}) e^{i(k_x z - k_z z - \omega t)} \\
E_{\text{dielectric}} &= (E_{x,d} \hat{i} + E_{z,d} \hat{k}) e^{i(k_x z + k_z z - \omega t)}
\end{aligned}
\]

From continuity requirements at the $z=0$ interface, we know that $k_x$ is equivalent for $z>0$ and $z<0$. Applying the appropriate boundary conditions and solving Maxwell's equations at the metal-dielectric interface reveals that

\[
k_x^2 + k_{z,i}^2 = \varepsilon_i \left( \frac{\omega}{c} \right)^2
\]

where $i$ is either the metal or dielectric side of the interface. From this dispersion relation we observe two critical features of modes supported at the surface for a system comprised of air ($\varepsilon_d = 1$) and metal ($\varepsilon_m < 0$ and $|\varepsilon_m| > 1$). First, $k_z$ is imaginary both into the metal and the dielectric half-planes revealing the evanescent nature of the
transverse portion. Since no fields exist within the metal (beyond the evanescent component), the field concentrates at the metal surface.

\[ E_z \sim \exp(-|k_z|z) \]

\[ \epsilon_d \]

\[ z = 0 \]

\[ \epsilon_m \]

Figure 2 Surface plasmons at a metal-dielectric interface evanesce in the z-direction while propagating along the interface (x-direction). The fields concentrate at the metal surface.

Second, the longitudinal oscillation propagates along the plane with

\[ k_z = \frac{\omega}{c} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} \]

the surface plasmon polariton (SPP) dispersion relation for a semi-infinite surface.

Figure 3 Surface plasmon (2D) dispersion relation and the light line.
At the air-metal interface, low values of \( k_x \) hold the dispersion near the light line, but as \( k_x \) increases \( \omega \rightarrow \omega_{sp} \) and never crosses the light line, \( k_x = \frac{\omega}{c} \), meaning the 2D, surface plasmon is nonradiative in the absence of a momentum matching mechanism. The asymptotic limit, \( \omega_{sp} \), is the surface plasmon frequency, which relates to the bulk plasma frequency of the metal by

\[
\omega_{sp} = \frac{\omega_p}{\sqrt{1 + \epsilon_d}}. \tag{2.9}
\]

In air, the surface plasmon is \( \omega_{sp} = \frac{\omega_p}{\sqrt{2}} \). Momentum matching can be achieved by gratings or prism coupling, but also requires films that are thin enough to allow coupling to the evanescent fields [32]. A critical difficulty working with 2D, metal films for surface plasmon applications is the momentum matching requirement, complicating the excitation and extraction geometry. Typically, gratings in the metal film require a) high resolution, reproducible lithographic features and b) a priori knowledge of the desired surface plasmon resonance (SPR) [33,36].

### 2.3 Localized surface plasmons – 0D metal sphere

Further confining the metal in three dimensions is most easily understood by examining an individual metal sphere whose optical behavior can be solved analytically using Mie theory [2]. Mie’s solution to Maxwell’s equations describes the scattering from a small metal sphere and yields the surface mode frequencies that can be supported by
an individual metal nanoparticle of a known bulk complex dielectric function. Rather than repeat Mie’s derivation here, I invite the reader to peruse his 1908 paper [2]. Here we will focus only on the final results of the derivation, namely the allowed plasmon modes of a spherical particle,

\[ \omega_l = \omega_p \sqrt{\frac{l}{l + \epsilon_d (l + 1)}} , (l = 1, 2, \ldots) \]  

where the angular momentum number, \( l \), originates from the spherical harmonic solutions to the problem of scattering from a sphere.

To derive some physical intuition about these localized plasmon modes, it is helpful to study the small particle limit (\( k \cdot a \ll 1 \)) and observe the convergence of the scattering problem (how a sphere perturbs a uniform, incident field) and the electrostatic approximation (the sphere, treated as a dipole in space, radiates a field) [26]. Series expansion of the spherical scattering of a homogenous incident field from a sphere produces absorption and scattering efficiencies

\[ Q_{abs} = k \cdot a \operatorname{Im} \left[ \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d} \right] \]

\[ Q_{sca} = \frac{8}{3} (k \cdot a)^4 \left| \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d} \right|^2 \]

and each resonates at \( \epsilon_m = -2\epsilon_d \) [26]. For the case of a sphere in air, the maximum absorption and scattering both occur at a frequency corresponding to \( \epsilon_m(\omega) = -2 \). The localized SPR resides at this resonance frequency,

\[ \omega_{sp} = \frac{\omega_p}{\sqrt{1 + 2\epsilon_d}} \]
Scattering from the sphere produces a far field potential with two contributions – one from the incident field and one perturbed field.

\[
\phi = -E_0 r \cos \theta + a^3 E_0 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \frac{\cos \theta}{r^2} \tag{2.13}
\]

Interestingly, the electrostatic potential of a dipole,

\[
\phi = \frac{p \cos \theta}{4\pi \varepsilon_0 r^2} \tag{2.14}
\]

relates to the perturbed component of the scattered field of equation [2.13] via the dipole moment,

\[
p = 4\pi \varepsilon_m a^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} E_0 \tag{2.15}
\]

Therefore, a scattering sphere can be described by an equivalent radiating dipole of radius \( a \). Continuing along this vein, the sphere/dipole’s polarizability is defined as

\[
\alpha = 4\pi a^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \tag{2.16}
\]

therefore the dipole is most strongly polarized at the resonance, \( \varepsilon_m = -2\varepsilon_d \). As such, spheres of diameter much smaller than the wavelength of light can be treated as dipoles that oscillate in response to electromagnetic excitation that appears homogenous to the electron density within the small sphere. In an incredible confluence of effects, a small metallic sphere resonantly absorbs, scatters, and radiates coincidentally at the surface plasmon resonance frequency of the free electrons confined within the volume oscillating in response to an incident EM field resonant with the plasmon resonant mode. Larger spheres are excited by nonuniform electromagnetic fields and therefore higher order
multipoles emerge \((l>1)\) and for very large \(l\) the solution approaches the 2D limiting condition, \( \omega_p = \frac{\omega_p}{\sqrt{2}} \).

![Dipole limit (l<<1, l=1)](image1.png)

![Multipole excitation (l>1)](image2.png)

Figure 4 Dipole and multipole excitation depends on the nanoparticle size with respect to the excitation wavelength, \(\lambda\).

Although the solution extrapolates to the 2D case, the localized plasmon modes manifestly differ from surface plasmons because of the scatterer’s spherical geometry and surface curvature; these modes are radiative and directly couple to photons in free space [37]. Prisms, gratings, or other momentum matching geometries are unnecessary to probe and exploit the optical response of plasmonic spheres and, by extension, plasmonic 3D structures.

### 2.4 Anisotropy and plasmon mode splitting

Expanding the analytical solutions described above beyond a sphere is challenging, but a more generalized case can be approximated by including a shape
factor \( \chi \) in equation [2.12] such that the resonance condition occurs at \( \varepsilon_m = -\chi \varepsilon_d \) where \( \chi \) changes with shape and size of the particles [38]. Including the shape/size effect in the particle polarizability,

\[
\alpha_i = V \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_d + \chi_i (\varepsilon_m - \varepsilon_d)} \quad [2.17]
\]

where \( V \) is the particle volume, \( 0 < \chi_i < 1 \), and the polarizability reduces to the spherical, dipole case at \( \chi = \frac{1}{3} \) [26]. Generally, the plasmon resonance redshifts with increasing nanoparticle size and increasingly nonspherical shape factor. Given that shape and size affects the polarizability, the plasmon resonance instead occurs at

\[
\varepsilon_m = -\frac{\varepsilon_d (1 + \chi_i)}{\chi_i}. \quad [2.18]
\]

For nonspherical particles, shape factors vary along the different axes causing the localized plasmon mode to split. Spatial asymmetry of the nanoparticles physically corresponds to differing contributions from the different polarizations of incident light along the different particle axes (figure 5).
Figure 5 Geometric anisotropy affects $s$- and $p$-polarized components of the incident field.

To physically intuit the shape effect, we consider nanoparticles with nonunity aspect ratios (e.g., nanorods or oblate spheroids), which exhibit anisotropic behavior depending on the polarization of the incident field with respect to the symmetric axes of the particle. Components of the incident field polarized along the two axes, parallel and perpendicular to the particle’s semimajor axis, excite different modes – longitudinal and transverse (figure 5). Typically, the longitudinal mode is defined as that which is along the semimajor axis of the spheroid and the transverse mode corresponds to the semiminor axis. Using this geometry, the longitudinal mode is redder than the transverse mode with the dipole mode located between the two, a designation we use for the multiple modes of the truncated spheroids investigated in this work [39].

The discussion thus far has only focused on single particles in an electric field, but in reality the substrate-supported, self-assembled metal particles grow within a larger collection of particles where growth conditions determine the interparticle separation and
Electromagnetic interactions between particles perturb the oscillation frequency of neighboring plasmons and shift the observed plasmon resonance.

Figure 6 Two particle interactions where the polarization along the long axis redshifts and vice versa.

In many ways, the impact of interparticle interactions on the SPR is akin to high aspect ratio particles [14]. Consider first two well-separated spherical particles (figure 6). As separation between two particles decreases, coupling along the length of the two particles or perpendicular to the long axis causes splitting of the longitudinal and transverse modes [40]. For polarization along the long axis, the plasmon resonance transitions from the single particle resonance at large interparticle distances to a redder resonance when the nanoparticles are closely spaced – e.g. center-center distance of close to the NP diameter. Transverse excitations along the short axis actually blueshift as the interparticle spacing (in the long axis direction) decreases. The polarization dependent plasmon shift for coupled NPs comes from the dipole-dipole attractive/repulsive forces and their respective impact on the electron density restoring force. Specifically, longitudinal excitations increase the attractive forces between the two particles therefore a lower energy excitation can induce electron cloud oscillations within the NPs, thus the redshift as the two dipoles begin interacting. Transverse excitations act in the opposite way. The positive charge of one particle attracts the negative charge
of the neighboring NP effectively lessening the charge separation within that dipole therefore a higher energy excitation is required to initiate electron density oscillations [40]. In practice, Rechberger, et al demonstrated that the coupled particle spectrum continuously transitions from that of a single particle to an elongated particle in the longitudinal case [40]. Interparticle coupling along chains of closely spaced metal nanoparticles has been exploited for use in plasmonic waveguides, which rely on the strong, localized fields at the particle surfaces facilitating evanescent coupling between particles thereby enabling the propagation of the signal, coupled into surface plasmon polaritons, along a chain of particles [5,15,21].

An additional source of anisotropy arises for nanoparticles not embedded in a uniform dielectric medium, but rather atop solid supports. Development of Mie solutions grew from a need to explain the changing color of metal colloidal solutions or cermets in glass due to variations in metal or particle size. Exploiting the plasmon modes for active devices and even passive sensing applications requires the metal particles be accessible, i.e. not embedded within a dielectric. Substrate-supported nanoparticles, even spheres, experience anisotropic dielectric environments causing their plasmon modes to split. The incident fields disparately couple to the substrate plane along the in-plane and out-of-plane directions when the substrate dielectric function is not index matched to the surrounding medium. The substrate polarizability, manifested as an image dipole, inhomogeneously perturbs the local fields, an effect that aggregates across the substrate for NP collections (figure 7) [41,42].
Figure 7 Dielectric anisotropy due to image charge in the substrate. The electric fields include NP dipole and image charge dipole causing mode splitting.

From a different perspective, local field components perpendicular and parallel to the substrate surface will unequally perturb the metal particle’s in-plane and out-of-plane polarizabilities creating unequal SPR modes corresponding to each polarizability component [43]. I.e. the substrate effect can be described as anisotropy of the particle dielectric function (and polarizability) due to interaction with the substrate polarizability [44].

Several factors contribute to plasmon mode splitting – both size-induced and anisotropy-induced. Large spherical nanoparticles support multipoles ($l > 1$) along with the dipole ($l = 1$). More prevalently, anisotropy-induced mode splitting originates from NP spherical asymmetry, interparticle electromagnetic interactions, and anisotropic dielectric environments created by solid substrates. For the self-assembled metallic NPs described herein, we will not deconvolve the multiple sources of anisotropy since their combined effect contributes to the observed SPR.

From the theoretical treatment, it is clear that the plasmon resonance is affected by the metal choice, size, and shape along with the chemical and physical (e.g.
refractive index) properties of the ambient environment [15,25]. Previous investigations [45] of the characteristics of metal NPs embedded in or supported on semiconductor or dielectric materials have shown that the plasmon resonance is red-shifted (relative to the same particles in vacuum), and the extent of the red-shift depends on the dielectric constant of the substrate and the fractional area of the particle in contact with the substrate [43,46].

2.5 Spectroscopic ellipsometry

Materials characterization during vacuum-based growth can be illustrated by surface-sensitive, nondestructive, optical, reflection-based techniques. However, an evolving surface with its time dependent roughness and morphology makes absolute intensity-based optical techniques limited in effectiveness due to signal scattering effects. Furthermore, details of the growth front’s microstructure can illuminate properties of the growth process. Spectroscopic ellipsometry (SE) avoids these pitfalls by comparing the relative amplitudes and phase changes of the s- and p-polarized components of an elliptically polarized signal after interacting with a sample surface [47].

The basic principle driving ellipsometric characterization is rooted in the anisotropic effect a surface has on a linearly polarized incident beam. Linearly polarized light is comprised of two components, defined by the polarization of the electric field, one perpendicular (s-polarized) and one parallel (p-polarized) to the plane of incidence (figure 8). Upon reflection from a surface, the incident field becomes elliptically polarized – that is the s- and p-polarized components reflect differently from a surface and they are no longer equal in magnitude or phase.
Figure 8 Comparison of the reflection of s- and p-polarized incident fields.

From the boundary conditions at the surface, the Fresnel equations describing the reflection and transmission of both s- and p-polarized components of the incident beam are

\[
\begin{align*}
    r_s & = \frac{E_{rs}}{E_{is}} = \frac{\tilde{n}_i \cos \theta_i - \tilde{n}_t \cos \theta_t}{\tilde{n}_i \cos \theta_i + \tilde{n}_t \cos \theta_t} \\
    t_s & = \frac{E_{ts}}{E_{is}} = \frac{2\tilde{n}_i \cos \theta_i}{\tilde{n}_i \cos \theta_i + \tilde{n}_t \cos \theta_t} \\
    r_p & = \frac{E_{rp}}{E_{ip}} = \frac{\tilde{n}_i \cos \theta_i - \tilde{n}_t \cos \theta_t}{\tilde{n}_i \cos \theta_i + \tilde{n}_t \cos \theta_t} \\
    t_p & = \frac{E_{tp}}{E_{ip}} = \frac{2\tilde{n}_i \cos \theta_i}{\tilde{n}_i \cos \theta_i + \tilde{n}_t \cos \theta_t}
\end{align*}
\]

where the complex refractive index (\( \tilde{n} \)) renders these complex values, which we present in polar form by

\[
\begin{align*}
    r_s &= |r_s| e^{i\delta_s} \\
    r_p &= |r_p| e^{i\delta_p} \\
    t_p &= |t_p| e^{i\delta_p}.
\end{align*}
\]

[2.19] [2.20]
Differences in the reflected amplitude and the phase shift experienced by both s- and p-polarized components, i.e. the polarization state change, fully define a surface’s optical response. The complex representations of the reflected coefficients provide the core observables measured by ellipsometry. Specifically, the amplitude ratio

$$\tan \Psi = \frac{|r_p|}{|r_s|}$$

[2.21]

and the relative phase shift

$$\Delta = \delta_p - \delta_s.$$  \hspace{1cm} [2.22]

The observable ellipsometric variables, $\Delta$ and $\Psi$, define the fundamental equation of ellipsometry [47],

$$\rho \equiv \frac{r_p}{r_s} = \tan \Psi e^{i \Delta},$$

[2.23]

an expression that encompasses all the relevant optical information to fully describe the interaction of light with the material in question. From $\rho$, the pseudodielectric function can be calculated

$$\langle \varepsilon \rangle = \langle \varepsilon_r \rangle + i \langle \varepsilon_i \rangle = \langle n > + i \langle k > \rangle^2 = n_0^2 \sin^2 \phi \left[ 1 + \frac{(1 - \rho)^2}{(1 + \rho)^2 \tan^2 \phi} \right]$$

[2.24]

assuming a semi-infinite isotropic system, where $n_0$ is the refractive index of the incidence medium and $\phi$ is the angle of incidence. The pseudo-optical constants, $\langle n \rangle$ and $\langle k \rangle$ can also be calculated from equation [2.24], which represents the effective
optical response of the semi-infinite system measured by spectroscopic ellipsometry.

More detailed interpretation of the pseudo-optical functions will follow in chapter 3.

Beyond the basic principles driving spectroscopic ellipsometry, competent application of spectroscopic ellipsometry requires additional understanding of the systems necessary for accurate collection of data. Physically collecting ellipsometric data involves polarizers and detectors sensitive to the amplitude of the polarized components and a mechanism by which the phase change of the two components can be evaluated. Fundamental differences in spectroscopic ellipsometry technology originate in the system by which the phase shift is measured. Because of our interest in collecting real-time data, the fastest measurement can be achieved by phase-modulated ellipsometry (PME), therefore UVISEL (Jobin-Yvon) systems, both in situ and ex situ, are employed throughout this work to exploit their speed [48].

![Figure 9 Schematic representation of in situ phase-modulated spectroscopic ellipsometer](image)

24
The schematic in figure 9 describes the PME system affixed to the MBE growth chamber. Starting on the incident side, a broad spectrum (1.5-6.5eV) Xenon source passes through a polarizer (P=45°) introducing linearly polarized light onto the sample surface. The reflected signal enters the detector via an analyzer (amplitude ratio) and a photoelastic modulator (phase shift). Unlike traditional rotating analyzer or compensator systems, photoelastic modulators (PEM) require no motor-driven parts and instead rely on the piezoelectric response of quartz to perform phase detection and analysis. Though faster than motor-driven systems, PEM systems can lose stability in variable temperature environments. The reflected signal is then monochromated (static measurements) or collected with a multiwavelength detector (for kinetic measurements) for spectral analysis. Static measurements collected through the monochromator boast higher resolution, while the kinetic measurements can be acquired over the full spectrum every second.

Real-time PME, though not widely used in materials deposition systems, MBE for instance, is a powerful technique able to monitor material evolution during growth. Despite this fact, kinetic monitoring of nanoscale metal particle formation and evolution has not been embraced by the plasmonics community.

2.7 Molecular beam epitaxy and nanoparticle ripening

Unlike standard wet chemistry-based synthesis processes for metallic nanoparticles, molecular beam epitaxy (MBE) can be performed directly onto solid substrates. An ultrahigh vacuum (UHV) evaporation process, MBE boasts atomic scale thickness control and high crystalline quality epitaxial films making it a desirable
deposition process for crystalline optical and electronic semiconductor materials. The basic principles enabling MBE require a UHV environment (base pressure~$10^{-12}$ Torr) in which evaporated (solid source) or cracked (gas source) constituent materials in their atomic form can diffuse freely. Solid source metals are heated until evaporation (or sublimation in the case of Mg) occurs at which point a shutter is released to allow unfettered diffusion from the source into the growth chamber where the atomic flux is monitored by an ion gauge to establish the beam equivalent pressure (typical BEP~$10^{-8}$). Adjusting the source temperature controls the atomic flux to ensure appropriate constituent ratios when growing compound semiconductors (the III-Vs) or metal alloys.

The UHV growth chamber allows the atomic/molecular species to diffuse toward the substrate surface with little scattering, thus the term molecular beam. The sticking coefficient of the impinging species depends on a variety of factors including substrate temperature, metal/substrate reactivity, substrate morphology, etc. In this work, all metal dosages are calibrated assuming a unity sticking coefficient at room temperature, which is reasonable for the group III metals.

Metal nanoparticles grown in this work evolve according to a Volmer-Weber (3D, island) growth mechanism, which arises when depositing species more readily bind together as opposed to the substrate [49]. Atomic species adsorbed on the substrate surface, adatoms, diffuse with a mean capture lifetime $\tau$. Adsorption takes two forms, chemisorption and physisorption, which exhibit different degrees of binding because of the different mechanisms causing the atom to adsorb. Chemisorption is characterized by bond formation while the weaker effect, physisorption, stems from physical
interactions, \textit{i.e.} van der Waals forces. These adatoms diffuse on the surface and eventually some nucleate, usually at surface inhomogeneity sites (defects, steps, \textit{etc}) [50]. Nuclei smaller than a critical nucleus size tend to shrink, minimizing the surface energy and eventually disappearing. Super-critical nuclei of surface density $N$ gradually increase in size as additional adatoms adsorb, diffuse on the surface, and attach. Under continued atomic impingement, an increasing population of adatoms adsorbs on the nucleated surface and the nucleation density reaches saturation, $N_s$, beyond which nuclei begin to aggregate and form clusters to minimize the surface energy causing $N$ to decrease with time. Gradually, the aggregates will begin coalescing much like droplets of water on a freshly waxed car. Large droplets can consume smaller clusters in close proximity, but not touching, in a process called Ostwald ripening, which is distinguished by an increasing island size and concomitant decrease in island density. This results from mass transport from the small droplet to the large droplet where the driving force is the adatom concentration gradient (figure 10).

![Ostwald ripening and sintering](image)

\textbf{Figure 10} Nanoparticle coalescence by Ostwald ripening and sintering.

Alternative ripening processes also exist. Sintering occurs between two touching droplets that experience a large surface energy gradient at the neck, which induces
atomic diffusion to the neck until the two droplets become one, minimizing the total surface energy/area and the concentration gradient at the neck [50]. The final process involves clusters, i.e. aggregated adatoms, which diffuse along the surface and coalesce after colliding. These dimer-like clusters can also migrate and continue to minimize the surface energy via other ripening processes.

Nanoparticles grown by MBE assemble on a substrate’s surface as a collection of nanoparticles with a Gaussian size distribution. The optical response of these nanoparticles is comprised of their individual plasmons and the interparticle coupling of modes, assuming they are closely spaced. Using a far-field technique such as spectroscopic ellipsometry, whose beam spot size is much larger than a single nanoparticle, the measured optical behavior will be indicative of the assemblage’s plasmon resonance and their interparticle interactions.
Chapter 3 Demonstration of real-time spectroscopic ellipsometry for plasmon monitoring during nanoparticle growth

Measurement of plasmon resonant nanoparticle (NP) optical properties is challenging due to the localized nature of the large, longitudinal surface-fields. Dark-field scattering or near-field scanning techniques have become the de facto standards for probing metal nanoparticle plasmons. Aspects of their optical set-ups limit the applicability of these measurement techniques for real-time monitoring during nanoparticle synthesis. We have demonstrated the novel use of nondestructive, in situ spectroscopic ellipsometry to accurately probe in real-time and thereby tune the surface plasmon resonance of metal nanoparticles deposited on various transparent and absorbing substrates by molecular beam epitaxy (MBE). Beyond enabling plasmon resonance tuning of metallic nanoparticle ensembles, real-time monitoring of their collective plasmon resonance can also be applied while modifying the nanoparticles’ surrounding environment such as for gas sensing or thermal treatment to understand the optical manifestation of physical modifications.

Molecular beam epitaxy of plasmonic metal structures is advantageous because of the potential for device integration, creating complex particles, and/or growing multilayered structures. Traditional growth of plasmonic nanostructures usually requires wet chemistry, nanolithography, FIB, or surface roughening. None of these techniques necessarily lend themselves to real-time monitoring and tuning of the nanostructures;
they all require prior knowledge of fabrication conditions to tune the nanostructures accordingly to the specifications of the desired application.

### 3.1 The pseudo-optical constants and optical modeling

To fully comprehend spectroscopic ellipsometry’s utility, the physical meaning derived from the ellipsometric variable, ρ, and pseudo-optical constants must be detailed. As shown earlier, all of the pseudo-optical constants can be determined from the spectroscopic variable, ρ, using the relation

\[
\langle \varepsilon \rangle = \langle \varepsilon_r \rangle + i \langle \varepsilon_i \rangle = \langle n \rangle + i \langle k \rangle = n_0^2 \sin^2 \phi \left[ 1 + \frac{(1 - \rho)^2}{(1 + \rho)^2} \tan^2 \phi \right],
\]

where \( n_0 \) is the ambient refractive index (vacuum = 1) and \( \phi \) is the angle of incidence (typically \( \sim 70^\circ \)). Ellipsometric measurements mathematically represent a material’s optical behavior via the pseudodielectric function, which describes the effective optical behavior of a multilayer system comprised of a substrate, the deposited layers and the ambient (figure 11). The pseudodielectric function therefore does not express the actual dielectric function of the individual layers, but rather the net behavior of the substrate/layer(s) system.

![Figure 11 The standard substrate/layer system described by the pseudodielectric function (\( \langle \varepsilon \rangle \)).](image-url)
Optically, the pseudodielectric function consists of contributions from the constituent materials’ complex optical constants, their spectral dependence, and their thicknesses. Extracting each layer’s properties from the measured optical response requires optical models based on effective medium approximations. Effective medium approximations depict the optical response of a material as a complex system comprised of several constituents and geometries distributed in different relative amounts whose net optical response is calculated from their relative fractions in the heterogeneous mixture by weighting their respective polarizabilities [51]. From the Clausius-Mossotti equation,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} n \alpha$$

(3.2)

a homogenous material comprised of \(n\) polarizable components possesses a dielectric function, \(\varepsilon\), that corresponds to its polarizability, \(\alpha\). In a heterogeneous material surrounded by an ambient, \(\varepsilon_h\), each component’s bulk polarizability is weighted by a volume fraction and they are summed to form the net polarizability, shown here by the Lorentz-Lorenz equation.

$$\frac{\varepsilon - \varepsilon_h}{\varepsilon + 2\varepsilon_h} = f_a \frac{\varepsilon_a - \varepsilon_h}{\varepsilon_a + 2\varepsilon_h} + f_b \frac{\varepsilon_b - \varepsilon_h}{\varepsilon_b + 2\varepsilon_h}$$

(3.3)

For the Maxwell-Garnet (MG) approximation, a small fraction of one constituent, defined by its species’ shape and small fill volume, is embedded in a homogeneous host matrix. The MG approximation is well suited for disperse metal inclusions in glass, but less so for high density metal nanoparticles on a solid support. An adequate representation for this system, the Bruggeman effective medium approximation (BEMA) describes a heterogeneous material comprised of evenly weighted individual components. In the
BEMA case, the effective material’s dielectric function, $\varepsilon$, is considered the host material and relates to its components by

$$\sum_i f_i \frac{\varepsilon - \varepsilon_i}{\varepsilon_i + 2\varepsilon} = 0$$

(3.4)

where $\varepsilon_i$ is the dielectric function of the $i^{th}$ constituent and the $f_i$’s are similar for all constituents. Through fitting algorithms, we can perform the inversion to extract the individual constituents’ optical behavior. Minimizing the error between the experimental data and the optical response of the EMA structure by adjusting fit parameters specific to the unknown layers of the EMA produces highly accurate representations of the constituent layers. Depending on the optical model and on the dispersion equation used to describe each layer (Drude, Lorentz oscillator, etc), intrinsic material properties, e.g. dielectric function, plasma frequency, oscillator energy and strength, and extrinsic properties, i.e. layer thickness, surface roughness (by void fraction), are tuned through the fitting process. Application of the EMAs requires care as they are mathematical constructs intended to mimic the optical response of multilayer systems and the fitted values should represent physical reality. Unrealistic values arise when the fit parameters approach a local minimum; therefore initializing the parameters well is a challenge to accurate material description.

Because spectroscopic ellipsometry is not an absolute measure of the light intensity and only relies on relative polarization states, the data is unaffected by macroscopic roughness and diffuse scattering from surface features. Spectroscopic ellipsometry’s utility derives from its extreme surface sensitivity and can identify sub-
monolayer material modifications including microstructure and atomic roughness of thin films and surfaces with size scales $< \frac{\lambda}{10}$. Combined with EMA modeling, spectroscopic ellipsometry can optically characterize and identify rough surfaces (modeled by incorporating a void fraction in the surface layer) and Ångstrom-scale interfacial layers (manifested as non-abrupt/graded interfaces). The pseudo-optical functions represent the net optical behavior of a system and are sufficient for situations such as observing the behavior of densely spaced metal particles supported on a substrate. Therefore, since the pseudoextinction coefficient accurately describes the absorption spectrum of the effective medium, kinetic monitoring of $\langle k \rangle$ facilitates real-time observation of the incident beam coupling into the metal nanoparticle plasmon modes manifested as a resonant absorption. We are not interested in extracting individual nanoparticle properties, such as its optical constants or size, rather we wish to describe the net population’s optical response and as such correlating the individual nanoparticle size to the modeling is beyond the scope of this work. Through the real-time $\langle k \rangle$ monitoring, we will see how the average nanoparticle diameter correlates linearly with the observed plasmon resonance and we can exploit kinetic measurements of $\langle k \rangle$ to tune the plasmon and, consequently, the average nanoparticle size.

### 3.2 Plasmonic interpretation of the pseudoextinction function

Spectroscopic ellipsometry, while powerful, has not enjoyed the same widespread use as RHEED (in MBE) or other traditional in situ monitoring techniques. While a small, but strong community of spectroscopic ellipsometrists exists their work
has primarily focused on the optical characterization of thin film semiconductors and dielectrics and, in even fewer cases, the dynamic evolution of nanostructured metals during growth [5255]. Application of spectroscopic ellipsometry to nanomaterials characterization has not garnered widespread popularity and this is partly due to an only nascent understanding of how spectroscopic ellipsometry can unveil nanoscale variations of materials properties. This section details the interpretation of pseudo-optical constants derived from ellipsometric data for metal nanostructure growth and the first UV measurements of substrate-supported gallium (Ga) localized surface plasmons.

We performed room temperature ultra-high vacuum (UHV) evaporation of Ga metal onto dielectric and semiconductor substrates to identify its plasmon resonance spectral range.

Ga nanoparticles were deposited onto single-side polished sapphire substrates in a Veeco GEN II plasma-assisted molecular beam epitaxy (MBE) system equipped with an in situ spectroscopic ellipsometer (UVISEL-Jobin-Yvon) at an angle of incidence of 70° and operating in the 1.5–6.5eV photon energy range. Under ultra-high vacuum (UHV) conditions, the nanoparticles were deposited at a constant Ga beam equivalent pressure of 2.043x10^{-7} Torr, corresponding to 41 ML/min of Ga in the thin film approximation. The evaporation was performed at ambient (chamber) temperature (~25°C) to minimize the metal-substrate interfacial interactions. Pseudoextinction spectra were collected both in real-time during deposition and after completing deposition. Ex situ spectra were also measured over a wider spectral range (0.75-6.5eV) using a separate UVISEL-Jobin Yvon system. Post-deposition imaging was
performed using a Digital Instruments Dimension 3100 atomic force microscope (AFM) in tapping mode and a Philips XL30 scanning electron microscope (SEM) employing beam energies between 2-5kV.

Models of a 2D Ga film based on the bulk dielectric function exhibit a significantly different optical response with increasing thickness compared to the observed temporal evolution of the Ga metal pseudoextinction function during room temperature metal deposition (figure 12).

Figure 12 Thin film layer model for increasing thickness (left) compared to measured Ga on SiC real-time ellipsometric spectra (right).

A distinct resonance emerges just as the deposition begins (fig. 3.1, right) while such features emerge with increasing film thickness (fig. 3.1, left) and since light from free space cannot couple into 2D plasmon modes without momentum matching gratings or prism coupling, the resonance cannot be attributed to thin metal film formation. Given the Drude nature of Ga metal (figure 13) and the previously reported plasmon activity of Al and In the resonance emerging during Ga deposition at room temperature must result
from incident photons coupling into plasmon modes of the Ga aggregates, i.e. 3D nanostructures [26,56,58].

Figure 13 The Ga bulk dielectric function measured by spectroscopic ellipsometry.

The plasmon peak continuously redshifts as the deposition time increases, which correlates to an increasing average particle size (figure 14), and never approaches the Drude metal characteristic spectrum implying that Ga follows a 3D growth mode and does not form a thin film at room temperature. In fact, the nanoparticle density observed by AFM imagery, temporally evolves in a fashion indicative of Ostwald coalescence of the Ga nanoparticles where a decreasing nanoparticle density accompanies increases in metal flux [50].
For completeness, other explanations for the pseudoextinction resonance must be considered. As previously discussed, spectroscopic ellipsometry is a polarization sensitive technique; therefore the measurement is immune to random scattering due to macroscale surface roughness. Coherent scattering due to underlying surface structure periodicity can yield resonant features in the spectra, however in the case of self-assembled metal nanostructures by UHV evaporation Bragg scattering does not occur. Post-deposition AFM imagery and fast Fourier transform analysis of the images confirms the random spatial distribution of Ga nanoparticles on sapphire. \textit{In situ} azimuthal angle
rotation and \textit{ex situ} variable angle of incidence (VAOI) spectroscopic ellipsometry measurements were also performed to confirm the absence of coherent scattering (figure 15). The resonance energy (wavelength) remains unchanged after both angular manipulations, which refutes the possibility of Bragg scattering from the surfaces.

![Graph showing plasmon resonance](image)

**Figure 15** The plasmon resonance measured by SE is insensitive to azimuthal rotations (left) and variable angle of incidence (VAOI) measurements (right).

Real-time data from spectroscopic ellipsometry provides a means by which the deposition can be monitored and the plasmon resonance tuned to specific photon energy without prior knowledge of the particle size or distribution. The real-time tunability enabled by spectroscopic ellipsometry is a powerful tool for plasmonic design as shown by our first demonstration of UV-vis-NIR tunable plasmonic Ga nanoparticles.

### 3.3 Extracting the absorption spectrum from the pseudoextinction function

We attribute the observed resonances in the pseudoextinction coefficient to a nanoparticle assembly’s collective plasmon resonance. The pseudoextinction coefficient, unlike the real extinction coefficient, is a function of the optical properties of
the deposited layer and its interactions with the underlying substrate and its dielectric function. The pseudoextinction function is an effective extinction function describing the optical behavior of the system assuming a simple two-phase sample/ambient optical model that reveals the energy at which the whole system’s plasmon resonance occurs [59].

To define the aggregate plasmon resonance of the metal nanostructures independent of the substrate interaction, optical modeling is necessary. Fitting the pseudoextinction function to a simple structure comprised of substrate/Ga NPs/air (figure 16) sufficiently describes the effective material when the substrate is sapphire, since room temperature metal deposition on inert sapphire substrates minimizes the formation of an interfacial mixed layer, as confirmed by XPS analysis.

![Multilayer System Diagram](image)

**Figure 16** The multilayer system to model the substrate/Ga nanoparticles/air samples.

To model a layer of plasmonic metallic nanoparticles, Lorentzian oscillators best describe the resonances exhibited by the plasmons [60]. Furthermore, since the sapphire is transparent ($k=0$) throughout the investigated spectral range, the real extinction spectrum ($k(\omega)$) of Ga on sapphire differs only slightly from the pseudoextinction coefficient (figure 17).
Figure 17 Extracted extinction spectrum for Ga nanoparticles on sapphire compared to the experimental pseudoextinction spectrum.

Clear differences arise when the substrate is no longer optically transparent throughout the measurement range. For example, Si substrates exhibit two interband critical points, E1 and E2, which interfere with the metal plasmon features (figure 18, left).

Figure 18 Extinction spectrum of bare Si (100) (left). Extracted plasmon resonance extinction spectrum of Ga nanoparticles on Si (100) compared to the experimental pseudoextinction spectrum (right).
These interband critical points obfuscate the real location of the plasmon resonances as evidenced by the distinct differences between the pseudoextinction function and the extinction spectrum after removing the substrate effect (figure 18, right).

From this work we demonstrated the use of spectroscopic ellipsometry for 'plasmonic ellipsometry' and modeling can reveal the real absorption spectra for the deposited plasmonic 3D metal nanostructures regardless of metal type, geometry, or substrate choice. The ability to model and extract the plasmonic properties of metal nanoparticles on any solid support gives SE-based measurements freedom with substrate choice that is advantageous with respect to traditional, transmission-based, far-field measurement techniques that limit the plasmonic nanoparticles' substrate to those that are transparent throughout the measurement range.
Chapter 4 Characterization of plasmonic group-III metals

The group-III metals are interesting for optical/plasmonic applications because their plasma frequencies, \( \omega_p \), of these Drude metals exceed those of Au or Ag (2.5eV and 3.8eV, respectively) suggesting they can excite UV plasmons (table I) [26].

![Figure 19](image)

The group III metal bulk dielectric functions are Drude-like. Ga and In were measured by SE (0.1-0.2mm Ga on glass, 1-2 µm In on Si) while Al is the Aspnes reference dielectric function.

While Al and In have been previously reported in plasmon studies, they are not widely used because they oxidize too much and become highly resistive, dampening the plasmon resonance [56,57,61,62]. Ga plasmonic applications are, however, still in their nascent stages [4,63].

Table I Bulk plasma frequencies and reported 2D surface plasmon resonances of the MBE metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \omega_p ) (eV)</th>
<th>( \omega_{sp} ) (eV, thin film)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al [26,58]</td>
<td>15-15.2</td>
<td>6.3-10.5</td>
</tr>
<tr>
<td>Ga [64]</td>
<td>13.9</td>
<td>unreported</td>
</tr>
<tr>
<td>In [26]</td>
<td>11.5</td>
<td>4</td>
</tr>
<tr>
<td>Mg [58]</td>
<td>10.5</td>
<td>7</td>
</tr>
</tbody>
</table>
4.1 Metal nanostructure and evolution revealed by plasmonic ellipsometry

Real-time monitoring of the metal deposition by plasmonic ellipsometry reveals details about the metal geometry and evolution during growth. The group-III metals are perfect case studies for observing metal evolution since each grows according to different modes.

Aluminum deposited on both sapphire (dielectric) and GaN (semiconductor) at room temperature behaves the same way – evolution from 3D droplets that coalesce and eventually form a continuous 2D film. This is visualized in kinetic SE spectra by a continuous transition from a plasmon resonance to a Drude-like pseudodielectric function (figure 20).

Figure 20 Real-time SE spectra during Al deposition on GaN proceeds from a 3D morphology with an observable plasmon resonance to a Drude-like thin film. SEM imagery confirms the nearly coalesced surface morphology (inset).
Concomitant with the Al plasmon redshift the resonance narrows – the dampening decreases – which is attributed to the increasing size of the Al structures before coalescence [65]. The percolation limit resides at the optical transition from the particle plasmon resonant pseudodielectric function to a Drude pseudodielectric function measured by kinetic SE and is defined by the corresponding metal effective thickness [60]. Beyond the percolation limit, the incident beam can longer momentum-match to the Al plasmon at which point the bulk Al behavior dominates the optical spectra. Post-deposition SEM images confirm the nearly coalesced thin film morphology of Al once the SE spectrum resembles a Drude dielectric function (figure 20, inset).

Conversely, large dosages of In and Ga sustain a particle plasmon resonance in their SE extinction spectra since neither metal coalesces into thin films; this is optically supported by their spectra never evolving into a Drude dielectric function – the optical indication of film coalescence. By observing the kinetic evolution of the group III metals on solid surfaces at room temperature, we can highlight the inherent differences in the wetting properties of these three metals as evidenced by their real-time plasmon resonance evolution.

As shown earlier, the in situ pseudoextinction functions of Ga nanoparticles for three selected equivalent thicknesses (650ML, 482ML, and 325ML) along with the corresponding AFM images are shown in figure 21.
Figure 21 Ga nanoparticles deposited on sapphire with effective thicknesses of (a) 650ML, (b) 482ML, and (c) 325ML.

A single UV mode emerges as Ga (and In) nanoparticle growth is initiated, which redshifts with increasing metal dosage. Eventually, a second high-energy mode emerges and Ga metal deposition never yields a Drude pseudodielectric function. As the deposition time increases, the average particle size increases while the particle density decreases. AFM and SEM images reveal that ripening involves smaller particles...
coalescing and forming larger particles with increasing deposition time. Histograms (figure 21, middle) from SEM imaging reveal a bimodal distribution of the particle sizes and an increasing size disparity between the large and small particle populations as deposition time increases [66]. The size distribution’s evolution confirms that Ga metal coalesces by Ostwald ripening [49, 67]. Thus, unlike thin metal films, e.g. Al, that coalesce after exceeding a percolation limit, room temperature deposited Ga does not produce a Drude-like pseudodielectric function [52].

Indium grows at room temperature onto solid supports in a 3D geometry as well, shown here on GaN substrates (figure 22).

Figure 22 The In nanoparticle on GaN plasmon resonance redshifts with increasing metal dosage. The nanoparticle size increases with dosage while the areal density decreases.

Also following an Ostwald ripening process, the In nanoparticles’ size increases with metal dosage and a concomitant decrease in nanoparticle density. Unlike Ga, however, In forms jagged, polygonal 3D nanostructures, as evidenced by AFM and SEM imagery.
The irregular, polygonal In nanoparticles evolve as such because of the solid, crystalline structure inherent to In deposited by UHV evaporation [57]. These sharp features can produce concentrated electric fields, but we have not measured that effect.

Through real-time plasmon resonance monitoring and post-deposition nanoparticle geometric characterization we have elucidated the stark contrasts in how the group III metals evolve during room temperature deposition. Al wets the substrate surfaces very well, it is known to adhere readily to many substrate surfaces during epitaxy, and as such the islands that initially form gradually coalesce into a thin film whose plasmon resonance is not measurable from free space.

Conversely, both Ga and In proceed in an Ostwald ripening regime whereby the nanoparticle geometry continues to evolve into lower density, large nanoparticles under continued metal flux. The two metals do, however, exhibit striking differences in resultant nanoparticle geometry. While polycrystalline In can be deposited by evaporation, the symmetry and curvature of the Ga nanoparticles is unexpected. We will elucidate the origin of the Ga nanoparticle geometry based on deposited Ga’s phase at room temperature in a later section.

4.2 Ga nanoparticle plasmon mode splitting

Tilted SEM images reveal that Ga nanoparticles are truncated spheroids (figure 23) that are best described as droplets. Based on the tilted SEM imagery and the AFM-probed morphology, the in-plane axis, on average, is larger than the nanoparticle height. The average Ga aspect ratio, defined here as the ratio between the mean diameter and the mean height, decreased with increasing dosage.
Figure 23 Tilted (45°) SEM image of the Ga nanoparticles deposited on sapphire illustrate Ga’s truncated spheroid shape.

From the extracted extinction spectra we can assign the two plasmon modes based on the nanoparticle size and orientation. The low energy peak corresponds to polarization along the longitudinal (in-plane) axis, which is the larger of the two main axes and the accompanying high energy peak corresponds to the transverse (out-of-plane) mode [31]. The two modes redshift throughout growth because the nanoparticles increase in size along both axes. Variable angle of incidence (VAOI) measurements reveal a changing plasmon strength, as measured by \( |\langle k \rangle| \), for the different incidence angles (figure 24).
Figure 24 The transverse plasmon resonance amplitude is sensitive to angle of incidence (5.5eV), whereas the longitudinal mode (2eV) is stable.

The changing amplitude is a manifestation of the polarization-dependent coupling along the two axes. A $p$-polarized incident field couples into both the in-plane and out-of-plane axes, but the extent varies and the component along the out-of-plane nanoparticle axis is sensitive to the angle of incidence. Therefore, the transverse mode amplitude varies more drastically compared to the longitudinal mode.

Anisotropic interaction of the electric field components parallel and perpendicular to the surface plane also occurs when the nanoparticles are surrounded by two different semi-infinite media, e.g. nanoparticles supported by a substrate, and causes mode splitting [42]. In the dipole limit, the nanoparticles are treated as small oscillating dipoles on the substrate surface. When the incident field excites the plasmon dipoles an image charge accompanies the dipoles in the solid support. The interaction between the surface dipoles and their image charges produce split radiative modes, as described in Chapter 2. The Ga nanoparticles produce split plasmon modes on a range of substrates
– dielectric and semiconductor – and deconvolving the two sources of anisotropy is beyond the scope of this work.

The plasmon resonance extends from the UV to the NIR, by any measure a wide range over which the nanoparticle resonance can be tuned. A third shoulder also exists between the two main plasmon modes, which we attribute to a higher order longitudinal mode (multipole) due to the large in-plane dimension of the particles since this feature only emerges for the largest nanoparticles ($d \sim \lambda$) well outside the dipole limit (figure 24).

In summary, the geometry (shape and size) and presence of solid supports all contribute to the final plasmon energy. The nonspherical geometry of the In nanoparticles induces a nonlinear plasmon resonance to mean nanoparticle diameter correlation both in the literature and by our investigations. Our measurements, however, extend far beyond the plasmon resonances described in the literature [68], as shown in figure 25, highlighting the wide tunable range of the longitudinal and transverse In nanoparticle plasmon resonance modes.
Figure 25 In plasmon resonance as a function of mean nanoparticle diameter. Lines are drawn to guide the eyes.

Unlike In nanoparticles, the Ga nanoparticle plasmon resonance linearly correlates with the mean nanoparticle diameter, which aligns with narrow spectral range measurements taken of Ga nanostructures embedded in an SiO$_2$ matrix reported by Tognini, et al (figure 26) [30].
Figure 26 The Ga nanoparticle plasmon resonance as a function of mean nanoparticle diameter. Ga nanoparticles were grown on (a) Si, (b) GaN, and (c) sapphire. Both the longitudinal and transverse modes are shown along side work from [30].

The error bars reflect the increasing size distribution as the mean nanoparticle size evolves and ripens. The nanoparticles whose transverse mode resides within the measurement range also linearly correlates with the mean particle diameter. The range of Ga plasmon resonances presented in figure 26 represent Ga nanoparticles deposited on a variety of substrates, including Si, GaN, and sapphire. The linear correlation with respect to nanoparticle diameter suggests that the shape factor, $\chi$, from equation [2.17] also linearly correlates with the nanoparticle diameter. The linear correlation between the shape factor and the nanoparticle diameter results from the liquid phase of the Ga nanoparticles, as will be discussed later, which ensures a consistently spheroidal shape during coalescence. More importantly, we have therefore determined the relationship between AFM measured mean Ga nanoparticle diameter and the longitudinal plasmon across wide spectral range.
4.2 Thermal annealing the plasmon resonance

To thoroughly explore the metal nanoparticle properties, plasmonic modification by thermal annealing (and cooling) was investigated.

4.2.1 Annealed Indium nanoparticles

SE spectra of oxidized indium nanoparticles ($T_{m,\text{In}} = 156.6^\circ\text{C}$) annealed between 25-300°C exhibit unchanged optical resonances (figure 27).

![Graph showing SE spectra of oxidized indium nanoparticles](image)

**Figure 27** In nanoparticles exhibit remarkable plasmon stability (energy and amplitude) up to 300°C, above which the plasmon redshifts slightly and decreases in amplitude.

Beyond 300°C, however, the plasmon resonance amplitude decreases irreversibly, even after cooling back to room temperature, although the In nanoparticle geometry is unchanged (figure 28).
Figure 28 Comparison of oxidized In nanoparticles before and after annealing up to 350°C.

The thermal annealing above 300°C can modify the nanoparticle’s conductivity, which in turn affects the plasmon resonance. Previous studies of sputtered indium oxide films for transparent conductive contacts reported annealing under vacuum and in air ambient caused a rapid resistivity increase around 400K due to crystallization of the amorphous film [62]. In our case, before annealing the In nanoparticles were exposed to air and developed a native oxide shell that causes the plasmon to redshift. Once heated, the native oxide may anneal and crystallize, further decreasing the nanoparticles effective conductivity explaining the small redshift and amplitude decrease above 300°C. The discrepancies between our observed critical temperature and the previously reported work can be attributed to the vastly different geometry of the indium oxide (nanoparticles vs. film) and chemical stability of each oxide species. The In nanoparticles oxidize when exposed to air with an undetermined stoichiometry and coverage and the oxidation can cause plasmon modification when annealed.
4.2.2 Annealed Ga nanoparticles

Earlier presented Ga bulk dielectric functions were experimentally collected by ex situ spectroscopic ellipsometry of liquid bulk Ga. Peculiar features in the solid Ga bulk dielectric function, deviations from the Drude metal model, triggered our interest in the phase and temperature response of Ga. Ga ingots melted onto glass slides remain liquid at room temperature, but placing the melted bulk Ga on glass into a standard household refrigerator for several hours solidifies the Ga into a specular, bulk film several millimeters thick. The acquired dielectric function of the solid, bulk Ga reveal mostly free electron behavior, but with a distinct bound electron contribution in the low energy range [26]. Conversely, the measured complex dielectric function of the bulk Ga left in liquid phase reveals no such low energy, bound electron contribution within the measurement range (figure 13). Optically, we observe free electron, metallic behavior of the liquid bulk Ga as opposed to the solid phase [69].

Given the bulk dielectric properties and the nearly room temperature bulk melting point, it is unclear whether the Ga nanoparticles are solid or liquid. However, the Ga nanoparticle plasmon resonance suggests their metallic character and given optical properties of the bulk, the nanoparticles are likely liquid phase. The near room temperature melting point (T_m=29.8°C) and expected drop in melting temperature at the nanoscale [70] substantiate the liquid phase of nanostructured Ga. Ga nanoparticles exposed to conditions ranging from -80°C to 600°C boast completely stable extinction spectra and unchanged morphology since the phase remains liquid and Drude-like throughout this range (figure 29) [71].
The Ga plasmon resonance is stable at temperatures ranging from -80°C to 600°C.

Given the bulk metallic behavior in the liquid phase coupled with the existence and extreme temperature stability of the nanoparticle plasmon resonance, the nanoscale Ga is liquid at room temperature. Solid Ga is known to be polymorphic; it boasts over 10 solid phases, of which only one is stable (α-phase), while four metastable (atmosphere) phases also exist (β, γ, δ, and ε) [72,75], but Ga’s low bulk melting point (T_m=29.8°C) combined with the well-known undercooling of Ga nanoparticles produces Ga liquid nanoparticles at room temperature [70,71], which do not coalesce into a thin film [52]. While the stable, solid α-phase exhibits semimetal behavior because of its bimetallic (covalent) molecular structure and accompanying pseudogap near the Fermi energy [75,76], Ga is a conductive Drude metal in its stable liquid phase with an almost free electron density of states [77], as evidenced by their respective bulk dielectric functions measured by spectroscopic ellipsometry. The liquid Ga droplets are stabilized by thin Ga oxide layer (predominantly amorphous Ga_2O_3) that can saturate at
thicknesses as low as 5Å [78]. Ga structural, electronic, and optical stability across a wide temperature range opens a myriad of opportunities where Ga nanoparticles can be exploited for applications used under extreme conditions.

4.3 Metal oxidation and the plasmon resonance

One major problem plaguing the widespread applicability of Ag plasmonic nanostructures is severe degradation that completely suppresses the plasmon resonance shortly after air exposure. The chemical activity of Ag in air renders the metal unstable, easily corroded and, ultimately, nonconductive, severely hampering the activity of the free electrons as manifested by the plasmon resonance’s complete disappearance within 36 hours of air exposure [29].

A plasmonic metal that can exist in an air ambient environment without detrimental oxidative properties would be advantageous in sensing, detection, and optical applications. Devices must exist in the real world – not in solution or vacuum. While Al and In both oxidize excessively, Ga does not. Comparison of the in situ and ex situ spectra of the Ga nanoparticles recorded after weeks and months of air exposure reveals a slight redshift (−0.4-0.5eV) for the transverse plasmon mode upon particle oxidation (figure 30).
Figure 30 The Ga nanoparticle transverse plasmon mode slight redshifts upon oxidation. The longitudinal mode is largely unaffected.

Though a small shift in the energy scale, these shifts represent between 20nm and 40nm shifts in the wavelength scale, a marginal issue in the UV, but lower energy modes clearly suffer longer wavelength redshifts. Nanoparticle design for specific optical applications should account for the extent of the oxidation-induced redshift to ensure maximized mode coupling. A combination of nanoparticle and optical incidence geometry yields a negligible oxidation effect on the longitudinal mode. Most importantly, the Ga nanoparticle plasmon mode remains active in the UV after oxidation and the nanoparticle optical response is remarkably stable – *i.e.* once oxidized, Ga nanoparticle oxidation does not persist *ad infinitum*.

*Ex situ* X-ray photoelectron spectroscopy (XPS) measurements confirmed a strong contribution of Ga$_2$O$_3$ bonds (figure 31).
The thickness of the oxide shell surrounding the metallic core mitigates extent of the redshift since liquid Ga oxidation has been shown to saturate once a thin (~5Å) oxide shell forms [78]. This represents an advantage over the Ag, Al, and Mg plasmon resonances which, in contrast, are very sensitive to air exposure [29,58,79].

4.4 Conclusions

We have reported experimental evidence of plasmon mode splitting for substrate-supported liquid Ga nanoparticles. The transverse and longitudinal modes that emerge can be tuned by real-time monitoring using in situ spectroscopic ellipsometry from the UV to the NIR. Both Ga plasmon resonance mode energies linearly correlate to average particle diameter. Unlike Al and In, liquid Ga nanoparticles are advantageous for applications because of their plasmon resonance oxidation stability and their temperature insensitivity across a wide temperature range. Limitations to the Ag and Au
plasmon tunable range prevent the demonstration of plasmonic applications in the UV and. Au in particular suffers from a strong, broad interband transition feature in its dielectric function, limiting the redshift of the plasmon resonance and preventing any mode splitting from emerging in the red to near IR [28]. Boasting strong local fields, the Ag plasmon is attractive for applications save for the high chemical reactivity that limits the lifetime and stability upon air exposure hindering its widespread commercial viability [29]. While the present reality is that Au and Ag still represent the ‘gold standard’ for plasmonic applications, Ga metal’s peculiar structural, electronic, and chemical properties make it an intriguing new facet in the plasmonic arsenal.
Chapter 5 Bimetallic Ga-Mg plasmonic nanoparticles

5.1 Limitations to geometry-based plasmon tuning

While the size and shape control of plasmonic nanoparticles is well understood—they require a great deal of control over the nanoparticle growth process. Traditional approaches to metallic nanoparticle synthesis involve either solution chemistry [14,15,80] or physical deposition [60,66,79,81,82]. Solution-based precipitation of constituent salts can produce alloying by mixing the constituent salts before precipitation [16,83], while core-shell formation simply requires sequential formation of the shell metal on core seeds [84,85]. Colloidal metal nanoparticles transferred onto solid-supports disperse and can overlap and/or cluster, modifying the observed plasmon resonance. The problems associated with solution-based nanoparticles necessitate the addition of ligand stabilizers that surround the nanoparticle surfaces and prevent clustering and aggregation in solution [86]. However the stabilizing molecules tend to limit the extent of nanoparticle size/shape control that the chemist can achieve [87,89].

Physical deposition methods can produce irregular shapes and sizes determined by the self-assembled coalescence processes governing metal deposition below the percolation limit [14,55]. Sputtered or evaporated metal thin films can be annealed at high temperatures to form irregular nanoparticles whose aggregate behavior is tuned to a broad resonance [90]. For better shape/size control, evaporation or sputtering onto templates of self-assembled polystyrene structures can produce various shapes, e.g. pyramids and hexagons [15]. E-beam or focused ion beam lithography can also make well-defined nanoparticle shapes and distributions [5,14,15].
Despite the high degree of control many groups have demonstrated over the size or shape of their noble metal nanoparticles, the achievable range of plasmon resonance tuning by size modification is limited. Considering the traditional noble metals, Ag offers a sharper plasmon bandwidth because of its smaller imaginary dielectric constant compared to Au over the visible wavelength range. Nevertheless, Ag nanoparticle device applications are limited by the poor chemical stability of Ag. On the other hand, spherical Au nanospheres offer very limited tunability of their plasmon resonance frequency [91]. With increasing nanosphere size, electromagnetic retardation effects hinder the plasmon resonance redshift to within a small spectra range [65]. Au nanospheres over a broad-size range have resonances between 520nm and 580nm [26,92], they are, therefore, not suited for NIR or UV applications. Modifying the shape, e.g. high aspect ratio nanorods, adds a degree of freedom for the electron density oscillations splitting the plasmon modes such that additional plasmon modes are redder than the dipole limit of the plasmon resonance [27,45]. From the bulk dielectric constants of Au and Ag, the dipole limit in air, $\varepsilon_r = -2$, limits each metals’ spectral range to wavelengths longer than 480nm (2.6eV) and 354nm (3.5eV), respectively. Broad interband transitions featured in the Au bulk dielectric function further limit its tunability to the blue, unlike other plasmonic metals [28,93]. Thus, Ag and Au nanoparticles’ tunable ranges are mostly limited to the visible and the near IR, smaller than the Ga plasmon’s range.

Despite its broad plasmon range, simply modifying the Ga plasmon resonance by size, which is controlled by total metal dosage, is untenable in situations that require
small particles with long wavelength plasmons such as plasmonic waveguides for optical communications systems. The subwavelength dimensions of plasmonic waveguides enable the transfer of optical signals along nanoparticle chains whose size falls below the diffraction limit, thus saving precious chip-level real estate [5,21,94]. To achieve sufficiently red plasmon resonances of the nanoparticles comprising these waveguides, the nanoparticles must be relatively large, but in this case the waveguide loses its size advantage. Alloying or mixing multiple metals to varying compositions is a natural alternative to modifying the metal properties without sacrificing nanoparticle size. Previous binary metal nanostructure studies typically produced core-shell \([17,84,95,96]\) or alloyed/mixed metal nanostructures \([16,63,83,96,101]\) comprised of two metals (Ag, Au, Al, Pt, Cu, Ga, \textit{etc}). Metal-dielectric core-shell structures are another alternative to tuning the plasmon independent of size. The plasmon resonance of core-shell structures depends on the total nanoparticle size, but more strongly on the relative radii of the two constituents (core and shell) \([102]\). Bimetallic nanoparticles have been demonstrated with varying degrees of plasmon sensitivity to composition and often across a \(\sim1\text{eV}\) plasmon range \([16,99,103]\).

\textbf{5.2 The Ga-Mg system for plasmonic alloys}

The technological advantages of Ga have been described previously \([4,54,55,63,104]\) and alloying Ga with other MBE metals to tune the plasmon resonance independent of nanoparticle size is the natural extension of our previously described work. Metal mixing with Mg provides interesting additional potential applications related to hydrogen storage and catalysis. It is well known that of the metal hydrides, Mg has
the greatest potential for hydrogen storage because of its high percent weight capacity [105,106]. Combined with Ga, which has been demonstrated to dissociate H₂ [107,108], the dissociative chemisorption of H₂ on Ga-Mg mixtures is a possibility [106]. From a materials science perspective, the Ga-Mg binary system has an interesting, featured phase diagram providing ample opportunities to form stable alloys and to manipulate the composition (figure 32).

![Ga-Mg phase diagram from [109]](image)

**Figure 32 Ga-Mg phase diagram from [109]**

Despite the variety of stable Ga-Mg alloys possible, this binary system has not been widely studied; indeed most studies focus on ternary or quaternary alloys that include Ga and Mg. As such the area is ripe for deeper understanding since the catalytic, hydrogenation, and optical properties are of interest for a variety of technological applications.
Based on the alloying demonstrated in the Ag-Au binary system, we expect that mixing Mg and Ga – of which the plasma frequencies are 10.7 and 13.9 eV, respectively, provides a additional controllable material parameter to tune the bimetallic plasmons [26][64]. How the two metals optically mix to shift the plasmon resonance is disputed in the literature. Some works have shown that a simple linear combination of the pure metal dielectric functions adequately describes the effective dielectric function of homogeneous bimetallic bulk as

$$\varepsilon_{\text{eff}} = x\varepsilon_a + (1-x)\varepsilon_b,$$  \hspace{1cm} (5.1)

which when applied to Mie simulations agrees well with the experimental data [97]. However, Link, et al, determined that the linear combination of the pure metal dielectric functions inaccurately described their experimental data and instead relied on the dielectric function of an alloy film of the same composition [16]. Straightforward theoretical treatment of the alloyed nanoparticles does not provide clear expectations of the resultant alloy plasmon resonance. Assuming the dielectric function (or the particle polarizability) is ultimately determined by some superposition of the constituent metals’ intrinsic properties, according to Mie theory, adding Mg to Ga nanoparticles should redshift the pure Ga plasmon resonance. But, this assumption ignores underlying differences between the alloy and a superposition of its constituents since bond formation between constituents can dramatically alter the final alloy’s characteristics. Such perturbations can also influence the mixed metal’s conductivity, which ultimately affects the plasmon resonance [110]. For example, a single work in 1975 revealed the room temperature resistivity of Ga$_2$Mg$_5$, a stable alloy, of $\rho=24\times10^{-8}\Omega\text{m}$, which is close to
the $\rho=13.6\times10^{-8}\Omega\text{m}$ value measured for pure Ga [111,112]. We are also motivated to investigate the Ga/Mg system to take advantage of the thermal and oxidation stability of the Ga nanoparticles to improve the chemical stability of the Mg nanoparticles. In fact, a drawback of the Mg plasmonic nanoparticles is their tendency to oxidize and redshift ($\Delta E=4\text{eV}$) and ultimately quench the Mg plasmon resonance [58].

Forming and synthesizing Ga-Mg alloyed nanoparticles by molecular beam epitaxy is challenging. Making alloys traditionally requires mixing high purity constituent metals in an inert crucible and melting them together at high temperatures [106,111]. MBE growth of metal nanoparticles is simply ultra-high vacuum evaporation and by this deposition process two extreme geometries define the limits of bimetallic nanoparticle metal distribution – homogeneous alloying or core-shell structures (figure 33).

![Core Shell vs Homogenous Alloy](image)

**Figure 33** Two extreme geometries of bimetallic nanoparticles – core-shell vs. homogenous alloy.

Specific control of the metal distribution relies on a variety of process conditions including constituent deposition order, deposition and/or annealing temperature, and metal flux ratio. Depending on the metal-metal solubility and indiffusion, sequential deposition of two metal constituents, absent any externally applied driving forces, will tend toward a core of the first metal surrounded by some coverage of the second species. The ordering effect can occur despite the Ga-Mg system’s tendency to
heterocoordinate [113] because the two metals' surface tensions differ – $\Gamma_{Ga} = 0.7N/m$ [112] and $\Gamma_{Mg} = 0.19N/m$. As such, metal deposition order along with thermally modifying the metal-metal solubility can also influence metal distribution, e.g. by elevating the deposition temperature or post-growth thermal annealing, which has been shown to alloy Au-Ag core-shell structures [17]. Substrate surface temperature also strongly affects the sticking coefficient since at elevated temperatures the desorption process competes with adatom surface diffusion,

$$\tau \rightarrow \tau_{\text{desorption}} \text{ at high temperatures}$$
$$\tau \rightarrow \tau_{\text{capture}} \text{ at low temperatures}$$

(5.2)

where $\tau$, the adatom lifetime, is no longer diffusion limited [49,114]. A thermally activated process, desorption,

$$\tau_{\text{desorption}} = \frac{1}{v} \exp \frac{E_{\text{desorption}}}{kT},$$

(5.3)

is a function of the adatom vibrational frequency, $v$, on the surface and the re-evaporation activation energy, $E_{\text{desorption}}$. Thus, substrate temperature can manipulate the surface metal composition. Directly manipulating the gas phase metal ratio also influences the sticking coefficient, through competitive adsorption of the multiple constituents and, by extension, the resultant composition. In this work, the gas phase metal flux ratio is used to describe the sample composition and should not be treated as absolute measures of bimetallic composition.

Beyond the materials science considerations, technological specifications motivate the need for alloyed structures as opposed to core-shells. While core-shell
structures can be produced more easily, for optical applications an outer shell of Mg is undesirable as the excessive oxidation and plasmonic quenching observed for pure Mg nanoparticles surely will plague Ga core/Mg shell structures as well. Fundamentally, the interesting potential applications, catalysis and hydrogenation, require stable Ga-Mg alloys rather than segregated nanostructures. Therefore, the following work is two-fold: 1) to manipulate bimetallic composition for plasmon tuning of both core-shell and alloy nanostructures and 2) to monitor the plasmon resonance as a measure of the nanoparticle composition and structure/phase (i.e. its chemical state) in order to exploit chemically active Ga-Mg alloys at the nanoscale, a scale where materials properties can become dramatically modified.

5.3 Composition-based bimetallic plasmon tuning

Plasmon resonance prediction for mixed metal nanoparticles is a tricky business – indeed previous studies conflict on the proper convolution of the constituent dielectric functions to accurately model the alloyed dielectric function and plasmon resonance [16,97]. Further confusion arises where core-shell geometries necessitate understanding how the relative radii of the constituent metals impacts their dielectric superposition [102]. To elucidate the effect of deposition order and effective metal dosage ratio, while minimizing substrate-metal interfacial layer formation and maximizing the metal sticking coefficients, we deposited bimetallic plasmonic nanoparticles at 25°C according to the conditions outlined in the following table (table II). Here, effective metal dosage is defined as total metal flux measured in nanometers and the effective Mg composition is measured by the relative dosages.
Table II Room temperature Ga-Mg bimetallic nanoparticle growth parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Effective total dosage range (nm)</th>
<th>Effective % vol. Mg</th>
<th>Metal sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>D532</td>
<td>15.5</td>
<td>3.4</td>
<td>Ga seed, Mg</td>
</tr>
<tr>
<td>D701, D702</td>
<td>12.4</td>
<td>5, 2</td>
<td></td>
</tr>
<tr>
<td>D707-710</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D721, D722</td>
<td>2.3, 1.5</td>
<td>27, 43</td>
<td>Mg seed, Ga</td>
</tr>
<tr>
<td>D723</td>
<td>2.3</td>
<td>23</td>
<td>Ga+Mg simultaneous</td>
</tr>
</tbody>
</table>

In contrast to pure Ga, pure Mg deposition proceeds in a regime where nanostructures evolve into a rough, nearly coalesced thin film. Therefore, to monitor the impact on the plasmon resonance, Ga seed nanoparticles were deposited to a) observe the plasmon resonance shift with a known starting geometry and b) to encourage nanoparticle formation upon Mg incorporation. This is confirmed by AFM imagery comparing the Ga-seeded growth with the Mg-seeded growth. Finally, simultaneous deposition of Ga and Mg was performed to discern which metal dominates the nanostructure morphology evolution. Since accurately predicting the bimetallic nanoparticle plasmon resonance, especially those with undefined geometries or metal distributions, is difficult, real-time plasmon monitoring by in situ spectroscopic ellipsometry renders predictive models unnecessary for our investigation.

5.3.1 Ga-seeded Ga-Mg bimetal epitaxy

Room temperature MBE deposition of bimetallic Ga-Mg nanoparticles effectively tunes the plasmon resonance by composition variation. Samples were grown at room temperature in vacuo by first depositing Ga nanoparticles on sapphire or Si substrates followed by Mg deposition.
**Figure 34** Real-time SE of pure Mg (black) deposited onto pure Ga nanoparticles (blue). Spectra are measured once per second and the Mg deposition clearly redshifts the Ga nanoparticle plasmon resonance for an effective Mg dose of 1.4Å.

To deconvolve the size effect from the composition effect on the plasmon resonance, we fixed the total effective metal dosage, defined as the total effective thickness of metal deposited (nm). Bimetallic nanoparticle size scales with total effective thickness and is independent of Mg/(Mg+Ga) dosage ratio, which we refer to as the effective Mg vol. %. As shown in the following AFM images, the nanoparticle diameter varied slightly from sample to sample for equivalent total effective dosages, but within the measurement error (figure 35).
Figure 35  Mean nanoparticle diameter measured by AFM as a function of effective Mg composition.

For comparison, pure Ga nanoparticle plasmon resonance varies with average nanoparticle diameter, but with sensitivity beyond the size error observed in the bimetallic nanoparticles (figure 36).
Figure 36 Ga nanoparticle longitudinal plasmon resonance as a function of average nanoparticle diameter on Si (A), glass (B), GaN (C), and sapphire (D) substrates (from Wu, et al, APL, 90, 103119 (2007) [30,54]).

Therefore, any plasmonic variation for nanoparticles of the same total effective dosage can be attributed to factors not related to geometry (shape or size), i.e. the metal composition. Shown in the spectra below, the plasmon resonance redshifts with increasing effective Mg vol. % on Si (figure 37).
Figure 37  The extracted extinction spectrum for Ga-Mg bimetallic nanoparticles as a function of effective % Mg. The pseudoextinction spectra (inset) are included to show the Si substrate effect.

For a small total effective dosage near 12nm, an effective Mg composition range of 2-10% tunes the plasmon across a range encompassing 3.6eV to 1.75eV. By comparison, Belotelov, et al. presented alloyed Au-Ag nanoparticles ranging from pure Ag to pure Au whose plasmon resonance only shifted within a < 1eV range [97]. Additionally, an equivalent plasmon range with pure Ga nanoparticles would require Ga doses ranging from 22nm to 74nm all larger amounts than necessary for the bimetallic system (figure 38).
Figure 38 Total effective bimetallic dosage of 12nm extends the plasmon resonance range the UV (3.6eV) to the near IR (1.75eV).

Quantitatively, the plasmon resonance sensitivity to relative metal dosages can be extracted from the figure below (figure 39). Whereas pure Ga nanoparticles exhibit a small (-9.3meV/nm) variation with respect to mean nanoparticle diameter, mixed Ga-Mg nanoparticles are highly sensitive to the Mg variation with no significant deviation of the mean nanoparticle diameter.
We exploit the plasmon resonance sensitivity to small variations in the effective Mg composition to demonstrate the size advantage for bimetallic nanoparticles compared to pure Ga nanoparticles. 10% vol. Mg effective composition bimetallic nanoparticles with a mean diameter of 50nm exhibit a plasmon resonance equivalent to 170nm pure Ga nanoparticles, a considerable size savings, as denoted by the green line in figure 39.

The plasmon resonance sensitivity to bimetallic composition also depends strongly on the average nanoparticle size suggesting that at larger sizes, the Mg doping impact is less pronounced. At low effective Mg compositions, the plasmon resonance linearly correlates to nanoparticle composition. But, the plasmon shift saturates at larger (≥10% vol. Mg) effective Mg compositions, suggesting that room temperature, Ga-seeded Mg epitaxy forms bimetallic core-shell nanoparticles comprising a Ga/Ga\textsubscript{x}Mg\textsubscript{y} core surrounded by an incomplete, conformal Mg shell. The bimetallic oxidation behavior
reflects this metal distribution as the resultant plasmon gradually quenches after several months of air exposure in a manner reminiscent of pure Mg.

Liquid Ga nanoparticles dissolve impinging Mg adatoms at room temperature. During the dissolution process, surface Ga-Ga bonds must first be broken before Mg atoms can incorporate and diffuse. Thus, the initial stage is bond energy limited, whereas the second stage is a diffusion-limited process [115]. The melting point of the bulk Ga-Mg alloy varies with Mg composition below which the surface solidifies and Mg cannot readily diffuse into the nanoparticle (figure 32). Absent the Ga-Mg alloy solidification, e.g. if the liquidus temperature is low enough at the nanoscale that the Mg solubility is the limiting factor [70], the relative surface tensions of both metals, $\Gamma_{\text{Ga}} = 0.7\text{N/m}$ and $\Gamma_{\text{Mg}} = 0.19\text{N/m}$, can explain the observed Mg segregation [112]. Once the Mg flux exceeds the solubility limit in Ga for a diffusion-limited process, the nanoparticle surface energy minimization will proceed by segregating any additional Mg outside the core nanoparticle. In this case, the nanoscale Ga-Mg system can therefore overcome its thermodynamic tendency to heterocoordinate in the bulk once the Mg population exceeds the solubility limit in liquid Ga; the lower surface tension constituent, Mg, segregates outside the strongly bound Ga core and heterocoordinated Ga-Mg network.

More likely, diffusion and segregation are two competing processes and determining the dominant factor requires further investigation, however, from this thermodynamic perspective, manipulating Ga and Mg distribution in a nanoparticle can be achieved by controlling the metal-metal solubility.
5.3.2 Mg-seeded Ga-Mg bimetal epitaxy

Given the surface tension disparity, we expected Mg-seeded Ga-Mg epitaxy above the solubility limit to proceed as a segregated system where the homocoordinated Ga preferentially forms droplet structures. In this case the Mg plasmon resonance blueshifts with increasing effective Ga composition, but at much higher effective compositions than in the Ga-seeded case (figure 40).

![Graph showing blueshift in plasmon resonance with Ga deposition on Mg seeds.](image)

**Figure 40** Ga deposited on Mg seeds blueshifts the plasmon resonance.

From our extensive experience characterizing pure Ga nanoparticles, the blueshift that accompanies the Ga deposition clearly is not related to increasing nanoparticle size. We therefore attribute the blueshift to an increasing electronic contribution of Ga during deposition since Ga's plasma frequency is larger than Mg's, 14eV and 10.5eV, respectively.
Metal order significantly changes the resultant nanoparticle morphology. Mg deposits as a nearly coalesced layer of nanoparticles and the extinction resonance for the pure Mg nanoparticles is quite broad. From the SE spectra and AFM imaging, we observe Mg evolving from a 3D nanostructure to a quasi-2D, textured film morphology. The subsequently deposited Ga assembles on the Mg surface, but AFM images reveal a final morphology resembling a rough, continuous film with RMS roughness of 0.75nm (figure 41).

![Figure 41 Phase AFM and plasmon resonance of pure Mg (0% Ga, left), 57% Ga (middle), and 73% Ga (right) Mg seeded epitaxy of Ga. Phase images are used to highlight surface texture.](image-url)
In the case of room temperature Mg-seeded Ga epitaxy, the solid Mg seed morphology ultimately drives the final morphology. Pure Mg evolves as a nanostructured, nearly coalesced, rough, thin film – not as distinct nanoparticles as is the case with pure Ga seeds. At room temperature the impinging Ga species adsorb on the seed surface as a liquid and penetrate the coalescence boundaries of the rough Mg seed film in a fashion similar to a process typically observed in Al-liquid Ga embrittlement [116]. As such the Ga liquid phase droplets do not readily form on the Mg surface, but rather they wet the textured surface and the high-density nanostructures resonate far into the red despite their small size.

5.3.3 Simultaneous Ga-Mg bimetal epitaxy

Room temperature simultaneous Ga-Mg deposition optically evolves like a Mg thin film with no distinct plasmon resonance, which suggests that Mg dominates the substrate wetting of the composite (figure 42). AFM imagery shows the formation of very disperse droplets of unknown composition with an image RMS surface roughness of 1.6nm.
Figure 42 Kinetic SE of simultaneous Ga and Mg deposition with the final spectrum (black) and no evidence of a plasmon resonance. Accompanying phase AFM is provided to highlight the surface’s texture.

Invoking the relative surface tension again can illuminate the formation process of the small disperse nanoparticles. Barring gas phase aggregation of Ga-Mg complexes, simultaneous deposition of Ga and Mg probably encourages the surface tension driven metal segregation where Ga nanoparticles form their characteristic liquid droplets on the predominantly Mg surface of RMS roughness ~ 0.3nm (measured between nanoparticles). Regardless of the composition, these nanoparticles are significantly smaller and more disperse than the standard plasmonic nanoparticles characterized by spectroscopic ellipsometry, which might limit whether the technique can probe the plasmon resonance.
5.3.4 Room temperature Ga-Mg epitaxy

From room temperature evaporation of Ga-Mg mixed metal nanoparticles we elucidated the impact of metal deposition order and metal flux ratios. Metal-metal solubility and metal-substrate wetting and mobility govern the resultant distribution of the constituent metals. Liquid Ga droplet-initiated growth produces plasmonic nanoparticles up to a limited effective Mg composition, beyond which Mg conformally covers the nanoparticle surface. We explained the limited alloy formation and subsequent Mg shell growth on the basis of alloy melting point augmentation as a function of Mg composition and the Ga-Mg surface tension difference. Ultimately, these two issues are rooted in the Mg solubility into the liquid Ga seeds. Conversely, Mg-initiated growth produces rough, nearly coalesced films with plasmon resonances blueshifted from the pure Mg case. Simultaneous Ga-Mg deposition exhibits no discernable plasmon resonance despite the formation of highly disperse and small droplets of unknown composition. Increasing Mg solubility into Ga while limiting conformal Mg layer formation will increase the plasmon redshift out of the visible to the IR and improve the plasmon stability of small (diameter<100nm) bimetallic nanoparticles.

5.3 Temperature-controlled alloy stabilization

Room temperature deposition limits the redshift of Ga seeded Ga-Mg bimetallic nanoparticles, which occurs when Mg dissolution saturates and a conformal Mg shell forms. Impinging Mg adatoms dissolve into the liquid Ga nanoparticles forming an alloy of increasing Mg composition whose corresponding liquidus point increases until the alloy solidifies. At 25°C, bulk Ga-Mg alloys solidify within 1-2% Mg, and although the
corresponding composition at the nanometer scale cannot be extrapolated directly from the bulk material properties, we expect surface solidification to limit the Mg indiffusion. Additional Mg conformally deposits an incomplete shell on the Ga nanoparticles and exceedingly large Mg dosages ultimately yield a bumpy, 2D system as opposed to distinct nanoparticles.

Figure 43 Amplitude AFM image of room temperature (25°C) grown Ga-seeded bimetallic nanostructures of Ga-Mg (a). An incomplete, rough Mg layer covers the underlying 3D nanostructure. SEM exhibits inhomogeneous metal coverage by image brightness (b). The plasmon resonance oxidizes over time and eventually becomes quenched (c)
While AFM imagery reveals the texture of the incomplete, conformal Mg coverage (figure 43a), SEM images highlight the inhomogeneity of the metal distribution by brightness contrast discernable within the individual nanoparticles (figure 43b). In addition to limiting the plasmon redshift, the conformal Mg coverage is undesirable because the pure Mg shell quenches the plasmon when exposed to air (figure 43c). By contrast, identical dosages of Ga and Mg deposited at 300°C caused the plasmon to redshift, but remained completely stable upon oxidation (figure 44c). SEM images reveal a symmetric image contrast within individual nanoparticles suggesting a more homogeneous metal distribution (figure 44b).
Figure 44 – Amplitude AFM (a) and SEM (b) of high temperature Ga-seeded deposition (300°C). The plasmon resonance is slightly redshifted after oxidation and is remarkably stable over a long period (c).

The disparate oxidation behavior reveals that Mg-rich shell formation occurs at room temperature while high temperature growths produce a mixed metal or Ga-rich material. As such, the oxidation is slight, does not induce a plasmon shift, nor does it quench the plasmon of high temperature deposited Ga-Mg bimetallic nanoparticles. Mg is not desorbed completely from the surface despite the high annealing temperature \(T_{\text{anneal}} > T_{\text{Mg,desorption}}\), as evidenced by the Mg contribution to the XPS spectra. By
extension, increasing the surface Mg composition by lower growth or annealing temperatures, \textit{i.e.} \( T < 250^\circ\text{C} \), may augment its incorporation and promote alloy formation.

Ga-seeded alloy epitaxy was performed at an elevated Mg deposition temperature (100°C), which redshifted the plasmon resonance, as expected (table III).

\begin{table}[h]
\centering
\caption{Elevated temperature Ga-seeded bimetallic epitaxy conditions}
\begin{tabular}{llll}
\hline
Sample & Effective dosage (nm) & Mg \% vol. & Thermal history (\textdegree C) \\
\hline
D764 & Ga = 23.25 \hspace{20pt} Mg = 0.81 & Ga seeded, sequential & 3.4 \% & Ga deposition = 25 \\
 & & & Mg deposition = 100 \\
 & & & \text{Anneal}_{\text{max}} = 300 \\
D766 & Ga = 20.14 \hspace{20pt} Mg = 0.36 & Ga seeded, simultaneous & 1.8 \% & Ga deposition = 25 \\
 & & & Mg+Ga deposition = 100 \\
 & & & \text{Anneal}_{\text{max}} = 100 \\
\hline
\end{tabular}
\end{table}

Despite slight differences in effective Mg composition, deposition order, and annealing temperature, the resultant nanoparticles exhibit similarly-sized asymmetric shapes that differ markedly from spheroidal pure Ga nanoparticles. Samples were grown by a Ga-seeded process, however Mg was deposited individually on D764, \textit{i.e.} sequential seeded epitaxy, and Mg and Ga were deposited simultaneously on D766. One discernable difference between their morphologies is the slight change in interparticle spacing with D764 exhibiting larger gaps between the neighboring particles (figure 45, top).
Figure 45 AFM and line profiles for D764 and D766 along with their respective in situ and post-oxidation plasmon resonance spectra.

The high temperature (300°C) post-growth anneal did not cause the slight decrease in nanoparticle areal density and increase in interparticle spacing on D764. The plasmon is stable throughout the high temperature (300°C) anneal, which indicates stable nanoparticle morphology during the high temperature anneal, as evidenced by real-time SE spectra. Pre- and post-anneal spectra are shown here, measured at 25°C (figure 46).
Figure 46 Pre-anneal and post-anneal spectra show the plasmon resonance stability.

Based on their respective mean size distributions, the nanoparticles on D764 are further along in the coalescence process than D766, which suggests the total effective dosage (20nm vs. 24nm) and/or the effective Mg composition modify the nanoparticle assembly kinetics (figure 47). D764 possesses a distinctly bimodal size distribution and its large diameter mode has a mean value of 95nm. The dominant mode of D766 resides near 98nm, while a second emergent mode exists at the low diameter tail. Despite their similar mean diameters, the two samples’ plasmon resonances differ because it is more strongly influenced by the nanoparticle Mg composition than the marginal size variations.
Most interestingly, the two samples oxidize in notably different ways. The D764 plasmon resonance quenches upon oxidation while D766 is unperturbed, as seen above in figure 45 (lower). Recall that room temperature deposited core-shell Ga-Mg nanoparticles quenched upon oxidation because of the Mg segregation to the exterior. Unlike the room temperature grown nanoparticles, the Ga and Mg in the D766 distribute homogeneously within individual nanoparticles as evidenced by energy dispersive X-ray spectroscopy (EDX) and energy-field transmission electron microscopy (EF-TEM) (figure 48). The D764 sample charges excessively during EDX measurement suggesting the nanoparticles become nonconductive upon oxidation either because of large Mg composition or the formation of a thin, segregated Mg shell. The disparate plasmon resonance oxidation behavior between D766 and D764 can result from segregated Ga-Mg distribution and/or contributions from the Mg composition and annealing temperature to their dissimilar chemical reactivity and oxidation products.
5.4 Chemical and structural analysis of Ga-Mg alloys

Alloy formation manifests itself chemically by core-level shifting due to charge state modification, which can be observed using X-ray photoelectron spectroscopy (XPS) [117]. Upon alloying, the Mg chemical state (EN = 1.2eV) shifts to a higher binding energy due to bond formation with a more electronegative Ga atom (EN = 1.6eV), while Ga core-levels will shift to a lower binding energy [112]. Mg-Ga nanoparticles annealed at both 300°C and 100°C reveal Mg 2p core level shifts to higher binding energies and an attendant Ga 3d shift to a lower binding energy – a hallmark of alloy formation (figure 49).
Figure 49 Comparison of alloy survey spectra between the Mg 2p and Ga 3d core levels. The binding energy difference between Mg 2p and Ga 3d are marked to show the charge transfer-induced core level shifting.

However, the Ga 3d core level deconvolution reveals differences in the homogeneity of the alloy stoichiometry depending on the Mg dosage. Ga alloying with Mg produces a Ga 3d component at a binding energy lower than the Ga-Ga metal state (18.5eV) (figure 50).
Figure 50 High-resolution Ga 3d core level spectra of D764 (upper) and D766 (lower) reveal alloy component(s) at binding energies <18eV.

At a larger Mg dosage (D764), the Mg-Ga alloy component can be deconvolved into two broad components suggesting inhomogeneous alloy formation and the presence of at least two Mg-Ga alloy stoichiometries. Conversely, a lower Mg dosage (D766) produces a narrow (FWHM=1.3eV) alloy component that is indicative of homogeneous, single
stoichiometry Mg-Ga alloy formation. The Mg-Ga nanoparticles exhibit O 1s core-level spectra representative of their differing oxidation behavior (figure 51).

Figure 51 High-resolution O 1s core level spectra of D764 (upper) and D766 (lower).

While the multiple Mg-Ga phases oxidize differently and produce nearly equal oxide components for the large Mg composition nanoparticles (D764), a single, strong contribution from the only Mg-Ga phase dominates the low Mg composition oxide population (D766). Since only a small additional contribution originates from residual
MgOx or GaOx, the XPS suggests the Mg and Ga are homogeneously distributed throughout D766. CO adsorption on the Mg-Ga nanoparticles varies with Mg composition as well reinforcing the assignment of different Mg composition to the two samples with different CO adsorption profiles.

![High-resolution C 1s core level spectra of D764 (upper) and D766 (lower).](image)

**Figure 52** High-resolution C 1s core level spectra of D764 (upper) and D766 (lower).

On the sample surface, we have determined clear differences in the chemical composition based on Mg dosage and annealing temperature. However, the XPS beam spot size represents the aggregate behavior over the measured area (large relative to
single nanoparticle size) and the specific metal distribution within a single nanoparticle is necessary to determine whether alloying is complete across the sample, i.e. from one particle to the next.

Single nanoparticles (100-200nm diameter) of D766 were structurally characterized by energy dispersive X-ray (EDX) analysis identifying the presence of both Mg and Ga in each nanoparticle, but the composition is unidentifiable without calibration. From electron energy loss spectroscopy (EELS) coupled with energy field transmission microscopy (EF-TEM) we have determined the Mg:Ga ratio for the low Mg composition sample (D766) to be 55:45 measured nanoparticles. Occasional bright spots in the high angle annular dark field scanning TEM (HAADF-STEM) image are small Ga droplets attached to the nanoparticles (figure 53).

![Image of D766 showing occasional bright spots](image)

**Figure 53** HAADF-STEM image of D766 showing occasional bright spots corresponding to higher mean atomic number regions.

Based on the EELS extracted compositional analysis and the occasional presence of Ga droplets on Ga-Mg nanoparticles of uniform composition, the low Mg dosage and low temperature annealing process of D766 yields MgGa nanoparticles of uniform...
composition within the individual nanoparticles. We have therefore demonstrated the MBE growth of stable, homogeneous, MgGa alloy nanoparticles that are metallic and therefore plasmon resonant even when oxidized. From the EF-TEM compositional analysis of D766 and the clear presence of multiple stoichiometries of Ga-Mg alloys in D764, we expect the higher effective Mg dosage nanoparticles (D764) to yield Mg$_x$Ga$_y$ alloys of x>y and we believe the larger Mg composition coupled with their inhomogeneity leaves the nanoparticles susceptible to oxidative quenching of the metallic alloy and plasmon resonance. While detailed compositional analysis is still needed, the final plasmon resonance is redshifted with respect to the MgGa nanoparticles, which further supports a Mg$_x$Ga$_y$ composition of x>y (figure 54).

![Figure 54 The extinction spectra of D764 (Mg$_x$Ga$_y$) and D766 (MgGa).](image)

The electronic properties of Ga-Mg binary alloys have not been well studied, but considering these characteristics is important to determine whether the alloys are metallic and plasmon resonant. For comparison, recall that at room temperature Ga$_2$Mg$_5$
has a resistivity of $22 \times 10^{-8} \Omega\cdot m$ [111], which is slightly larger than that of pure Ga ($\rho_{RT} = 13.6 \times 10^{-8} \Omega\cdot m$) [112]. This single reference point combined with our knowledge of the relative plasma frequencies of bulk Ga and Mg, imply that metallic, stable Ga-Mg binary alloys do exist and should therefore possess a plasmon resonance, albeit redshifted compared to pure Ga. From our preliminary work, it is clear that MgGa is a metallic alloy phase with a plasmon that is also stable after air exposure.

We have identified a low temperature, low Mg flux process to grow stable, homogeneous, plasmonic MgGa alloy nanoparticles. From the chemical analysis we have determined that the MgGa alloy Ga 3d core level corresponds to 17.7eV with a FWHM of 1.3eV. Variations in the Mg-Ga stoichiometry will shift the Ga 3d component according to the composition ratio and electronegativity differences of Mg and Ga. Most surprisingly, the real Mg composition in D766 far exceeds the gas phase 1.8% vol. Mg composition. Differences in nanoparticle distribution and composition can be affected by electronic modification of the metal sticking coefficient, the control of which can provide better control over resultant nanoparticle composition. Continued study of the nanoparticle formation kinetics during low temperature growth and variable temperature annealing will illuminate the nanoparticle distribution differences.

We have designed a dry chemistry-based method to grow plasmonic, MgGa nanoparticles. A great deal of work still remains, however, to understand the fundamental processes governing the intermixing, alloy formation, and nanoparticle distribution on the substrate surface as a function of metal ordering and deposition/annealing temperatures. Once these factors are understood, we can
manipulate these processes to control the Mg$_x$Ga$_y$ phase formation and size to tune our nanoparticles to technology-driven specifications. We know that the surface sticking competition between the two constituents determines the final alloy’s composition, but there are many factors that contribute to the competitive process including surface temperature, coverage-related surface energy modification, gas phase charge transfer modification of solid phase sticking, etc. Much experimental work is left to clearly articulate the driving mechanism(s) for Ga-Mg alloy formation before we can fully manipulate the growth process.
Chapter 6 Ga nanoparticle-polar semiconductor interface charge and metal nanoparticle assembly

We have detailed material composition manipulation to tailor the plasmon mode in the previous chapters. Here we will examine the electronic interactions at the metal/substrate interface to elucidate the mechanisms driving nanoparticle formation on the surface and their influence on the resultant plasmon resonance. Because plasmon enhancement of UV emitting solid-state devices can be realized by coupling the surface-bound free electron oscillations of metallic nanoparticles to wide bandgap semiconductor structures, effectively increasing the photon density of states, there is a need to understand the metal/semiconductor interface chemical and electronic interaction.

While vast body of knowledge provides insight into the optical interaction of plasmonic nanostructures with dielectrics, little understanding of their interaction with polar, wurtzite semiconductors relevant to the development of UV photonic devices exists. This chapter will present direct evidence that the interface potential characteristics of polar semiconductors (SiC, GaN, and ZnO) and electronic interactions between plasmonic nanoparticles (gallium) and their substrates influence metallic nanoparticle dynamics and their size and shape on polar surfaces. To elucidate the mechanisms controlling nanoparticle assembly dynamics, we exploit the Lippman electrowetting framework and determine that the intrinsic charge transfer at the Ga nanoparticle/polar semiconductor
interface controls nanoparticle wetting and geometry and, by extension, the surface plasmon resonance.

Unlike their interaction with dielectric materials, the interaction of metal nanoparticles with semiconductors is more complex since electronic transfer can also affect metal chemisorption [118] and, by extension, the growth mode and geometry of the nanoparticles and, consequently, their localized surface plasmon resonance. So far, Au and Ag nanoparticles have been coupled with Si-based optical devices for applications in the visible range [119,121], but Si is not applicable to short wavelength photonic devices and is limited in operation temperature and voltage.

6.1 Polar semiconductors

In this context, SiC, GaN and ZnO are scientifically fascinating and technologically advantageous semiconductors for optoelectronics, microelectronics, plasmonics and sensing devices operating at high temperature, high power, high voltage, and high frequency [122,126]. Both GaN and ZnO are ideal for realising high efficiency blue-UV lasers [127,128]. Fundamentally, SiC, GaN and ZnO are intriguing because unlike cubic semiconductors, e.g. Si, they are polar semiconductors. Polarity is a bulk characteristic of hexagonal wurtzite materials manifested as two inequivalent c-directions resulting from a lack of a symmetry center [129,130] as shown in Fig. 55.
Figure 55 Bonding structures and polarity schematics for wurtzite GaN, ZnO, and 4H-SiC. Ga-polar, Zn-polar and Si-polar (0001) faces and N-polar, O-polar and C-polar (000-1) faces for GaN, ZnO and SiC are shown. The corresponding polarization and sign of fixed polarization charge is also reported, pointing out the inversion of polarization for SiC with respect to GaN and ZnO.

The non-centrosymmetric structure augments the partial ionicity of the bonds resulting from the differing Pauling electronegativity of the constituents (see Table I), yielding a net spontaneous polarization field along the c-axis. Therefore, the Si-polar SiC(0001) and C-polar SiC(000-1), the Ga-polar GaN(0001) and N-polar GaN(000-1), and the Zn-polar ZnO(0001) and O-polar ZnO(000-1) are characterized by different properties, such as morphology, dipole moments, surface charge, band bending and chemical stability [130,132]. Most significantly, a strong polarization-induced surface charge of opposing sign characterizes the (0001) and the (000-1) polar surfaces (see also Table IV).
Table IV Properties of wurtzite ZnO, GaN, and 4H-SiC along (0001). Ref. a) [133], b) [134], c) [135], d) [136].

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Lattice Constant (Å)</th>
<th>Bandgap (eV)</th>
<th>$\varepsilon_{\infty}$</th>
<th>Pauling Electronegativity</th>
<th>Spontaneous Polarization (C/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>$a=3.249$, $c=5.207$</td>
<td>3.37</td>
<td>3.71&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Zn=1.65, O=3.44</td>
<td>$\Delta=1.79$</td>
</tr>
<tr>
<td>GaN</td>
<td>$a=3.189$, $c=5.185$</td>
<td>3.45</td>
<td>5.35&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Ga=1.81, N=3.04</td>
<td>$\Delta=1.23$</td>
</tr>
<tr>
<td>4H-SiC</td>
<td>$a=3.08$, $c=10.08$</td>
<td>3.26</td>
<td>6.55&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Si=1.90, C=2.55</td>
<td>$\Delta=0.65$, $\Delta=0.043$</td>
</tr>
</tbody>
</table>

Because the permittivity of opposing polarity surfaces of the same substrate is constant, Mie theory predicts the nanoparticle plasmon resonance to be independent of surface polarity. In this work, we show for the first time that for metal/polar semiconductor nanostructures, substrate polarity-mediated surface charge and interface potential govern the nanoparticle formation dynamics and, consequently, their localised surface plasmon resonance. We explain the observed polarity-dependent phenomena using novel, robust, and technologically significant metal/semiconductor systems, i.e. Ga nanoparticles coupled with polar SiC, GaN and ZnO surfaces, enabling us to extend our conclusions in a generalisable fashion. Ultimately, we aim to evaluate the impact of electronic phenomena at the semiconductor/metal interface on the nanoparticle assembly and plasmon resonance. To demonstrate the importance of the polarity-charge driven plasmonic behaviour, we utilise these three comparable direct and wide bandgap semiconductors amongst which various factors can be considered and ruled out. Specifically, the defect density of the two GaN surfaces can be considered along with the
relative bond strengths of Ga adatoms on opposing SiC or GaN surfaces or metal reactivity on ZnO surfaces to elucidate the observed differences in nanoparticle formation and assembly on the polar surfaces.

6.2 Ga nanoparticle assembly dynamics on polar semiconductor supports

In order to discern the effect of polarity on the resultant plasmon resonance, Ga nanoparticles were deposited by molecular beam epitaxy at room temperature under ultrahigh vacuum conditions onto polar 4H-SiC, GaN, and ZnO substrates of both (0001) and (000-1) orientation. The use of in situ spectroscopic ellipsometry enables the investigation of plasmon dynamics whereas previous studies were limited to ex situ, post-growth characterization of supported nanoparticle ensembles [137,138].

The real-time pseudoextinction coefficient spectra recorded during Ga nanoparticle formation on the Si-polar and C-polar SiC are shown in figure 56 to contrast the different plasmon dynamics for the opposing polarity surfaces. Indeed, for equivalent Ga dosages, the position and amplitude of the plasmon resonance vary for the opposing polarity surfaces despite the constant refractive index for the given substrate material.
Figure 56 Real-time evolution of ellipsometric spectra of the pseudoextinction coefficient, $<k>$, recorded during Ga nanoparticle formation on (a) C-polar and (b) Si-polar SiC (140s total deposition time corresponding to 96ML of Ga): spectra are shown every 20s (corresponding to 14ML); only the longitudinal plasmon mode is visible in the investigated photon energy range; (c) C-polar and (d) Si-polar SiC (475s total deposition time corresponding to 325ML of Ga): spectra are shown every 50s (corresponding to 34ML); both the longitudinal and the transverse mode (at higher energy) are visible.

Closer inspection of kinetic spectra for the Ga/Si-polar SiC (and similarly Ga/N-polar GaN and the Ga/O-polar ZnO) revealed that, for the equivalent Ga dosage, the Ga nanoparticle plasmon resonance is larger in amplitude and red-shifted on Si-polar SiC, N-polar GaN and O-polar ZnO. To more clearly emphasize the difference in nanoparticle
plasmon evolution on the opposing polarity surfaces, the longitudinal plasmon mode was extracted from the real-time data and plotted as a function of total Ga dosage (in MLs) (figures 37a-c). The Si-, N-, and O-polar surfaces exhibit faster Ga plasmon evolution compared to their respective opposing polarity surfaces, implying that red-shifted plasmon resonances are observed for the Si-polar SiC, the N-polar GaN and O-polar ZnO surfaces for equivalent Ga dosage. Clearly, the different plasmon resonance dynamics are associated with different nanoparticle ensemble geometry, also shown in figure 37, wherein the nanoparticle assembly density and mean nanoparticle diameter is also shown to depend on the substrate polarity. For all polarities, the nanoparticle density decreases with increasing Ga dosage, while the average nanoparticle diameter increases, indicating that the Ga nanoparticles evolve by adsorption, surface diffusion, coalescence according to the Ostwald ripening mechanism [139]. Most illustrative, the Si-polar SiC and N-polar GaN surfaces reveal lower densities and larger diameters relative to their opposing polarity surfaces, suggesting the nanoparticles more readily diffuse and coalesce on those surfaces. Thus, the rate at which the plasmon mode evolves and the nanoparticles coalesce (diffuse) are intimately tied together. As such, we infer that the nanoparticle wetting, substrate interaction, and plasmon behaviour are not specifically related to the cation- or anion-polarity of the substrates.
Figure 57 The plasmon resonance extracted from kinetic measurements as a function of Ga dosage (ML) for (a) SiC, (b) GaN, and (c) ZnO. Associated nanoparticle density and mean diameter as a function of Ga dosage are included.
In order to evaluate possible common attributes of the different polarity surfaces with comparable nanoparticle and plasmon behavior, we must consider substrate-related factors that may influence nanoparticle synthesis and assembly. Substrate defect density, metal-substrate bond strengths, or metal-substrate reactivity and their relation to substrate polarity may drive the nanoparticle assembly. During nucleation, the critical nuclei density, \( N \), covering the surface when a metal flux, \( F \), impinges on a surface is given by

\[
N = (\frac{40F}{D_0})^{1/2}
\]

where \( D_0 \) is the surface diffusion coefficient of the metal atom [140]. The impinging Ga flux is fixed for the nanoparticle deposition on all the polar surfaces, therefore nanoparticle larger densities (i.e., larger value of \( N \)) on the C-polar, Ga-polar, and Zn-polar surfaces suggest that the Ga surface diffusivity and density on these surfaces is inhibited with respect to the opposing polarity surfaces. By extension, morphology and plasmon resonance dynamics in figures 37a-c suggest the Ga surface diffusivity should be higher on the Si-polar, N-polar, and O-polar surfaces. Consideration of substrate defect density and reactivity does not reflect the above expectations of relative Ga surface mobility on SiC and GaN. First, AFM comparison of bare Ga-polar and N-polar surfaces prior to Ga nanoparticle deposition reveal the N-polar surface is significantly more defective than the Ga-polar surface and this has previously been demonstrated in the literature (figure 58).
Figure 58 Ga nanoparticles deposited on Ga-polar and N-polar GaN substrates. The bare N-polar GaN is more defective than the Ga-polar surface.

The Ga surface mobility has in turn been shown to relate to GaN surface morphology; the smoother, less defective Ga-polar surface should exhibit a higher Ga surface mobility relative to the rough, N-polar surface [140]. Accounting for metal/substrate reactivity reveals that Ga-Ga bonding is less energetically favorable compared to Ga-N bonding [141], as such the N-polar surface should interact more readily with the Ga nanoparticles and ultimately decrease their surface mobility. Conversely, Ga is highly reactive with Si-polar SiC forming Ga-Si euctetic at room temperature [142], whereas no stable Ga-carbides have been reported, which suggests the C-polar surface should interact less with the Ga nanoparticles and ultimately yield larger surface mobility on the C-polar surface. As for the impact of substrate surface morphology, it is known that the contact angle and, hence, wetting, of a droplet shows a strong dependence on the morphology of the surface on which it rests as described in detail by Bahadur and Garimella [143].
Indeed, we used epitaxial quality substrates, which are atomically flat (RMS roughness <0.3nm). Si-polar SiC with an RMS roughness of 0.14nm, smaller than the 0.163nm RMS roughness measured on C-polar SiC, exhibits a larger Ga wetting and surface mobility disqualifying any strong influence by the substrate surface morphology. Substrate defect density, reactivity, or morphology considerations are not supported by our observations of nanoparticle density and plasmonic nanoparticle evolution and assembly.

### 6.3 Electrowetting and the intrinsic interface potential

The final commonality between the different polar substrates relates to the sign of the polarisation-induced surface charge, which indicates the polarity dependent plasmonic behaviour is driven by surface charge of the opposing polarity surfaces. Electronic interactions at a liquid droplet-solid interface can be described by the Young-Lippmann theory of electrowetting [144], where surface mobility, wetting (θ is the contact angle) and interface energy depend on the interface potential according to

\[
\cos \theta = \cos \theta_v + k \left( U - U_{pzc} \right)^2
\]

where \( k \) is a constant reflecting the dielectric constants, \( U \) is the externally applied potential, \( U_{pzc} \) is the potential of zero charge, and

\[
\cos \theta Y = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{sv}}
\]

(\( \sigma_{sv}, \sigma_{sl} \) and \( \sigma_{sv} \) are the surface free energies of the semiconductor solid, semiconductor/liquid gallium interface and of liquid gallium, respectively, that define the Young contact angle \( \theta_Y \)). As such a larger interface potential resulting from differing
polarisation-induced surface charge and charge transfer at the metal/semiconductor interface increases the liquid Ga nanoparticle wetting on the solid surface and consequently reduces the surface mobility.

In our system, where the externally applied potential is zero, $U_{\text{pzc}}$ is analogous to the barrier potential at the metal/semiconductor interface, i.e. the Schottky barrier, which for various metals on SiC, GaN, and ZnO has been reported [145,148] to be polarity-dependent and detailed examination of polar interfaces has shown that the polarisation-induced surface charge perturbs the barrier potential [149]. From X-ray photoelectron spectroscopy and the method described by Waldrop, et al., we have determined the barrier potential, $U_{\text{pzc}}$, at the Ga nanoparticles/semiconductor interface by evaluating the substrate core-level shift of opposing polarity SiC, GaN, and ZnO after equivalent Ga dosage [148]. The obtained data reported in Table V reveals larger barrier potentials at the C-polar, Ga-polar and Zn-polar surfaces. Note these are the negative polarization-induced surface charge polarities. These data are consistent with other data present in literature. For example, larger barriers have been reported for Au and Ag on Zn-polar surfaces compared to those on O-polar ZnO [145]; similarly, larger Schottky barrier heights have been reported for Pt and Au on Ga-polar surfaces relative to N-polar GaN [146,150]. C-polar SiC also forms larger barriers with Ti, Ni, Al than Si-polar SiC [148].
Table V Schottky potentials at the Ga/semiconductor interface determined from X-ray photoelectron spectroscopy core-level measurements, and the sign of the polarization-induced surface charge for each polar surface.

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>SiC</th>
<th>GaN</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>polarity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>barrier height (eV)</td>
<td>1.81</td>
<td>0.72</td>
<td>1.5</td>
</tr>
<tr>
<td>polarization-induced</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>surface charge sign</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
</tbody>
</table>

According to the Young-Lippman theory and equation (5.2), the larger \( U_{pzc} \) potential measured at the C-polar, Ga-polar, and Zn-polar interfaces induces more wetting of Ga nanoparticles on those surfaces, decreasing their surface mobility, and ultimately increasing the final nanoparticle density, but decreasing their diameter, as schematised in Fig. 59 for Ga nanoparticles on N-polar and Ga-polar GaN. As such, the barrier potential, determined by the substrate polarity and surface charge, drives Ga nanoparticle formation, assembly, and plasmon dynamics.
Figure 59 The contact angle varies with $U_{pzc}$ (interface potential) strength. Representative 3D AFM images Ga nanoparticles (325ML) on GaN reveal variation in Ga nanoparticle wetting on the two polar surfaces.

The present data examined under the electrowetting Lippmann lens, a fundamental physics concept that has thus far been neglected at metal NP/semiconductor interfaces, demonstrates that NP assembly and plasmon dynamics are affected by the presence of the polarisation-induced surface charge and by charge transfer to/from the polar substrate from/to the Ga NPs. The interface charge determines the metal NP/semiconductor coupling strength and, hence, the metal cluster surface mobility that ultimately determines particle size and geometry. These data reveal that tailoring the semiconductor surface charge is an important, intrinsic, parameter for tuning the localised surface plasmon resonance of metal NP ensembles. Thus, Lippmann electrowetting formalism, a well-established theory first articulated over a century ago, can now be applied to highlight and rationalise new phenomena at the nanoscale. Our
collaborators have extended the present study to plasmonic indium and gold nanoparticles deposited on the same semiconductors proving the present results are not limited to Ga, but can be generalised to polar semiconductor/metal systems.
Chapter 7 Applications of Ga plasmonic nanoparticles

We have thus far treated plasmonic gallium nanoparticles as mere curiosities – an unexplored metal with peculiar materials properties and a convenient growth method enabling \textit{in situ} monitoring of their plasmon resonance. However, the scientific realm ultimately requires a measure of applicability and demonstrable utility from any scientific findings. Herein, we have shown potential interesting behaviors from the Ga nanoparticles and foreshadowed control of the Ga nanoparticle properties for sensing or optoelectronic device applications. Grown by MBE, the Ga nanoparticles could easily lend themselves to integrated solid-state semiconductor-based devices. The long-term stability of their phase and oxidation layers implies these Ga nanoparticles may be beneficial for sensing applications under extreme conditions.

Toward these ends, we have initiated studies of plasmon-induced surface-enhanced Raman scattering and plasmon-mediated GaN-based QW emission enhancement with Ga nanoparticles.

7.2 Surface-enhanced Raman scattering

C.V. Raman first described his eponymous scattering effect in 1928, garnering him a 1930 Nobel prize in physics [151]. In his Nobel prize-winning work, Raman demonstrated the inelastic scattering of light from molecular bonds. Molecules are most simply described by a dipole with dipole moment $\overrightarrow{p} = \varepsilon_0 \alpha \overrightarrow{E}_0$ where $\alpha$ is the polarizability. Intuitively, the polarizability is a measure of the ease with which a molecule’s electron cloud is distorted or displaced by an incident electric field, $\overrightarrow{E}_0$, away from equilibrium to form a dipole. The Raman effect involves incident light imparting some amount of energy on a molecule and exciting a vibrational state, and the scattered field is then
Stokes or anti-Stokes shifted relative to the incident field. The inelastic scattering is the manifestation of a Raman transition when a molecule is perturbed such that its polarizability changes, which can be visualized as the stretching or compression of a bond’s electron cloud. These perturbations to the molecule’s polarizability cause the incident electromagnetic field to lose energy or gain energy, which causes the scattered field to exhibit a shift relative to the exciting field. That energy absorbed (or sometimes contributed) by the vibrating molecule is manifested by a Stokes/Anti-Stokes shift of the scattered field.

Figure 60 Energy diagram depicting the Raman scattering shifts.

In figure 60 the incoming field from the left is the incident laser line and the outgoing field on the right is the scattered field after the molecule’s vibrational state transition that modifies its polarizability. Raman scattering is a powerful sensing mechanism because those modes to which it is sensitive will all resonate at a signature energy and selective detection is possible through this chemical ‘fingerprinting’. Raman spectroscopy is an important analytical technique for chemical and biological analysis due to the vast information on molecular structures, surface processes, and interface reactions that can be extracted from experimental data. But, Raman scattering lacks sensitivity due to low transition probabilities of the Raman active modes. For a molecule with an initial state
|\langle i | f \rangle|, selection rules dictate the transition probability between the ground state and the excited state, |\langle i | f \rangle|. The Raman transition probability can be determined from perturbation theory

\[ P_{\langle i | f \rangle - | f \rangle} \sim \left| \langle f | \hat{H}_R + \hat{H}_0 | i \rangle \right|^2 \]  

(7.1)

where the Raman perturbation, \( \hat{H}_R \), constrains the allowable transitions and defines the selection rules.

Although the Raman cross-section is inherently weak, hampering its detection limit, the observation of enormous Raman enhancements (10^6-10^{14}) for molecules adsorbed on special metallic surfaces has renewed interest in Raman spectroscopy [152,153]. The use of nanostructured metallic surfaces to enhance the Raman scattered signal is termed surface-enhanced Raman scattering (SERS), a highly sensitive and selective detection mechanism extensively studied over the past 30 years, with new applications frequently being reported [152,157].

When experimental observations of extreme Raman intensities were revealed for pyridine on textured Ag films, initial reports concluded the remarkable Raman intensities resulted from the larger surface area available on the Ag enabling larger numbers of adsorbed molecules for probing [10,156,157]. In reality, two mechanisms are invoked to explain the SERS effect – one chemical and one electromagnetic – both of which contribute to the scattering spectrum. The chemical mechanism involves charge transfer inherent to molecular adsorption to a metal surface and therefore depends on the metal’s Fermi level relative to the ground and excited vibrational states of interest (figure 61). The charge transfer results in a modification of the molecule’s vibrational response to incident electromagnetic fields modifying the Raman intensity. The charge transfer
effect therefore requires the molecule to adsorb to the metal surface to allow charge transfer.

Figure 61 The chemical enhancement (charge-transfer) mechanism partially enables SERS [158].

For an adsorbed molecule on a metal of Fermi level, $E_F$, charge transfer-induced modification of the molecular polarizability can proceed in two ways. An incident field can excite ground state electrons to a state above the metal Fermi level, followed by the vibronic coupling of the metal to the excited molecular state. Conversely, ground state transition mediated through a metal state by vibronic coupling followed by incident field-induced transfer of charge from the metal to the excited molecular state can also occur [158]. Effectively, this metal-mediated charge transfer excites the molecule to a vibrational state and modifies the molecule’s polarizability. Either way, the transition to an excited state is augmented by the presence of the metal, thus enhancing the intensity of the measured Raman signal.

The second mechanism (electromagnetic) induces a stronger SERS enhancement and does not necessitate molecular adsorption onto the metal surface [10]. When an incident field excites a localized surface plasmon of the metal nanostructures, proximate molecules experience the strong fields characteristic to particle plasmon modes at the metal surface (figure 62).
Figure 62 The electromagnetic mechanism governing SERS.

The strong, localized fields in turn excite Raman active modes of the detected molecule and resonantly induce large scattering cross sections, especially important for modes whose transition probability is extremely low. The scattered fields are many orders of magnitude stronger than from the same molecular concentration of surface-adsorbed species not in proximity to a nanostructured plasmonic metal. In this paradigm, two enhancements occur – first of the incident field at the nanostructure surface with field enhancements usually scaling with $|E|^2$, and second of the molecule’s Raman scattered signal that can be enhanced by its proximity to the plasmonic structures, also an $|E|^2$ factor [157]. Thus, in a resonant system enhancements scaling with an approximate factor of $|E|^4$ are expected. Typically, this electromagnetic mechanism is the stronger of the two SERS mechanisms, although both can contribute simultaneously.

Among the metal nanostructures used for SERS, Ag and Au are the most frequently used: they exhibit strong SERS enhancements and have been incorporated into a variety of sensing schemes for chemical or biological applications [10]. Ag nanoparticle SERS enhancements range from $10^6$-$10^{14}$ depending on nanoparticle geometry and spatial configuration, making them the most widely used material, while
Au nanoparticles generally exhibit lower enhancements ($10^4$-$10^5$) and are red-shifted with respect to their Ag counterparts [159,161]. Au does have advantages over Ag, notably immunity to oxidation. SERS measurements are typically performed in solution, which consists of colloidal metal nanoparticles, or on dry substrates formed by metal deposition. Various groups have studied the size and shape control of nanoparticles in dispersed solution [162,166], which effectively protects the metallic surface from reactive environments, e.g. air, that would otherwise oxidize and render the nanoparticles ineffective. Dry substrates, however, lack surface protection and maintaining SERS activity represents a considerable challenge, especially for Ag. The fact that surface-deposited Ag nanoparticles readily corrode in ambient limits their utility; indeed ambient-induced corrosion can severely quench the Ag plasmon resonance even to the point of complete damping. Consequently, the SERS effect for solid-supported Ag nanoparticles degrades over time following exposure to air and a recent study has shown this lifetime of utility is only 36 hours [29]. For this reason, there is interest in other metal nanoparticles that can serve as SERS substrates, especially those that resist the effects of oxidation and are widely tunable.

In this work, we demonstrate the plasmon-based SERS effect as a measure of the Ga nanoparticles’ applicability for biological/chemical sensing.

### 7.3 SERS proof of concept

Gallium has been recognized as an alternate SERS substrate metal, but previous SERS investigations have been made with rough Ga films, evaporated at low temperature (80K), that exhibited slight ($10^3$) enhancement, but no enhancement for room temperature evaporated Ga [167]. Plasmonic gallium nanoparticles (nanoparticles), however, are promising SERS candidates because of their previously
described broad plasmon tunability, stability across a wide temperature range, excellent plasmon resiliency when oxidized, and simplicity of deposition – even at room temperature [54,55]. Moreover, Ag and Au nanoparticles tend to aggregate during growth causing instability and irreproducibility of the SERS substrate plasmon wavelength while Ga nanoparticles exhibit no post-deposition aggregation or attendant modification of the plasmon. That Ga can be deposited directly onto solid supports, such as sapphire or Si, and does not necessitate an additional adhesion layer, is advantageous compared to Ag and Au. Therefore, stable Ga nanoparticles can overcome the drawbacks associated with uncontrolled nanoparticle aggregation, yielding reproducibly tunable SERS substrates. We synthesized geometrically-controllable Ga SERS substrates through the MBE deposition of Ga metal nanoparticles onto sapphire substrates, producing Ga nanoparticles whose size distribution, particle density, and plasmon resonance can all be easily adjusted during growth to specified values. The SERS enhancement and longevity from Ga nanoparticles substrates were tested using the standard Raman dye Cresyl fast violet (CFV) and a polymer used in electroluminescent devices, poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV), with a weaker Raman signature.

The Ga nanoparticles were grown at room temperature on inert, sapphire substrates, which exhibit significantly less fluorescence interference in Raman measurements than glass, and tuned using real-time monitoring by in situ spectroscopic ellipsometry. A series of Ga nanoparticles/sapphire substrates was grown with plasmon modes respectively tuned to 400nm (3.1eV), 633nm (1.96eV), or 785nm (1.58eV) (figure 63, top), in accordance with the various laser excitation sources available.
Figure 63 Absorption spectra corresponding to a) 3.1eV (442nm), b) 1.96eV (633nm), and c) 1.58eV (785nm) Ga nanoparticle on sapphire plasmon resonances with corresponding SEM images and accompanying nanoparticle diameter distribution. The decrease in the nanoparticle density as a function of increasing mean nanoparticle diameter is evident from the SEM imagery. FWHM of the size distributions, derived from Gaussian fit, are 23nm, 84nm, and 33nm/81nm from smallest to largest mean nanoparticle diameter, respectively.

Since SE beam spot (~1x2mm²) is large relative to the nanoparticle diameters, the SE signal represents the collective behavior of the nanoparticles. Substrates were half metallized and half unmetallized for direct comparison between the Ga nanoparticles’ influence and the bare sapphire. Scanning electron microscopy (SEM) confirms the nanoparticles visibly increase in average size as the plasmon resonance redshifts (figure 63, middle). The nanoparticle size distribution functions reveal a gradual nanoparticle diameter transition at various metal dosages from a single mode size distribution (e.g.
the 3.1eV sample) to a bimodal distribution (e.g. the 1.58eV sample), another hallmark of Ostwald ripening (figure 63, bottom).

CFV has a well-defined Raman signature with its strongest mode at 590cm$^{-1}$. Initial studies with a Raman dye are advantageous as they allow the experimentalist to easily discern whether or not the SERS effect occurs with a particular metal nanostructure and if so, to perform quantification of the enhancement factor in a well-controlled manner. A 1µL volume of 100ppm CFV in ethanol (EtOH) was dropwise placed on fully oxidized Ga nanoparticles/sapphire substrates and dried for approximately 15 minutes to ensure complete EtOH evaporation and to minimize the distance between the CFV molecules and the metal nanoparticle surfaces. CFV and sapphire possess distinct, strong, and well-separated Raman active modes (figure 64a).
Figure 64 (a) Full spectrum of surface-enhanced CFV Raman on sapphire. Sapphire only contributes the Raman features between 1350-1450cm\(^{-1}\). (b) High resolution SERS spectra for the strongest CFV mode at 590cm\(^{-1}\) for Ga nanoparticles with plasmon resonance at (i) 3.1eV (442nm), (ii) 1.58eV (785nm), (iii) 1.96eV (633nm) and (iv) bare sapphire without Ga nanoparticles.

EtOH easily wets the substrate surface and the solution spreads over a circular area of approximately 5x5mm = 25m\(^2\). The strong Raman-active CFV mode at 590cm\(^{-1}\) was measured at five different positions on the metallized surface of each sample (figure 64b). To ascertain the SERS enhancement, the average intensity of these five measurements were normalized to the weak Raman signal from a 100 ppm CFV solution on bare sapphire. The clear difference with and without Ga nanoparticles on the surface indicates that the nanostructured Ga induces an enhancement of the Raman scattering. The strongest SERS enhancement (~30) was measured from the 3.1eV plasmon
sample, followed by the 1.58eV and 1.96eV samples. Although this was an unexpected observation – the nanoparticles tuned to the laser excitation energy (1.96eV) were expected to provide the strongest enhancement – optimizing the Ga nanoparticle geometry will improve the enhancement factor. Note that the SERS measurements were performed through a 50x microscope objective with a beam spot diameter ~2μm, probing an aggregate, heterogeneous collection of nanoparticles of varied sizes and separations. The measured SERS signal effectively represents the sum of individual SERS signals arising from the interactions between the adsorbed molecules and individual nanoparticles, the majority of which are non-resonant and exhibit only a weak enhancement.

To quantify the SERS sensitivity and post-oxidation stability of the 3.1eV nanoparticles, CFV solutions ranging from 10-200ppm were deposited onto Ga nanoparticles on sapphire for Raman measurements (figure 65).

![Figure 65 Calibration of CFV SERS on Ga nanoparticles. Calibration measurement error bars range from 4-20% (mean = 12%), quite small even at the largest concentrations, implying reproducibility. The Raman mode at 590cm\(^{-1}\) CFV is shown for each concentration solution (inset).]
As expected, the Raman intensity weakens linearly with decreasing CFV concentration, but even the 10ppm sample exhibits a measurable SERS signal. In stark contrast to Ag SERS substrates, the Ga SERS intensity did not degrade even after several days of air exposure.

Several factors contribute to the varying enhancements among the three plasmonic Ga nanoparticle/sapphire substrates. Since the SERS effect relies on the electromagnetic enhancement from strong localized surface modes of plasmonic nanoparticles, and given the consistent spheroidal geometry of all the Ga nanoparticles, the dominant effect on plasmon energy and field strength is the size of the nanoparticles. Inspection of the Ga nanoparticle imagery supports this correlation between nanoparticle size and SERS signal. The strongest SERS response came from the 3.1eV sample whose nanoparticles had the smallest mean diameter (88nm), which suggests that narrowly distributed nanoparticles in the 85 ± 15 nm diameter range are primarily responsible for the SERS signal. The 1.58eV sample, comprised of a bimodally distributed nanoparticle diameter with one peak centered at ~85nm, had the next strongest SERS signal. The 1.96eV sample, whose plasmon resonance coincided with the excitation energy of the laser, had the weakest SERS signal, and the sample had the fewest nanoparticles of diameters between 70 - 100nm. The SERS enhancement therefore correlates with the excitation of a particularly-sized nanoparticle at a given laser wavelength; importantly, the SERS signal can be optimized by tuning the Ga nanoparticle diameter during growth to maximize the number of nanoparticles of that diameter.

The intricate spatial distribution of the Ga nanoparticle population, characterized by density and interparticle distance, produces E-field coupling between adjacent nanoparticles. The aggregate behavior of the Ga nanoparticle population influences
their efficacy for SERS: the smallest nanoparticles exhibit the largest areal density, the narrowest size distribution, and the smallest nanoparticle separations. The size and areal density of Ga nanoparticles can be tuned during growth to optimize the Raman scattering intensity [65]. Increasing the nanoparticle areal density increases the SERS signal in two ways: 1) higher density surfaces contribute more resonant nanoparticles, and 2) reduced interparticle distances increase the electromagnetic coupling and concentrate the surface fields between nanoparticles [40,166,168,169]. In addition to providing a greater percentage of optimally-sized nanoparticles, a narrow distribution of nanoparticle diameters increases the opportunity for resonant interparticle electromagnetic coupling between nanoparticles of similar size. Concomitantly, the interparticle distances increase with nanoparticle size. The nanoparticle interparticle distances in the 3.1eV sample are most narrowly distributed around a mean separation of 16nm, small enough to induce strong interparticle E-field coupling to enhance the local fields ultimately strengthening the SERS signal [169]. As the nanoparticles increase in size, so does the interparticle spacing – 20nm for the 1.96eV substrate and 40nm for the 1.58eV substrate – weakening any SERS enhancement derived from interparticle electromagnetic coupling. For all these factors, it is reasonable that the 3.1eV substrate with a large number of small, similarly sized, closely spaced nanoparticles produces the strongest SERS signal for a given concentration of CFV. More importantly, these insights suggest how to optimize Ga nanoparticle size and distribution to maximize SERS signal.

These data show that Ga nanoparticles are a compelling candidate for a SERS substrate material with considerable spatial consistency and significant SERS enhancement. The work presented here represents the first demonstration of Ga SERS with self-assembled Ga nanostructures. Should size distribution control be attainable by
controlled UHV evaporation of Ga, the tunability of the Ga plasmon resonance by SE would enable the development of even stronger SERS enhancements with resonant Ga nanoparticles.

7.4 Demonstration of SERS with MEH-PPV

To demonstrate the viability of Ga nanoparticle SERS for real applications, a molecule that is not a Raman dye must be examined. While CFV is an excellent marker for Raman measurements, MEH-PPV is a more compelling candidate for SERS since it is an electroluminescent polymer currently being used in hybrid polymer/solid state emitter devices [170,171]. The strongest Raman-active mode of MEH-PPV occurs at 1583cm\(^{-1}\) [171].

To measure the SERS signal of MEH-PPV, a thin, low concentration (0.1% wt.) solution of MEH-PPV in toluene was spin cast onto Ga nanoparticle/sapphire substrates and stored under vacuum for 24 hours to ensure toluene evaporation. Spin casting at 500 rpm yields a homogeneously thin layer of ~70nm – on the order of the nanoparticle height. The thin MEH-PPV deposition ensures that the nanoparticles are not completely embedded in the polymer layer such that the incident beam can still couple directly to the metal nanoparticles. Figure 66 depicts (a) thin MEH-PPV on Ga nanoparticles and (b) the identical MEH-PPV film on bare sapphire. For a 5mW HeNe excitation, the strong MEH-PPV mode ~1583cm\(^{-1}\), along with several weaker modes, emerges only when in contact with Ga nanoparticles, so the enhancement factor could not be quantified.
Figure 66 Raman spectra of MEH-PPV thin films spin cast onto (a) Ga nanoparticles on sapphire compared to identical MEH-PPV on (b) bare sapphire. Sapphire modes are removed between 1300-1400 cm\(^{-1}\) for clarity. Characteristic features (966 cm\(^{-1}\), 1112 cm\(^{-1}\), 1283 cm\(^{-1}\), and 1583 cm\(^{-1}\)) are observed only in the presence of the Ga nanoparticles. All other features are sapphire background.

This result highlights the SERS activity of Ga nanoparticles for a diversity of molecules and demonstrates that Ga surface modes can effectively couple with electroluminescent polymers.

**7.6 Ga plasmon coupling with III-N quantum well emitters**

Prior efforts to couple quantum well (QW) emitters with 2D surface plasmon modes yielded strongly enhanced emission for InGaN active regions (tuned to the visible) and Ag thin films[8]. In the work performed by Neogi, et al, plasmon-mediated radiative recombination lifetime enhancement was demonstrated on chemical vapor deposition grown GaN/InGaN QW structures emitting in the visible at 2.8eV. The presence of plasmon modes at the Ag film/QW interface was shown to effectively increase the photon density of states thereby increasing the dipole transition probability with respect to free space emission directly from the QW.
Harnessing Ga’s UV resonant plasmon modes, AlGaN/GaN QWs emitting close to 3.4eV were grown with Ga NPs deposited on the QW surface in vacuo. The Ga NP effective plasmon resonance was tuned to match the exciton peak of the QW structure, but time-resolved photoluminescence (TRPL) measurements were unable to discern a radiative recombination rate enhancement. The difficulty lay, in part, in the inherently fast recombination rate of the AlGaN/GaN QWs that were initially grown. With recombination lifetimes close to the resolution limit of the TRPL system, any potential enhancement (shortening) of the lifetime would not be measurable.

Switching to the InGaN QW grown by MBE, the intrinsic carrier lifetime could be readily measured by TRPL, but exhibited no discernable enhancement in the presence of the plasmonic Ga nanoparticles. Compared with an identical sample covered with a thin Ag film that accelerates the lifetime by a factor of $10^2$, the Ga NPs were exhibited an enhancement near 2. The weakness of the Ga NP enhancement can be attributed two issues. Firstly, the difficulty in coupling the InGaN QW emission to the Ga NPs might be related to the broad size distribution of the Ga NPs. Similar to the SERS enhancement, the net population of NPs resonant at the appropriate wavelength is only a fraction of the assembly deposited on the sample surface. As such, improving the deposition process to decrease the NP size distribution of tuned Ga NPs is necessary to proceed. Furthermore, decreasing the distance between the active region and the Ga NPs can improve the extent of the evanescent coupling between the emission mode and the plasmon modes. Successful demonstration of Ga plasmon-mediated emission enhancement both in the visible and the UV requires much continued effort to improve growth, tuning, and coupling control over the Ga NPs.
7.5 Discussion

Size-controlled Ga nanoparticle substrates for SERS detection have been grown using our simple, MBE-based fabrication protocol with *in situ* SE monitoring, without the need for nanosphere or lithographically-defined templates. Raman measurements of CFV and MEH-PPV on these substrates represent the first demonstration of reproducible, tunable, self-assembled Ga nanoparticles for SERS applications. A SERS enhancement factor of ~30 was measured and SERS signals were observed for CFV dye solutions as dilute as 10 ppm. While the enhancement factor for these Ga nanoparticles is much smaller than reported for Ag nanostructures, our continued work to understand the characteristics of the Ostwald ripening mechanism will illuminate how optimal substrates may be grown. This ability to monitor and control Ga nanoparticle growth conditions can potentially yield more uniformly sized nanoparticles or more controllable nanoparticle densities, which could greatly improve the strength of the Ga SERS signal. Gallium’s resilient performance following oxidation is inherently advantageous compared to Ag for practical *ex vacuo*, non-solution applications and, in concert with its characteristic temperature stability, makes it an interesting candidate for diverse sensing environments. As such, we believe that Ga nanoparticles are an effective tool for SERS sensing applications and their stability over a wide temperature range and even after oxidation suggests the nanoparticles could be used in certain harsher environments in which Au or Ag are simply inadequate.

Many challenges remain for Ga nanoparticle coupling with QW emitter devices for emission enhancement, but several potential solutions have already been mapped out to succeed in this ongoing effort. A diversity of Ga nanoparticle applications still
remain to be explored to ensure their place within the plasmonics and broader nanotechnology community.
Chapter 8 Final thoughts and the future

8.1 Conclusions

The work described here has progressed the field of plasmonics in several ways. The application of UV-vis in situ spectroscopic ellipsometry to real-time plasmonic monitoring enables accurate control over evolving plasmonic nanostructure assemblies to tune their resonance without prior knowledge of their resultant geometry. Spectroscopic ellipsometry can be widely applied to various metals, substrates, and growth systems – a powerful characteristic of this unheralded characterization method. Through the use of real-time plasmon monitoring of the group III metals, Al, Ga, and In, we demonstrate its ability to discern the plasmonic evolution during disparate growth processes – thin film coalescence and Ostwald ripening. Based on our assessment of the Ostwald mechanism driving Ga nanoparticle formation and development, we have shown that Ga metal is a flexible plasmonic metal whose size-dependent tuning can cover a remarkably wide spectral range, well beyond that of pure Ag and Au. We assessed the thermal, oxidative, and geometric properties of In and Ga and uncovered several unique features of Ga nanoparticles making them applicable in situations untenable for traditional Ag-based plasmonic technology. They are liquid at the nanoscale and the plasmon’s stability after oxidation means plasmonic Ga nanoparticles’ lifetime far exceeds that of Ag. We moved beyond simple size-dependent plasmon tuning by growing bimetallic nanoparticles of varying effective composition to manipulate the plasmon resonance. By growing at elevated temperatures, we successfully deposited homogenous alloy nanoparticles of MgGa, a surprising composition given the effective composition (gas ratio) is approximately 2%. This initial demonstration opens the door for continued work to fully manipulate the alloy composition during growth. The
development of alloyed nanoparticles has implications for plasmonics along with catalysis and hydrogen storage.

In addition to our work characterizing and growing nanoparticles of various metals, shapes, sizes, and compositions, we also performed fundamental scientific investigation of interfacial science, the results of which also have implications for a variety of fields encompassing surface chemistry and interfacial physics. Using kinetic ellipsometry to monitor nanoparticle growth on polar semiconductor surfaces, we have presented the electrowetting interaction controlling Ga ripening as a function of the intrinsic barrier potential at the metal-semiconductor interface. This work uncovers a previously untapped intrinsic tuning parameter.

Finally, the first demonstration of surface-enhanced Raman scattering with Ga nanoparticles is presented with both CFV and MEH-PPV to show the technical application of these new plasmonic metal nanoparticles. For sensing applications their unique chemical and thermal stability will expand the sensing environments possible for SERS-based sensing devices. Furthermore, these Ga nanoparticle SERS substrates can potentially be integrated with solid-state III-V semiconductor laser devices by MBE. Emission enhancement of InGaN quantum wells with plasmonic Ga nanoparticles has been initiated, but the effect is slight. The proper tuning of the nanoparticle size distribution and sufficient coupling of the evanescent fields with the emitter active region are two areas that require further investigation.

8.2 Future directions

Direct continuation from this work can progress from several of the key findings. The surface level interactions driving nanoparticle formation and aggregation are an important process that still requires study. Specifically, quantitatively detailing the barrier
potential interaction with the metal nanoparticles ripening on polar semiconductors will go far to expand the tunability of the nanoparticles during their growth. More generally, understanding the growth mechanisms driving the formation of homogenous alloy Ga-Mg nanoparticles can be exploited to ultimately manipulate the alloys to any composition and size. The immediate question relates to the relative composition in the final nanoparticles and its correlation to the gas phase (effective) metal ratio. The final EF-TEM confirmed composition of MgGa indicates that the Ga and Mg may combine in two ways. It is possible the Ga and Mg fluxed simultaneously may bind in the gas phase before adsorption and nucleation on the substrate surface. Or, the Ga and Mg adatoms adsorb in a competitive process controlling the final composition. Regardless of their binding, whether it occurs in the gas phase or on the substrate surface, a competitive nucleation process is occurring since highly Ga-rich deposition conditions were able to yield MgGa homogenously across the surface and within the individual nanoparticles.

To expand interest in Ga and Ga-based plasmonic nanoparticles, we must continue seeking impactful applications for their use. Improving the Ga nanoparticles’ SERS enhancement by improving their geometry and mixing with other SERS metals, e.g. Ag, are natural first steps. Eventual development of integrated SERS devices based on Ga-NPs and nitride-based lasers is just one long-range technological advancement borne of the work started here that can have a direct impact on sensing and detection for medical and military applications. From an emission enhancement standpoint, the nanoparticle geometry and their spatial separation from the emitter active regions must be improved. The ultimate goal of which is to improve the radiative recombination lifetimes of quantum well structures in the visible and the UV – a region in which Ag cannot be utilized. The enhancement of UV emission from nitride-based optoelectronic structures has broad implications from solid-state lighting to water purification – both
highly profitable in the current environmental sustainability-oriented climate. These extensions are simply the beginning. Our vision is to continue expanding the role Ga plays in the plasmonics and overarching nanotechnology communities while continuing to delve into the fundamental science of the underlying processes governing nanoparticle surface assembly.
Appendix

Appendix A Characterization methods

The materials characterization presented in this work were primarily collected at the Duke University Shared Materials Instrumentation Facility (SMIF) unless otherwise noted.

Atomic Force Microscopy

Atomic force microscopy (AFM) is a nanometer resolution scanning microscopy technique. A mechanical imaging technique, AFM involves scanning a sharp probe across a sample surface to measure the 3D topography and surface features. Two measurement modes are possible by AFM – contact and tapping. Since contact mode leaves the tip on the sample surface throughout the measurement it is limited to hard surfaces. Tapping mode images, however, are performed by tapping the tip along the sample surface near the tip’s resonance frequency, which is controlled by a piezoelectric scanner. Adjusting the piezoelectric controller’s PID parameters can tune the tip oscillation to minimize noise and artifacts in the image. Additionally, tapping mode AFM can also collect tip controller amplitude (mV) and phase (º) images that provide different contrast images that improve topographical resolution on some types of samples (e.g. nanoparticle samples shown in this work). Both of these control parameter images collects the piezoelectric controller’s feedback system parameters as it responds to the sample topography, thus, while not an absolute measure of the surface height and roughness, the images are an accurate representation of the tip/surface interaction and provide an additional dimension to the visual interpretation of the sample surface. The tapping mode images presented within this work were collected on a Digital Instruments Dimension 3100 and Veeco TESP (Sb-doped n-Si) tips.
Raman spectroscopy

Two Raman systems were used to perform the surface-enhanced Raman scattering measurements. A Horiba-Jobin-Yvon Horiba LabRam ARAMIS system with variable source capabilities was used with a 100x microscope objective and CCD detector. Of the 3 visible lasers – 785nm, 633nm, and 442nm (25mW, 5mW, and 1mW, respectively) – the HeNe (633nm) source was the primary source. A second system, an inVia Renishaw Raman system housed the Vo-Dinh Lab at Duke University’s Biomedical Engineering department, comprising an inverted microscope equipped with a 50x objective and a 0.2mW 633nm (HeNe) laser, was also used. In both cases, the laser power can be mitigated to protect the sample surface from burning by utilizing optical filters.

Scanning Electron Microscopy

Unlike AFM, SEM uses electromagnetic interactions to probe a sample surface. The secondary electron SEM in this work employs a highly focused electron beam of energy 1-5kV that is raster scanned across the sample surface wherein the electrons interact with the material’s lattice, experiencing absorption and scattering within the interaction volume. Emitted secondary electrons, inelastically scattered by the incident electron beam, are collected and whose total count varies the brightness of the image revealing sample topography details. Tilting the sample surface with respect to the electron beam can increase the contrast along z-axis features improving the topographic contrast and clarifying the form of 3D. Typically, the magnification can range from $10^1$ to $10^6$x with a resolution on the order 1nm. For image clarity, highly conductive samples produce the best images, but surface charging effects can be slightly mitigated by limiting the beam energy as we have done here with the FEI XL30 SEM-FEG.
Transmission Electron Microscopy

As the name suggests, transmission electron microscopy requires that samples be thinned down (~10^-1 nm) to allow detection of transmitted electrons. An electron beam impinges on the sample surface and the transmitted electrons can be Z-filtered (atomic number) to discern the precise location of different elements. We employed energy filtered TEM (EF-TEM) to measure the compositional distribution of the alloyed nanoparticles and can resolve the homogeneity down to within a single nanoparticle (and below). With the atomic-scale resolution EF-TEM can discern composition and homogeneity of nanoscale structures. Coupling diffraction mode TEM with electron energy loss spectroscopy (EELS) measures the energy of transmitted electrons that have inelastically interacted with the sample lattice the analysis of which can quantify elemental composition to high lateral resolution. High angle annular dark field scanning TEM (HAADF-STEM) was also performed on samples for atomic number contrast imaging. From these images for which the electron beam is raster scanned across the sample surface, the bright features correspond to regions of higher mean atomic number, Z. Dr. Alexandra Suvorova at the University of Western Australia performed the TEM analysis on plan view samples using a JEOL 2100 TEM equipped with a Gatan Image Filter and Tridiem digital camera.

X-ray Photoelectron Spectroscopy

Chemical analysis of samples can be performed with precision using x-ray photoelectron spectroscopy. Based on the photoelectric effect, XPS detects the kinetic energy of emitted photoelectrons from a sample to determine the binding energy of the surface with which the incident x-rays has interacted. From the binding energy, the chemical state of the present elements can be discerned and relative ratios of the
Elements can provide more detailed analysis of the surface stoichiometry. The Kratos Analytical Axis Ultra was employed here with a monochromatic Al source.
Appendix B Abbreviations

AFM  atomic force microscopy
NIR  near infrared spectrum
NP   nanoparticle
SE   spectroscopic ellipsometry
SERS surface-enhanced Raman scattering
SEM  scanning electron microscopy
SPR  surface plasmon resonance
TEM  transmission electron microscopy
XPS  X-ray photoelectron spectroscopy
UV   ultraviolet spectrum
vis  visible spectrum
References


Nanoscale Gate Lengths. Journal of Nanoscience and Nanotechnology 2, no. 3-4: 325-32.


Biography

Pae Wu is a North Carolina native who grew up rooting for Duke Basketball. After graduating cum laude with a B.S.E in electrical engineering from Princeton, she moved to the Centre National de la Recherche Scientifique (CNRS) in France. After one year, she returned to North Carolina to pursue her graduate studies at Duke. While she cultivated her scientific chops she simultaneously nurtured her love of Duke basketball, coaching rowing, playing ultimate, studying the djembe, planning the DOUGHMAN, and enjoying life in dirty Durham.

Publications and presentations


