Study of Strain-Tunable Optical Properties of Metal Thin-Films on Elastomeric Substrates

by

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A thesis submitted in conformity with the requirements

for the degree of Master of Applied Science

Graduate Department of Electrical and Computer Engineering

University of Toronto

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2016

Abstract

Metal thin-films have unique optical properties and play a pivotal role in many photonic, plasmonic and metamaterial devices. The optical properties of metal thin-films cannot be easily modulated however, and as such the potential for tunable devices using metal thin-films layers is limited. We demonstrate the tunability of the optical properties of metal thin-films deposited on elastomeric substrates by way of applied tensile strain. Silver thin-films seeded by dielectric aluminum nitride layers are shown to exhibit strain actuatable infrared plasmonic resonances as a result of film crumpling when under strain. Silver thin-films seeded by chromium are shown to have local surface plasmon resonances as well as reduced infrared reflectivity when compared to smooth silver thin-films. Under strain, we show how the reflectance of these films is further decreased, and their transmittance enhanced. We conclude with a list of potential tunable optical devices that could utilize strain-tunable metal thin-film layers.
Acknowledgements

I would like to first acknowledge my parents, James and Glenda Clark for their support throughout my academic career. I would further like to thank my father for inspiring me to pursue the profession of engineering and always pushing me to do better than before.

Without the support of my supervisor, Prof. Nazir Kherani, I would not have been able to complete my Masters graduate program successfully. I would first like to thank Prof. Kherani for taking me on as a student, and giving me the freedom to pursue a topic of interest to me. I would also like to thank Prof. Kherani for the opportunities he gave me to attend international conferences and be exposed to a broader range of research being undertaken worldwide as well as in his group.

In addition to the support of my supervisor, I was also greatly aided by the other members of our research group. I would like to specifically thank Andrew Flood for always helping to troubleshoot equipment problems and help me reason through theoretical problems during my degree program. For training me on various pieces of equipment, I would like to acknowledge Brett Ramautarsingh and Remy Ko. For her academic and professional advice I would also like to thank Dr. Hui-Lin Hsu.

Finally, I would like to thank the University of Toronto, Department of Electrical and Computer Engineering for allowing me to pursue a Masters of Applied Science and supporting me financially throughout the past two years. For funding my work, I would also like to thank the Natural Sciences and Engineering Research Council and specifically through the Discovery program and the Smart Net-Zero Energy Buildings Research Network of NSERC.
# Table of Contents

Abstract........................................................................................................................................... ii  

Acknowledgements........................................................................................................................ iii  

List of Figures...................................................................................................................................... vii  

Table of Tables ................................................................................................................................... xiii  

List of Acronyms and Symbols ......................................................................................................... xiv  

List of Appendices.......................................................................................................................... xvi  

Chapter I: Introduction .................................................................................................................. 1  

Chapter II: Plasmonics................................................................................................................... 5  

2.1 Dielectric Function of Metals .................................................................................................. 5  

2.1.1 Drude Model...................................................................................................................... 5  

2.1.2 Limits of the Drude Model ............................................................................................... 8  

2.2 Surface Plasmon Polaritons.................................................................................................... 8  

2.2.1 Dispersion Relation .......................................................................................................... 9  

2.2.2 Coupling to SPPs ............................................................................................................ 14  

2.3 Localized Surface Plasmons.................................................................................................... 18  

2.4 Tunable Plasmonic Devices..................................................................................................... 21  

Chapter III: Strained Metal Thin-Films ....................................................................................... 25  

3.1 Growth of Metal Thin-Films on Polymer Substrates ............................................................. 26  

3.2 Studies of Strained Metal Thin-Films.................................................................................... 30
Chapter IV: Microscale Fracturing of Strained Silver Thin-Films

4.1 Mechanical Structure ................................................................. 38
4.2 Electrical Properties ................................................................. 43
4.3 Optical Properties ................................................................. 44
4.4 Multilayer Coatings ................................................................. 52
4.5 Conclusion ............................................................................ 54

Chapter V: Nanoscale Fracturing of Strained Silver Thin-Films

5.1 Mechanical Properties ................................................................. 56
5.2 Electrical Properties ................................................................. 59
5.3 Optical Properties ................................................................. 60
5.4 Electromagnetic Simulations ....................................................... 64
5.5 Effect of Film Thickness ............................................................. 73
5.6 Conclusion ............................................................................ 76

Chapter VI: Applications

6.1 Tunable SPP Sensors ................................................................. 77
6.2 Flexible and Strainable Plasmonic Devices ................................. 79
6.3 Tunable Metallo-Dielectrics ....................................................... 80
6.3.1 Metamaterials ................................................................. 80
6.3.2 Solar Control Coatings ....................................................... 81
6.4 Strain Activated Sensors

Chapter VII: Conclusion and Future Work

References

Appendix A: Derivation of the Drude Model

Appendix B: Guided Wave Solution at an Interface and Surface Plasmon Frequency

Appendix C: Fabrication Methods

Appendix D: Microscale Fracturing of Strained Silver Thin-Films - Supplemental Information

Appendix E: Refractive Indices used in Simulation
List of Figures

Figure 1: Relative permittivity of a lossless metal obeying the Drude model................................. 7

Figure 2: Electric field intensity of an SPP mode at the interface of a metal and a dielectric. The components of the wavevector in the metal and dielectric are shown at the bottom and top respectively .................................................................................................................................. 11

Figure 3: Real component of the normalized tangential component of the wavevector at the metal-dielectric interface (the surface plasmon wavevector normalized by the free space wavevector). .................................................................................................................................................. 13

Figure 4: Diffraction of normally incident light upon striking a metallic grating. The horizontal arrows illustrate a diffracted order propagating along the metal-dielectric interface....................... 16

Figure 5: The penetration of an evanescent mode when TIR occurs (left). The coupling of the evanescent mode at the prism-air interface coupling into an SPP mode at the metal-air interface. (right) ...................................................................................................................................................... 17

Figure 6: Quasi-Static approximation of the polarizability of a metallic nanosphere. A strong resonance in the polarizability is seen at \( \omega/\omega_p = 1/3 \) ........................................................................................................................................... 19

Figure 7: Increase in reflectance and red-shift of a film with constant nanoparticle density as the particles are brought closer together (left). Illustration of the field intensity between the metal nanoparticles with 100nm interparticle spacing of the figure on the left (centre). Illustration of the field intensity between the metal nanoparticles with 10nm interparticle spacing of the figure on the left (right)........................................................................................................................................ 21

Figure 8: Mechanism for silver thin-film growth on an amorphous substrate. Illustrating the connection between island dimensions and film roughness......................................................... 28
Figure 9: Film smoothness can be improved by using a high surface energy seeding layer that alters the contact angle, flattening out the islands (left). Another mechanism for improving smoothness is by using a seeding layer with good adhesion to the metal in order to limit the growth of the islands (right).

Figure 10: Nanoscale cracking pattern observed with a well adhered 25nm Ag thin film deposited atop a 5nm Cr seeding layer and a 1mm PDMS substrate.

Figure 11: Microscale cracking pattern observed for poorly adhered 30 nm Ag thin film deposited atop a 3nm AlN seeding layer and a 1mm PDMS substrate.

Figure 12: Optical phenomena in a strained metal thin-film on an underlying elastomeric substrate. (A) Reference pre-fractured unstrained Ag thin film (10 nm) on PDMS (1 mm) with schematic representation of incident (yellow arrow), specular transmitted (blue) and specular reflected (red) light. (B) Scanning electron microscopy (SEM) plan view of the microstructure of the Ag film in (A). (C) Specular and total transmittance, and specular and total reflectance of the film in (A). (D) Reference post-fractured unstrained thin film. (E) SEM plan view of film in (D) show fracture lines. (F) Optical properties of film in (D) essentially identical to those of (A). (G) Strained post-fractured thin film illustrating the presence of scattered transmitted and reflected light (green), and formation of NIR SPPs (bright red) along the undulations and MIR SPPs (dark red) along the microcracks of the film. (H) SEM plan view of film in (G) revealing undulating morphology and microcracks. (I) Optical properties of film in (G) reveal presence of diffuse transmission and reflection, and absorption at specific frequencies due to formation of SPPs. Insets in (E) and (H) show photos of the film in the unstrained (transparent) and strained (translucent) states.

Figure 13: Surface structure of strained metal thin-films. SEM images show surface morphology of post-fractured metal thin-films of different thicknesses (10, 20 and 30nm Ag) under a range of conditions.
strains (0, 5, 10 and 15%). Insets show higher magnification images focusing on the periodic undulations parallel to the direction of strain. ................................................................. 39

Figure 14: 30nm thick Ag thin-film on PDMS with 15% strain applied. The distance between adjacent cracks is on the order of 10s of μm. ................................................................. 41

Figure 15: Electrical properties of strained films. (A) Measured resistance of the strained Ag films. (B) Inferred effective resistivity of the Ag films under strain. Red squares, blue diamonds, and green triangles correspond to 10, 20, and 30nm Ag films, respectively. ......................... 44

Figure 16: Optical appearance of a 30nm Ag thin-film on PDMS (A) when unstrained showing a large amount of specular reflection, and (B) when strained where most of the reflected light is scattered, and no reflected images are visible. Comparison of the two films clearly shows an increase in diffuse scattering of transmitted light and reflected light after being strained......... 45

Figure 17: Optical transmittance and reflectance of 10nm, 20nm and 30 nm Ag films under strain. (A), (B) and (C) show specular transmittance, specular reflectance and total transmittance of 10nm Ag films under strain, respectively. The black, red, green and blue curves correspond to 0, 5%, 10% and 15% strain, respectively. Similarly, (D), (E) and (F) show the spectra for 20nm Ag films under strain, and (G), (H) and (I) show the spectra for 30nm Ag films under strain. ............ 47

Figure 18: Structure of the undulated 10nm Ag thin-film simulated in COMSOL................... 49

Figure 19: Modelled and experimental reflectance and transmittance spectra of planar and undulating 10nm Ag films on PDMS. (A) Modelled spectra: Total transmittance (solid blue) and total reflectance (solid red) for unstrained film; total transmittance (dotted blue) and total reflectance (dotted red) for 15% strained film; specular transmittance (dashed blue) and specular reflectance (dashed red) for 15% strained film. (B) Experimental spectra with identical legend of (A)........................................................................................................................................... 49
Figure 20: Comparison of experimental and simulated optical spectra for a 10nm Ag thin-film seeded by AlN and deposited on PDMS. Good qualitative agreement between the experimental and simulated results as to the wavelengths at which various changes occur in the spectra can be observed.

Figure 21: Optical spectra of a multilayer thin-film structure with a 1mm PDMS substrate, a 3nm AlN seeding layer, a 10nm Ag thin-film and a PDMS capping layer of an unknown exact thickness. Unstrained samples are shown in blue, and 15% strained samples are shown in black. (A) specular transmittance, (B) total transmittance, (C) specular reflectance, (D) total reflectance.

Figure 22: SEM image of a 25nm thick Ag thin-film with a 5nm Cr seeding layer deposited on PDMS. Inset show a higher magnification of the same strained film.

Figure 23: SEM image of the film from Figure 18 with >15% strain, illustrating a periodic undulation in the horizontal direction.

Figure 24: Resistance (left) and approximate resistivity (right) of the film under varying amounts of strain. Clearly illustrating the maintaining of conductivity even as large amounts of strain (up to ~20%) are applied.

Figure 25: Optical transmittance and reflectance of 25 nm Ag films under strain. (A), (B), (C), and (D) show UV-Vis specular reflectance, total reflectance, specular transmittance, and total transmittance under strain, respectively. The black, red, green and blue curves correspond to 0, 5%, 10% and 15% strain, respectively.

Figure 26: Absorbance of the 25nm Ag thin film, the optical properties of which are shown in Figure 24.
Figure 27: MIR Reflectance of a 25nm thick Cr Seeded Ag thin-film on PDMS. Illustrating how in the long wavelength limit, the nanocracked Ag thin-film has metallic reflection and behaves as a homogenous conductive film. ......................................................... 63

Figure 28: Unit Cell Proposed in Lacour et. al.[28] ................................................................. 65

Figure 29: Simulated Reflectance and Transmittance from the Unit Cell shown in figure 28. .. 67

Figure 30: (A) Comparison of the reflectance peak wavelength for the experimental measurements and the simulated structure. Showing good agreement between the reflectance peak wavelength in simulation and experiment. (B) Comparison of the transmittance dip wavelength for the experimental measurements and the simulated structure. ............................................... 69

Figure 31: Structure of the Strained Nanoscale Cracked Metal Thin-film............................... 71

Figure 32: Simulated change in VIS-NIR transmittance and reflectance of Ag-Cr thin-film under 10% strain (unstrained structure shown in Fig. 28, strained structure shown in Fig. 31............ 72

Figure 33: SEM image of the surface of a 20nm (right) and 30nm (right) thick Ag thin-film seeded by Cr and deposited on PDMS. ................................................................. 73

Figure 34: (A) reflectance, and (B) transmittance, of Ag thin-films of varying thickness seeded with Cr and deposited on PDMS. ........................................................................ 74

Figure 35: SEM of the surface of 30nm Ag thin-film seeded by Cr under 15% tensile strain. A transition between micro-cracking and nano-cracking behaviour is observed, including the formation of undulations aligned parallel to the applied strain. .............................................. 75

Figure 36: Schematic of a simplified SPP prism coupled sensor. The shift in refractive index caused by the binding of the green molecules changes the SPP wavelength and results in the light being reflected at the prism interface instead of coupled to the SPP................................. 78
Figure 37: Illustration of how a strain based tunable SPP grating can operate. Initially the period is short and green light can be coupled to SPPs on the grating surface. As strain is applied, the period of the grating increases and the grating can now couple red, instead of green, normally incident light.
Table of Tables

Table 1: Summary of undulation dimensions for 10nm, 20nm, and 30nm thick Ag thin films seeded by AlN and deposited on PDMS................................................................. 42
# List of Acronyms and Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>AlN</td>
<td>Aluminum Nitride</td>
</tr>
<tr>
<td>B</td>
<td>Magnetic Flux Density</td>
</tr>
<tr>
<td>c</td>
<td>Speed of Light</td>
</tr>
<tr>
<td>c₀</td>
<td>Speed of Light in Vacuum</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
</tr>
<tr>
<td>D</td>
<td>Electric Flux Density</td>
</tr>
<tr>
<td>E</td>
<td>Electric Field</td>
</tr>
<tr>
<td>EOT</td>
<td>Extraordinary Optical Transmission</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>H</td>
<td>Magnetic Field</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>j</td>
<td>Imaginary Number (engineering notation)</td>
</tr>
<tr>
<td>J</td>
<td>Free Current Density</td>
</tr>
<tr>
<td>kₚₛ</td>
<td>Surface Plasmon Wavevector</td>
</tr>
<tr>
<td>LSP</td>
<td>Local Surface Plasmon</td>
</tr>
<tr>
<td>LSPR</td>
<td>Local Surface Plasmon Resonance</td>
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<tr>
<td>mₑ</td>
<td>Electron Effective Mass</td>
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<tr>
<td>MIR</td>
<td>Mid-Infrared</td>
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<td>N</td>
<td>Electron Density</td>
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<td>Near-Infrared</td>
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<tr>
<td>P</td>
<td>Polarization Density</td>
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<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
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<tr>
<td>r</td>
<td>Reflection Coefficient</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>SPP</td>
<td>Surface Plasmon Polariton</td>
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<tr>
<td>t</td>
<td>Transmission Coefficient</td>
</tr>
<tr>
<td>TE</td>
<td>Transverse Electric</td>
</tr>
<tr>
<td>Symbol</td>
<td>Name</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>TIR</td>
<td>Total Internal Reflection</td>
</tr>
<tr>
<td>TM</td>
<td>Transverse Magnetic</td>
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<tr>
<td>(\alpha)</td>
<td>Normalized Tangential Wavevector</td>
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<td>Normalized Perpendicular Wavevector in Dielectric</td>
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<tr>
<td>(\gamma)</td>
<td>Normalized Perpendicular Wavevector in Metal</td>
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<tr>
<td>(\gamma_f)</td>
<td>Damping Frequency</td>
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<tr>
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<td>Permittivity/Dielectric Constant</td>
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<tr>
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<td>Relative Permittivity</td>
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<tr>
<td>(\theta_c)</td>
<td>Critical Angle</td>
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<tr>
<td>(\lambda)</td>
<td>Wavelength</td>
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<tr>
<td>(\lambda_{sp})</td>
<td>Surface Plasmon Wavelength</td>
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<tr>
<td>(\mu)</td>
<td>Permeability</td>
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<td>(\mu_0)</td>
<td>Vacuum Permeability</td>
</tr>
<tr>
<td>(\mu_r)</td>
<td>Relative Permeability</td>
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<tr>
<td>(\nu)</td>
<td>Poisson's Ratio</td>
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<tr>
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<td>Electric Susceptibility</td>
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<tr>
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<td>Local Surface Plasmon Frequency</td>
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<tr>
<td>(\omega_p)</td>
<td>Plasma Frequency</td>
</tr>
</tbody>
</table>
List of Appendices

Appendix A: Derivation of the Drude Model.................................................................93

Appendix B: Guided Wave Solution at an Interface and Surface Plasmon Frequency.........95

Appendix C: Fabrication Methods..................................................................................98

Appendix D: Microscale Fracturing of Strained Silver Thin-Films - Supplemental Information .........................................................................................................................103

Appendix E: Refractive Indices used in Simulation..........................................................106
Chapter I: Introduction

Since before the fundamentals behind electromagnetic theory were understood, metals have always played a key role in optical and electromagnetic devices. From their use as reflective layers in mirrors since the time of antiquity to their use in the study of diffraction phenomenon in the 18th and 19th century[1], the optical properties of metals have fascinated scientists and laymen alike.

For the most part, these initial uses of metals dealt with bulk metal objects and films and were limited to using metals as either broadband reflectors or opaque barriers to electromagnetic radiation. With the development of more sophisticated thin film fabrication technologies, such as electron-beam evaporation[2] and sputter deposition[2], it became possible to make metal films as thin as several nanometers[3]. In addition, new micro and nano scale lithography techniques such as electron-beam lithography and focused ion beam lithography have made it possible to pattern these thin-films to nanoscale dimensions[4]. Together, these two revolutions have led to the study of a wide range of new fields of optics, one of which is plasmonics.

Plasmonics in a general sense is the study of how electromagnetic radiation interacts with the surfaces of materials that have an abundance of free charge carriers[5]. One class of materials in which there are a large number of free charge carriers is metals[6]. In a metal, the electrons in the valence band of the metal act as a free electron gas that can move under the influence of an incident electric field, such as electromagnetic radiation[6]. When an electromagnetic field is incident on a bulk metal, the free electrons within the metal oscillate collectively with the incident field, generating their own induced electric field and reflecting the incident light[6]. This reflection over
A broad range of wavelengths is used in a large variety of applications, including metallo-dielectric heat mirrors[7], electromagnetic shielding[8] and high-energy laser optics[9]. In addition to the bulk properties of metals, the surfaces of metals also exhibit the very unique surface phenomena of Surface Plasmon Polaritons (SPP) and Localized Surface Plasmons (LSP)[1].

Surface Plasmons are the coupled oscillation of conduction electrons at a metal surface with electromagnetic radiation[1]. These oscillations can be propagating in the case of SPPs or localized oscillations in the case of LSPs, however, in both cases they have the unique property of confining light to sub-wavelength dimensions resulting in resolution greater than the diffraction limit and high electric field intensity[1]. A wide variety of new applications have opened up based on the properties of these phenomena, including sub-wavelength waveguides[10], bio-molecule sensors[11], photo-luminescence enhancement[12], near-field imaging[13] and second harmonic generation[14].

In order to realize these applications, many different device architectures have been proposed and built. Structures such as metallic gratings[1], metal nanoparticles[15], metallo-dielectric multilayers[16], perforated metal films[1], arrays of metal nanostructures and metal tips are all examples of structures that have been shown to demonstrate plasmonic resonances[1]. Though these devices vary in many ways, there are a few features that many share in common. One feature in common between many of these plasmonic devices is the use of noble metals as their functional materials[1]. A major hurdle to the use of noble metals in plasmonics however is the inability to tune their properties. This limits the functionality of metals such as gold and silver to a narrow range in the visible and infrared[1]. In addition, the lack of elasticity in metals means that in the past they could not be implemented in flexible and strainable devices that are often used for the
tuning of other photonic resonances, such as the photonic bandgap devices[17] and diffraction gratings[18].

Metals are also used prolifically in electronic devices as conducting layers for electrical interconnects and contacts[19]. In recent years, there has been a large focus on developing flexible electronics for use in wearable electronics and non-planar devices[20]. A major hurdle in this field has been the large amount of strain experienced by the conducting layers and the damage this causes to metallic layers[20]. To solve this problem, a large amount of research has been done in recent years on developing strainable metal films that retain their conductivity even when a significant amount of mechanical strain is applied to them[20]–[23]. It has been shown that metal thin-films deposited on elastomers can retain their electrical connectivity even when strains as high as 30%[21] are applied. The resistivities are additionally still orders of magnitude lower than alternatives such as organic conductors[21], [24], thus reducing electrical losses.

The investigation of strained metal thin-films has focused mostly on their application as conductive layers in flexible electronics[25]–[27], however they also have the potential to be of use in the field of optics as well. When metal thin-films are strained, significant changes to the microstructure of the films has been observed[28], and this is expected to have a large impact on their optical properties. In addition, the ability to strain the films and maintain the connectivity of the film allows the potential to use these devices in strain tunable photonic devices such as those mentioned above. A thorough investigation of the optical properties of strained metal thin-films can not only allow the realization of a broad range of new strain tunable plasmonic devices but also be used to add tunability to current plasmonic devices using metal thin-films.
The following thesis is a first in-depth investigation into the optical properties of strained metal thin-films on elastomeric substrates. The investigation has focused on the properties of silver thin-films on polydimethylsiloxane (PDMS). However many of the conclusions drawn are applicable to other metal thin-films as well as films deposited on alternative elastomeric substrates. Chapter II and III focus on the fundamental theory behind the behavior of strained metal films, with Chapter II outlining the basic theory of plasmonics and Chapter III explaining the growth of metal thin-films and the impact of seeding layer on the mechanical structure of strained metal thin-films. Chapter IV outlines the mechanical, electrical and optical properties of silver thin-films deposited on PDMS with an Aluminum Nitride (AlN) seeding layer and discusses the fundamental origins of the various optical phenomena observed. Chapter V introduces an alternative seeding material, Chromium, and demonstrates how the use of this material drastically impacts the morphology of the strained silver films as well as their optical properties. Chapter VI discusses several potential applications for strainable metal thin-films based devices in optics. Chapter VII concludes the key results of the investigation and proposes future work that needs to be done in order to develop a more complete understanding of the optical properties of a variety of metal thin-films with various seeding layers. Details of the experimental procedures used are available in Appendix C.
Chapter II: Plasmonics

Plasmonics is a field of electromagnetism that deals with the interaction between the surfaces of materials with an abundance of free charge carriers, and electromagnetic radiation[5]. Due to the properties of these materials, there exist unique solutions to Maxwell’s equations that allow for high confinement of light, negative refraction and many other extraordinary properties[5]. We will focus on metals as a specific example of a plasmonic material.

2.1 Dielectric Function of Metals

At the heart of the plasmonic properties of metals and other conductors is the dielectric function of the bulk material. The unique solutions to Maxwell’s equations such as SPPs and LSPs that exist are only possible because of the values of the dielectric function of conducting materials[5].

2.1.1 Drude Model

One rudimentary model for the dielectric constant of metals is the Drude model. In the Drude model, the free electrons in the metal are treated as an electron gas and are assumed to be entirely responsible for the optical properties of the metal[5].

The goal of any model for the dielectric function of a material is to determine the value of the dielectric constant (\(\varepsilon\)). When an electric field (\(\mathbf{E}\)) is applied to a material, the free and bound charges respond to the field and set up an internal electric field within the material[6]. This internal field can be described as resulting from a polarization density (\(\mathbf{P}\))[6]. Using \(\mathbf{P}\), it is possible to relate the other electrical vector in Maxwell’s equations, electric flux density (\(\mathbf{D}\)), to the electric field by way of the constitutive relation[6].
\[ \mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \]  \hspace{1cm} (2-1)

This can be rewritten in terms of an electric susceptibility \((\chi_e)[6]\),

\[ \mathbf{D} = \varepsilon_0 \mathbf{E} + \varepsilon_0 \chi_e \mathbf{E} \]  \hspace{1cm} (2-2)

and upon simplifying the above expression\([6]\),

\[ \mathbf{D} = \varepsilon_0 (1 + \chi_e) \mathbf{E} = \varepsilon_0 \varepsilon_r \mathbf{E} \]  \hspace{1cm} (2-3)

Finding the relative permittivity \((\varepsilon_r)\) is essential for understanding the interaction between a material and light, as the time harmonic solution to the electric field inside a non-magnetic material will be of the form\([6]\),

\[ \mathbf{E} = A e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} + B e^{i(\omega t + \mathbf{k} \cdot \mathbf{r})} \]  \hspace{1cm} (2-4)

where \(|\mathbf{k}| = \sqrt{\varepsilon_r k_0}, k_0\) is the vacuum wave vector\([6]\). In order to solve for the dielectric constant, we start by treating the free electrons of the metal as free classical charged particles experiencing an electrical force from an incident electric field\([1]\). In addition there is a frictional force that accounts for electron-electron collisions and electron-phonon collisions that slow the free electrons\([1]\). After solving for the electron displacement and determining the polarization density, we obtain the dielectric constant shown below\([5]\),

\[ \varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2 - \gamma_f \omega} \]  \hspace{1cm} (2-5)

where \(\omega_p = q \sqrt{\frac{N}{m \varepsilon_0}}\), is the plasma frequency, \(\gamma_f\) is the damping frequency, \(N\) is the density of free electrons in the metal, \(m\) is the electron effective mass, and \(q\) is the charge of an electron\([5]\). For a full derivation of the Drude model, see Appendix A. From the dielectric response of a non-lossy metal, shown in Fig. 1, we clearly see that there is a unique property when the frequency approaches the plasma frequency. At this point, the value of the dielectric constant reaches zero,
and the dielectric constant goes from being negative to positive. This is an important point, as it represents a frequency where the free electrons of the metal are resonant with incident radiation. For the non-lossy metal, the metal is perfectly reflective below this frequency, and transmissive above it.

![Graph](image)

*Figure 1: Relative permittivity of a lossless metal obeying the Drude model.*

This dielectric constant can also be related to the DC conductivity of the metal when we allow the frequency to be arbitrarily small, and the equation of the dielectric constant reduces to[5],

\[
\varepsilon_r = 1 - \frac{j\sigma}{\varepsilon_0 \omega} \quad (2-6)
\]

where \(\sigma\) is the DC conductivity. This clearly demonstrates that the conductivity of the metal has a significant impact on its dielectric properties[5].
2.1.2 Limits of the Drude Model

Despite the versatility of the Drude model for the dielectric constant of metals, there are limitations to its applicability. With regards to predicting the optical properties of a metal, a major inadequacy of the Drude model is the assumption that the only method of interaction between the metal and an incident electric field is through the free electrons\(^5\). In reality there are many other charged particles present within the metal, and at certain frequencies these can also interact with the incident field\(^5\).

At visible and ultraviolet (UV) frequencies, the inner shell electrons of the metal atoms can be excited to high energy bands by incident light\(^5\). These transitions are known as interband transitions and represent another mechanism by which the metal can interact with incident light\(^5\). For this reason, the Drude model does not give a complete picture of the dielectric constant of metals in the UV and visible regions. The effect of interband transitions on the dielectric constant is primarily to introduce additional loss into the material, however it also causes a slight shift in the location of plasmon resonances such as SPPs and LSPs that are discussed subsequently\(^5\). In order to present a phenomenological explanation of the various plasmonic phenomena, the subsequent discussion will focus on an ideal metal obeying the Drude model, although the ways in which to account for non-ideality will clearly be identified.

2.2 Surface Plasmon Polaritons

A surface plasmon polariton (SPP) is a bound electromagnetic state in which an electromagnetic wave in a dielectric is coupled to the collective oscillations of the free charges at the surface of a conductor\(^1\). The SPP is confined to a region around the surface of the conductor, and propagates along the interface\(^1\). Within the dielectric, the SPP manifests as a confined electromagnetic
wave propagating along the interface, and in the conductor it manifests as a wave of electron
density. SPPs can exist for any conductive material within a certain wavelength range [1],
however we focus on SPPs in metals.

2.2.1 Dispersion Relation

Like all classical electromagnetic phenomena, the properties of SPPs are fully explicable by
Maxwell’s equations[6].

\[
\nabla \cdot \mathbf{D} = \rho \quad (2-7)
\]

\[
\nabla \cdot \mathbf{B} = 0 \quad (2-8)
\]

\[
\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (2-9)
\]

\[
\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \quad (2-10)
\]

In a source free, current free and isotropic medium, such as the dielectric and metal being
considered in the solution of an SPP, the four equations take the form[6],

\[
\nabla \cdot \mathbf{D} = 0 \quad (2-11)
\]

\[
\nabla \cdot \mathbf{B} = 0 \quad (2-12)
\]

\[
\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (2-13)
\]

\[
\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} \quad (2-14)
\]

By utilizing the constitutive relationships discussed previously, these four equations reduce to a
simple wave equation in terms of the electric field[6],

\[
c^2 \nabla^2 \mathbf{E} = \frac{\partial^2 \mathbf{E}}{\partial t^2} \quad (2-15)
\]

which has a solution of the form,
\[ E = A e^{j(\omega t - kr)} + B e^{j(\omega t + kr)} \]  \hspace{1cm} (2-16)

where \( A \) and \( B \) are constants, and \( k \) and \( \omega \) are related by the relation \(|k| = n \omega / c_0\), and \( n \) is \( \sqrt{\varepsilon_r} \) in a non-magnetic medium[6]. When applied to an interface between two materials, this solution provides an equation each for the electric field on either side of the interface, where each is comprised of a backward and forward propagating wave. After applying the boundary conditions for Maxwell’s equations, it is possible to determine relations between the amplitude of incident, reflected and transmitted waves, known as the Fresnel equations[6].

\[ r = \frac{n_1 \cos \theta_2 - n_2 \cos \theta_1}{n_1 \cos \theta_2 + n_2 \cos \theta_1} \]  \hspace{1cm} (2-17)

\[ t = \frac{2n_1 \cos \theta_1}{n_1 \cos \theta_2 + n_2 \cos \theta_1} \]  \hspace{1cm} (2-18)

It is possible to find a unique solution for TM polarized light where \( t \) and \( r \) go to infinity (when the denominator goes to zero)[1]. This condition is known as the pole of the transmission and reflection coefficients, and represents the case when there is no incident electromagnetic wave. When we additionally choose a solution where the electromagnetic wave in both materials is decaying away from the interface, we obtain a guided wave solution as illustrated in Fig. 2 below.
To simplify the expression of the solution, the electromagnetic field will be described by the magnetic field perpendicular to the plane of incidence, which in time harmonic form is[1],

\[ H = H_0 e^{-j k_0 (\alpha x - \beta y)} \] (2-19)

in the dielectric, while

\[ H = H_0 e^{-j k_0 (\alpha x + \gamma y)} \] (2-20)

is in the metal, where \( n_1 \cos \theta_1 = k_0 \alpha \) and \( n_1 \sin \theta_1 = k_0 \beta \) and \( n_2 \sin \theta_2 = k_0 \gamma \)[1]. By making these substitutions, it is possible to solve for \( \alpha, \beta, \text{and} \ \gamma \) using the Fresnel equations and we obtain.
\[
\alpha = \pm \frac{n_2}{n_1} \sqrt{1 + \frac{n_2}{n_1}^2} \quad \beta = -\frac{1}{\sqrt{1 + \frac{n_2}{n_1}^2}} \quad \gamma = \frac{\left(\frac{n_2}{n_1}\right)^2}{\sqrt{1 + \left(\frac{n_2}{n_1}\right)^2}}
\]

If the metal described by \( n_2 \) is governed by the lossless Drude model, and \( n_1 \) is 1 (vacuum), then we can derive a relation between \( \alpha, \omega \) and \( \omega_p \), which is [1],

\[
\alpha = \pm \sqrt{1 - \frac{\omega_p^2}{\omega^2}} \quad (2-24)
\]

The real portion of \( \alpha \) can be plotted against the frequency to observe the surface plasmon dispersion relation [1]. We also note that as \( \omega_p^2/\omega^2 \) approaches 2, the value of \( \alpha \) will approach a maximum, meaning \( \alpha \) will have an asymptote at \( \omega = \frac{\omega_p}{\sqrt{2}} \). This value of \( \omega \) is known as the surface plasmon frequency, and although it is simply described by the equation above, for lossy Drude materials \( \alpha \) has a more complex form [1]. See Appendix B for a detailed analysis. The dispersion relation for a lossy Drude Model metal is plotted in Fig. 3 below.
Based on the dispersion relation for the SPP, there are a few interesting properties of SPPs that we notice immediately. The first is that the SPP is truly a guided mode, without the need of another dielectric interface, and it is possible to strongly confine the electromagnetic energy to the surface of the conductor[1]. This can be seen by the imaginary components of $\beta$ and $\alpha$. As the imaginary components are negative, the field intensity will decrease as you move away from the interface (denoted as $y = 0$)[1]. This not only allows the SPP to propagate along the interface without being dissipated due to radiation, but means that the electric field intensity will be highest at the interface[1].
The final two properties relate to the fact that the component of the wavevector parallel to the interface \((\alpha k_0)\) for the SPP has a real component greater than \(k_0\) (i.e. \(\alpha > 0\))[1]. Primarily, this means that the effective wavelength of the SPP in the direction of propagation is smaller than the value in the dielectric[1]. Not only this, as you approach the surface plasmon frequency this value approaches a minimum value[1]. As the minimum distinguishable spot-size that can be made is limited by the diffraction limit \(R = \frac{\lambda}{2\sin\theta}\)[4], and the effective wavelength of the SPP, \(\lambda_{sp} = \frac{2\pi}{k_{sp}}\), where \(k_{sp}\) is given by the tangential component of the wavevector \((\alpha k_0)\), is shorter than that in the dielectric, it should theoretically be possible to focus SPPs on a metal-dielectric interface to a resolution greater than the diffraction limit in the dielectric material[1].

This means that the perpendicular component of the wavevector in the metal and dielectric for any electromagnetic wave that can excite the SPP must be imaginary to satisfy the relations \(k_0 = \sqrt{\alpha^2 k_0^2 + \beta^2 k_0^2}\) and \(n_2 k_0 = \sqrt{\alpha^2 k_0^2 + \gamma^2 k_0^2}\)[1]. This restriction means that a plane wave incident on the metal-dielectric interface cannot excite the SPP and special means are necessary to couple a plane wave into a SPP.

### 2.2.2 Coupling to SPPs

There are a variety of different structures and objects that are capable of coupling a propagating plane wave into an SPP mode. The inability for a plane wave to couple into an SPP is solely due to the fact that \(k_{sp} (\alpha k_0)\) of the SPP is greater than \(k_0\), and therefore any means that can impart momentum into a plane wave and give it momentum greater than \(k_0\) may be capable of coupling incident radiation into an SPP[1]. There are a variety of structures that can achieve this, however
we will focus on three examples, diffraction gratings, sub-wavelength structures and devices with total internal reflection (TIR).

Diffraction gratings are a common structure used to couple incident electromagnetic radiation into SPPs[1]. Diffraction gratings are a surface structure where either the surface height is periodically modulated, as in the case of a surface relief grating, or the refractive index of the material is periodically modulated, as in the case of a volume grating[9]. When electromagnetic radiation is incident on a diffraction grating, in addition to reflection and transmission occurring at the specular angles, the periodic structure of the grating also imparts momentum on the incoming photons allowing for transmission at a variety of angles described by the diffraction equation[1].

\[ \sin \theta_m + \sin \theta_i = \frac{m \lambda}{nd} \quad (2-25) \]

where \( \theta_i \) is the angle of incidence, \( \theta_m \) is the angle at which the diffracted order emerges, \( \lambda_o \) is free space wavelength of the incident radiation, \( n \) is the refractive index of the medium in which the diffracted order propagates (the incident medium for reflected light, and the grating medium for transmitted light), \( m \) is the diffraction order, and \( d \) is the period of the grating[1].

The component of the wavevector parallel to the interface for these diffracted orders is given by[1],

\[ k_{xm} = k_{x0} + \frac{m \lambda}{d} \quad (2-26) \]

When observing the radiation that emerges from the diffraction grating in the far-field, only diffracted orders with an angle less than 90 can be detected, however in reality an infinite number of diffracted orders exists in the near-field with \(-\infty < m < \infty\). In the near-field, this allows for the existence of modes where \( k_{xm} \) is greater than \( k_0 \), and therefore when the grating material is a metal,
for a certain wavelength a certain diffraction order could have a \( k_{xm} = \alpha k_0 \) and therefore the grating could couple incident light with a TM polarization to an SPP propagating along the direction of the grating[1].

When incident light is coupled into an SPP, the electromagnetic energy for this order is trapped in a propagating SPP along the surface of the grating. As a portion of the electric field penetrates into the lossy metal, energy is dissipated into the metal as the SPP propagates. The wavelength at which this resonance occurs can be noted by an increase in the absorption of light at the wavelength for a certain angle of incident light[1]. This phenomenon is known as Wood’s anomaly and has been observed since the beginning of the 20\(^{th}\) century[1]. For normally incident light at wavelengths significantly far away from the Surface Plasmon frequency, where \( k_{sp} \) has a real component only slightly greater than \( k_0 \), this anomaly occurs very close to where a diffracted order would diffract at 90\(^\circ\), a point known as the passing off[1] as illustrated in Fig. 4 below.

Another approach to coupling incident radiation to an SPP is through the use of a sub-wavelength nanostructure. When electromagnetic radiation is incident upon a structure much smaller than the wavelength of radiation, the structure scatters the incident radiation and produces an infinite

\[ \text{Dielectric} \]
\[ \text{Metal} \]
number of new waves with a different tangential wavevectors[1]. For a spherical particle, the additional horizontal momentum given to these waves is,

\[ \Delta k = \frac{n^2 \pi}{a} \]  \hspace{1cm} (2-27)

Where \( a \) is the radius of the sphere, and \( n \) is the refractive index of the medium. Once again we note that it is therefore possible in the near-field to observe scattered radiation with a \( k_x \) greater than \( k_0 \). By means of these excited waves, it is possible to couple radiation from an incident plane wave into an SPP. This is often done using a nanoparticle atop a metallic film, where the near-field of the nanoparticle excites an SPP in the metal film. The polarizability of the nanoparticle plays a key role in the intensity of the nanoparticle’s near-field, and thus the efficiency of the coupling to the SPP[1]. For this reason, metallic nanoparticles are often used due to their high polarizability near their resonant local surface plasmon frequency, which will be discussed subsequently in the Local Surface Plasmon (LSP) section[1].

The final common approach to coupling incident radiation to an SPP is through the use of the TIR phenomenon by use of a prism. The coupling mechanism is schematically illustrated in Fig. 5 below.

![Figure 5: The penetration of an evanescent mode when TIR occurs (left). The coupling of the evanescent mode at the prism-air interface coupling into an SPP mode at the metal-air interface. (right).](image-url)
The incident radiation enters the prism at the first air-glass interface with an incident angle of 0. The radiation then propagates until it reaches the second glass-air interface. The new angle of incidence is given by $\theta$, and if this angle is greater than the critical angle $\theta_c = \sin^{-1} \left( \frac{n_2}{n_1} \right)$, where $n_1$ and $n_2$ are the refractive index of the prism and the air respectively, then $k_x$ in the air will be greater than $k_0$. If a metal film is placed beneath the prism, then the evanescent wave in the air below the prism can couple into a propagating SPP on the surface of the metal. Ordinarily the prism will completely reflect the incident radiation due to the TIR at its bottom interface, however at a specific angle for each frequency of radiation, an SPP will be excited, and the reflected intensity will significantly decrease.

### 2.3 Localized Surface Plasmons

When dealing with metallic nanostructures with sub-wavelength dimensions, speaking of propagating SPPs becomes meaningless. When the size of the nanostructure is sub-wavelength, the SPP will interfere with itself, and a localized mode of oscillation at a specific frequency will result. This type of oscillation is known as a localized surface plasmon (LSP).

The constructive interference of SPPs is the fundamental source of the resonant behavior of metallic nanoparticles, however it is often more convenient to consider the polarizability of the metal nanoparticle as a whole when deriving the LSP properties. For small particles, the polarizability can be derived using a quasi-static approximation. When we do this, we see that the polarizability for a nanoparticle made of a material obeying the Drude model has a very strong frequency dependence and reaches a maximum value at a resonant frequency $\omega_{\text{sp}}[1]$, which
occurs when the dielectric constant of the nanoparticle medium is equal to -2\[1\], as shown in Fig. 6. The fact that all materials obeying the Drude model will have a dielectric constant of -2 at some frequency, and metals obey this model, allows them to exhibit this strong resonant behavior\[1\].

**Figure 6**: Quasi-Static approximation of the polarizability of a metallic nanosphere. A strong resonance in the polarizability is seen at $\omega/\omega_p = 1/\sqrt{3}$.

There also exist additional higher order resonance modes at higher orders, and for a spherical particle these are given by,

$$\omega_l = \sqrt{\frac{l}{2l+1}} \omega_p (2-28)$$

where $l$ is the order of the multipole (i.e., 1 for the dipole mode), and $\omega_p$ is the bulk plasmon frequency.

In reality this does not fully describe the resonant frequency of metallic nanoparticles, as the geometry and size cause a slight retardation of the plasmon oscillations and change the resonant
frequency. The resonances of many other nanoparticle shapes have been studied, including nanocubes[29] and nanoprims[30], however for understanding the work in this thesis, a full understanding is not necessary, and it is satisfactory simply to understand that sub-wavelength metallic nanostructures will have LSP resonances and what the effects of these resonances will have on the optical properties of the material.

There are once again three key properties of LSPs that are useful in their use in nanophotonic devices. The first was discussed previously, and that is that LSPs represent a mode of electromagnetic radiation where the horizontal wavevector is greater than the free space wavevector. This allows LSPs which are localized in space around a nanoparticle to couple incident radiation into propagating SPPs on a nearby metal film.

In addition to this coupling, similar to an SPP, the electric field of an LSP is strongly confined to the surface of the metallic nanoparticle. This results in a very strong electric field and high sub-wavelength resolution at the interface of the particle. Depending on the geometry, it is possible to further enhance the field intensity and resolution using structures with a very small radius of curvature, such as cones and subwavelength apertures[10].

Another important aspect of LSPs is their ability to couple to each other. Similar to two atoms whose electron resonances couple and create bonding and anti-bonding states when the atoms are brought close together, the LSP resonances of two metal nanoparticles can couple to each other and interact when they are brought close together[31]. This coupling is a result of the near-field of the two particles interacting with each other and creating a lower energy state in which the conduction electrons of the two particles oscillate in phase with each other[31]. With this coupling, two effects are observed. First the resonant frequency of the particle pair shifts to a lower
frequency (lower energy)[31], and second the field intensity between the two particles is greatly enhanced[31], as seen in the illustration of the field intensity around a pair of 20nm silver nanorods infinite in length separated by 10 nm in Fig. 7.

![Graph and Illustrations]

**Figure 7**: Increase in reflectance and red-shift of a film with constant nanoparticle density as the particles are brought closer together (left). Illustration of the field intensity between the metal nanoparticles with 100nm interparticle spacing of the figure on the left (centre). Illustration of the field intensity between the metal nanoparticles with 10nm interparticle spacing of the figure on the left (right).

### 2.4 Tunable Plasmonic Devices

Plasmonic nanostructures are extremely useful due to their ability to strongly confine radiation to sub-wavelength regions as well as the very sharp and intense resonances they exhibit. Further work has sought to expand these capabilities of plasmonic materials even more by adding the ability to actively tune their properties. In order to make plasmonic based sensors, filters, lenses and other such devices that can adapt their resonances in order to operate at different wavelengths, tunable plasmonic devices are desired. There are a variety of approaches used in order to actively change the plasmonic resonances of metallic/conductor nanostructures. Some of these include, changing the dielectric medium, changing the carrier concentration in the conductor and bringing nanostructures closer together to alter the coupling efficiency of their LSP resonances.
One of the most common methods of tuning the plasmon resonances of a SPP or LSP based sensor is by changing the refractive index of the surrounding dielectric medium. As shown previously, the magnitude of the wavevector of a propagating wave is dependent on the index of the medium that it is propagating in[6]. With regards to plasmonic structures, this causes two effects. First, it changes the interference conditions for periodic structures such as gratings, altering their diffracted orders[1]. This results in a change in the frequencies of radiation that can be coupled into SPPs by a grating structure[32]. Often this is used in sensors to detect the presence of biomolecules on a surface based on the refractive index change they induce near the metal surface[32]. The same effect can be seen when using a prism to couple SPPs to a metal surface, as the angle required to couple the SPPs will change with the refractive index change that the binding of biomolecules causes[32]. Second, the dielectric constant shifts the resonant frequency for metal nanoparticles[11]. This shift in the resonant frequency results in a change in the frequency of radiation that the nanoparticles scatter, and can be observed as a change in their colour[11]. This is observed when nanoparticles are submerged in solvents of different refractive indices for example[11].

Another approach to changing the plasmonic properties of conducting materials is by changing the plasma frequency of the material itself. This can be done by changing the carrier concentration within the material. Semi-conductors being conductors also have Drude like properties and can exhibit plasmonic phenomena at certain frequencies, however as a result of their low carrier concentrations, these are shown at much lower frequencies, usually in the infrared[33]. Materials such as indium tin oxide (ITO) have also been shown to have a conductivity dependent plasma frequency[34], and through electrically biasing ITO nanocrystals, tuning of the carrier concentration and hence the reflective properties has been shown[35].
In an attempt to extend these electrical approaches to tuning the plasma frequency of semiconductors to metals, a new field of electrochemical plasmonic materials has developed. This began through an extension of the metal-hydride battery technology to the optics field in the 1990s[36]. Using electrochemical cells to reversibly hydrogenate rare earth metals, it was demonstrated that a transition from metallico-reflective properties to transparency could be achieved in metal films[36]. This was attributed to a change in the free carrier concentration as a result of the hydrogen inclusion in the metal lattice, resulting in a shift in the plasma frequency to longer wavelengths of radiation[36]. Initially, this was only observed in rare earth metals such as ytterbium, however more recently metal alloys and oxides have been shown to demonstrate the same properties when used in hydrogen and lithium ion electrochemical cells[37]. Despite the fact that technologies based on these methods have even been commercialized[37], they have been limited due to the complexity associated with electrochemical devices.

One final method in which plasmonic properties are often tuned is by taking advantage of the coupling between individual metallic nanostructures. As discussed earlier, metallic nanostructures brought into close proximity experience a coupling between their plasmonic resonances that results in a shift of their resonant frequencies[31]. Mechanically tunable devices have been designed based on this principle that can adjust the coupling intensity between arrays of metallic nanoparticles. Demonstrations such as achieving a transition between the highly specific resonances of gold nanoparticles to the broadband reflection of a metal thin-film have been made using a Langmuir Blodgett technique to mechanically bring nanoparticles closer together[38]. Similar tunable devices relying on the coupling between metallic nanostructures have also been shown using metallic nanostructures deposited on elastic substrates as well[39]. A major limitation with this technique however, is that it relies on the coupling of isolated gold
nanoparticles. This means that until extremely close separation distances are achieved, there exists simply an array of LSP resonant structures, and the film does not have the same properties as a solid metal film that can support SPP propagation.
Chapter III: Strained Metal Thin-Films

Metal thin-films are planar metal layers with thicknesses on the order of tens of nanometers. Due to their finite thickness, metal thin-films have optical and electrical properties that vary greatly from the properties of bulk metals.

In bulk metals, the electrical resistivity is highly dependent on the resistivity of the bulk of the metal. This is largely due to the fact that the mean free path of conducting electrons is incomparable to the thickness of the film, and most electrons are scattered by bulk events rather than the metallic surfaces[40]. As the film thickness becomes comparable to the mean free path of electron scattering, then the surface scattering becomes significant, and contribute greatly to the resistivity of the films[2]. In addition to this, the roughness of the film surface can further enhance the scattering causing an even greater increase in the resistivity[3]. Further increases in the resistivity of the thin-film are caused by the fact that average grain size increases with film thickness, and therefore when the films are thin and thus the average grain size small, bulk scattering events become more frequent[2].

The electrical properties are not the only unique and important properties of metal thin-films. They also exhibit very unique optical properties as well. Although bulk metals are highly reflective and opaque to electromagnetic radiation, as they are made extremely thin, due to the imperfect reflection at the metal surface and the partial penetration of electromagnetic radiation into the metal, radiation can partially penetrate when the thickness of the metal is below a characteristic thickness known as the skin depth[41]. The amount of penetration and transmission is highly dependent on the dielectric constant of the metal. For longer wavelengths where both the imaginary and real part of the metal dielectric constant is large in magnitude, there is very
little penetration and the bulk of the electromagnetic radiation is still reflected[41]. As the plasma frequency is approached however, the magnitude of the dielectric constant decreases and for metal films with thicknesses on the order of 5-20 nm, a significant amount of visible light transmission is possible[41]. At extremely low thicknesses, the metal films become discontinuous and extremely rough, resulting in the creation of LSP resonances in the film that strongly scatter visible light[42]. The thicknesses at which this occurs is generally referred to as the percolation threshold, and is highly dependent on the surface roughness of the film[42]. In order to obtain high clarity optical films that utilize metal thin-films, it is essential to optimize the metal growth conditions in order to achieve a low percolation threshold.

### 3.1 Growth of Metal Thin-Films on Polymer Substrates

As discussed above, the optical and electrical properties of metal thin-films are extremely sensitive to the surface roughness, film continuity and lateral grain size. Therefore, for most applications it is necessary to grow films with low surface roughness, few discontinuities and a large grain size. Initially, the growth of such films was limited to growth on crystalline substrates using epitaxy[2], however in more recent years much research has been done on depositing ultrathin metal films on amorphous dielectric substrates. This progress was greatly hindered by the fact that the growth of metal thin-films on amorphous substrates differs greatly from that of epitaxial growth on crystalline substrates.

Epitaxial films are crystalline films that grow in a Frank Van-der Merwe growth mechanism where each layer deposits one by one atop a crystalline substrate[2]. During growth, individual atoms impinge on the substrate, then migrate to preferential binding sites, such as crystal ledges and form a single layer. Once a single layer is complete, isolated atoms will be deposited on the
smooth layer and then another atomic layer will form in a similar manner[2]. In order to form such epitaxial films however, there are many limitations on the substrate and the material being deposited[2]. The substrate and the deposited material must have a similar crystal structure, the two materials must be able to form a strong bond, the deposited material must be able to wet the substrate well, and the deposited atoms must have high mobility in order to migrate to the defects[2]. A match between the crystal structure of the substrate and deposited material is necessary in order to allow a strain free film to form and prevent internal stress from generating defects in the grown crystal. Strong bonding between the substrate and the film is necessary in order to achieve interfacial adhesion. This bonding often takes the form of alloying at the interface for metal films on metallic substrates[2], and chemical bonding with oxygen and nitrogen atoms in the case of oxide or nitride based substrates[43]. Wettability is essential to allow the film to deposit in a smooth complete layer instead of forming islands, and high mobility is essential to allow the atoms to diffuse to the preferential growth sites[2]. These requirements mean that epitaxy on crystalline substrates is often performed at elevated temperatures, however when the substrates are amorphous as in the case of polymers, these requirements drastically change.

When growing metal thin-films on amorphous substrates as opposed to crystalline substrates, the growth mechanism changes in several ways. Unlike in the case of crystalline substrates where an ordered crystalline plane with preferential growth sites is presented to the metal atoms being deposited, in the case of an amorphous structure the surface is random and uniform. This lack of distinct binding sites results in the metal remaining or sticking where it strikes the surface of the substrate and thus prevents the formation of a smooth defect-free crystal film. Instead the film grows as many isolated islands of the metal. As the number of islands increases, the separation
distance between adjacent islands decreases, and eventually a solid film forms. This growth mechanism is illustrated in Fig. 8 below.

![Figure 8: Mechanism for silver thin-film growth on an amorphous substrate. Illustrating the connection between island dimensions and film roughness.](image)

Based on this growth mechanism, the height of the islands is extremely important in determining both the minimum percolation threshold, as well as the ultimate film roughness. To minimize this height, two factors must be considered. First, the wetting of the metal thin-film on the substrate is extremely important, as it determines the contact angle of the islands and therefore their width-height ratio. In order to achieve this, the substrate should have a higher surface energy than the deposited metal to ensure that the formation of a metal-substrate interface is thermodynamically preferred over metal-air and substrate-air interfaces. Second, the size of individual islands must be limited in order to ensure that percolation occurs with a minimal island height. This can be achieved by limiting the diffusion of the deposited metal atoms when they strike the surface of the substrate. One way this can be done is by reducing the kinetic and thermal energy of the atoms, for example by altering the plasma chemistry in sputtering[42], or by using a low substrate temperature. Alternatively, the sticking coefficient of the deposition process can be enhanced by ensuring the substrate material can form a strong chemical bond with the deposited material. The different methods of improving layer smoothness are shown in Fig. 9.
When attempting to deposit metal thin-films on amorphous polymeric substrates as opposed to simply amorphous substrates, the complexity of the growth mechanisms is even greater. It has been shown that for polymeric materials, metal islands form preferentially at the locations of oxygen and nitrogen rich functional groups, and that the adhesion and bonding between the metal thin-film and the polymer is directly proportional to the nitrogen and oxygen concentration within the polymer. This is as a result of the ability for metals to form Metal-Oxide/Nitride-Polymer bonds between the polymer backbone and the metal. Metals with more negative enthalpy of formation for the formation of oxide and nitride compounds have also been shown to bond more strongly with polymer substrates. For metals that do not form oxides and nitrides as readily, such as silver and gold, this makes it difficult to form low roughness and thin metal thin-films on polymeric substrates. In addition to this, polymers have extremely low surface energies, resulting in very large contact angles and large island formation when metal thin-films are deposited on them. Due to the difficulty of achieving high quality metal thin-films directly on polymer substrates, additional layers that improve film quality need to be introduced.

In order to achieve high quality metal thin-films on both ordinary amorphous materials as well as amorphous polymeric substrates, wetting (also known as seeding) layers are required. Seeding
layers are an additional extremely thin layer that is deposited prior to the desired metal layer in order to improve the quality of the metal thin-film. This is achieved by two means. Primarily, the wetting layers improve the wettability of the metal on the substrate by providing a higher surface energy surface and thus reducing the contact angle between the substrate and the metal islands that form during growth[3]. In addition, for materials that do not adhere well to the substrate, a wetting layer that can strongly bond to the substrate as well as bond tightly with the deposited metal is chosen in order to improve the adhesion between the metal thin-film and the substrate and thus reduce the mobility of the metal clusters that are deposited, discouraging the growth of individual islands and promoting fewer and smaller islands. A variety of potential materials are possible, including metallic wetting layers such as chrome, titanium and copper, as well as dielectric wetting layers such as aluminum nitride and titanium nitride.

3.2 Studies of Strained Metal Thin-Films

Though a large amount of research was undertaken to develop deposition techniques for depositing ultrathin and smooth metal thin-films on amorphous polymers, this alone was insufficient for their implementation in flexible electronics. Although using the techniques described above, high quality metal thin-films can be deposited, in actuality with flexible electronics, there are additional complexities. When a flexible film is bent, it creates both compressive and tensile strain in the device. For polymer substrates, this strain is not a concern, as the substrate can usually undergo significant elastic deformation before being damaged. However metal thin-films cannot undergo strain without being damaged. As metal thin-films often serve as electrical interconnects in electronic devices, in order to develop low-loss flexible
electronics it is essential to develop a structure that will allow the straining of the metal film without catastrophic mechanical failure of the layer.

In recent years it has been found that when metals are deposited on elastomeric substrates, tensile strain can be applied to the elastomeric substrate while still maintaining electrical conductivity in the metal thin-film even when strains as high as 30% are applied[21]. When strain is applied, resistivity of the film increases ‘elastically’, and when the strain is removed, the film regains its initial electrical properties. The reason for this elastic change in the electrical properties is that although the straining of the elastomeric substrate causes local tearing of the metal thin-films, the elastic nature of the substrate ensures that when the strain is removed, the metal thin-film segments, which are adhered to the polymer substrate, are pulled back together and the isolated segments of the film are once again brought into electrical contact. Depending on the geometry of the initial cracks that form in the metal thin-films, the change in electrical resistance with strain can vary greatly, and thus many investigations have been carried out in order to understand the mechanisms for film cracking, as well as the factors affecting it.

In the rest of this chapter, we will briefly review some of the literature describing different strained metal thin-films and their mechanical properties and give a description of some of our own conclusions with regards to the causes of different cracking behaviours observed.

Depending on the way in which the metal thin-films are deposited on elastomeric substrates, different cracking geometries have been observed when strain is applied. In general, there are two types of cracks that form, linear microscale cracks[20], and nanoscale cracks[28]. Microscale cracks are long linear cracks perpendicular to the direction of strain, and are in general separated by distances of tens of micrometers[23]. Nanoscale cracks are much more frequent, and have a
zig-zag pattern. They are not directly aligned with the strain direction, however cracks are aligned predominantly perpendicular to the strain direction and open in the direction of the strain, as would be expected[23]. The nanoscale cracks can have a total length of several micrometers, however the lengths of the zig-zag branches are on the order of hundreds of nanometers[23], [28]. The mechanism governing the type of crack formation is attributed to the adhesion of the polymer to the substrate[23]. When the film is not well adhered to the substrate, the metal film behaves like a strained free-standing metal thin-film, and necking in the metal thin-film begins at highly localized areas centred around defects[23]. As the local strain reaches the maximum tensile strain of the metal, a crack forms and propagates perpendicular to the strain direction[23]. In the case of the well adhered film however, the compliance of the elastomeric substrate prevents the local strain from affecting the stress in other locations of the film, and necking occurs in a large number of areas[23]. These necking locations then form small cracks that propagate and link up to form a network of small cracks that mostly maintain the connectivity of the film[23], [28].

As the adhesion of the metal thin-film is extremely important in determining the cracking behaviour of the metal films, the quality of the seeding/wetting layer utilized is extremely important in determining the cracking geometries that are observed in the strained metal thin-films. Chromium is a well-known seeding layer for noble metals, and the cracking pattern observed when a 5nm Cr layer is deposited on PDMS prior to a 25nm Ag layer is shown in Fig. 10 below.
As can be seen there are many small cracks that have formed, and although there are a large number of cracks ultimately a clear path of conduction is nevertheless maintained. When a seeding layer with a poorer adhesion is utilized, for example AlN, we see that instead of the nanoscale cracks of Fig 10, we observe large linear microscale cracks as shown in Fig. 11. Ultimately connectivity is still maintained as the cracks do not propagate across the entire film, however the conduction pathway is drastically lengthened, and the resistivity significantly increases as will be shown later.
Despite the large amount of research in this field, the focus of the reported research has been on the development of flexible and strainable electrical conducting films. Examination of the optical properties of such films has been limited to simple visual analysis that do not provide intricate details and insight into the optical spectrum including information about the infrared and UV properties of the films[44]. In the following chapters, we will detail our research into the optical properties of these strained metal thin-films.
Chapter IV: Microscale Fracturing of Strained Silver Thin-Films

We have discussed briefly the two types of cracking behaviour observed in strained metal thin-films deposited on elastomeric substrates. As mentioned in the previous chapter, these two behaviours are understood in the literature to be dependent on the adhesion strength of the metal thin-film to the elastomeric substrate. In the next two chapters, we investigate the optical properties of metal thin-films that crack by the poorly adhered mechanism and the well adhered mechanism. This chapter will focus on the case of a poorly adhered metal thin-film on an elastomeric substrate.

In order to objectively examine the effect of solely the cracked structure on the optical properties of the metal thin-film, a key consideration must be made. For most poorly adhered metal thin-films, the smoothness and continuity of the metal thin-film will also be very poor. In order to decouple the effect of the film roughness and continuity from the optical properties induced by the cracking behaviour, we have chosen to use AlN as a seeding layer. AlN can be used to improve the smoothness of a metal thin-film deposited over top, however it is known to have poor adhesion to glass[45]. As the adhesion between a polymer substrate and a material is often determined by the formation of interfacial bonds[46], and that the PDMS surface has a silica like surface chemistry, we can deduce that AlN should also have poor adhesion to the PDMS substrate –which we later demonstrate by the observed cracking patterns in the AlN seeded films.

Commencing with a Ag metal thin-film deposited on PDMS (Fig. 12A) we obtain the reference pre-fractured unstrained thin-film microstructure (Fig. 12B) and its optical properties (Fig. 12C)
of specular and total transmittance and specular and total reflectance. Next, we strain the metal thin-film beyond its tensile strength and then remove the strain to obtain the reference post-fractured unstrained thin-film (Fig. 12D), its microstructure (Fig. 12E) and its optical properties (Fig. 12F). The underlying elastomeric substrate in the unstrained state draws the fractured metal thin-film segments together, resulting in a film which appears uniform, with the exception of the pattern of visible fracture lines between the microscale film segments, and optical properties which are essentially identical to those of the reference pre-fractured unstrained film. Thereafter, application of a 15% strain to the post-fractured film opens the crack pattern perpendicular to the direction of applied strain and develops a pattern of undulations in height in the film fragments which are parallel to the direction of strain (Fig. 12G, H). In the visible wavelength region, the undulations scatter and diffract transmitted and reflected light, illustrated schematically by the green arrows at oblique angles (Fig. 12G) and evident by the fact that the specular reflectance and transmittance are much lower than the total transmittance and reflectance (Fig. 12I), and thus lead to a change from the visibly transparent (unstrained state) (inset Fig. 12E) to visibly translucent (strained state) appearance (inset Fig. 12H). Further, it is believed that these undulations enable the metal thin-film to couple incident light to travelling surface plasmon polaritons (SPPs), illustrated as bright red arrows on the undulating surface (Fig. 12G), in the near infrared (NIR) region, resulting in an increase in absorption at specific frequencies. Additionally, medium infrared (MIR) SPPs are coupled by the micro scale cracks resulting in an increase in the MIR absorption and hence emissivity of the film. The resistivity of the film is additionally increased by the disruption of the electron conduction pathway caused by the cracks.
Figure 12: Optical phenomena in a strained metal thin-film on an underlying elastomeric substrate. (A) Reference pre-fractured unstrained Ag thin film (10 nm) on PDMS (1 mm) with schematic representation of incident (yellow arrow), specular transmitted (blue) and specular reflected (red) light. (B) Scanning electron microscopy (SEM) plan view of the microstructure of the Ag film in (A). (C) Specular and total transmittance, and specular and total reflectance of the film in (A). (D) Reference post-fractured unstrained thin film. (E) SEM plan view of film in (D) show fracture lines. (F) Optical properties of film in (D) essentially identical to those of (A). (G) Strained post-fractured thin film illustrating the presence of scattered transmitted and reflected light (green), and formation of NIR SPPs (bright red) along the undulations and MIR SPPs (dark red) along the microcracks of the film. (H) SEM plan view of film in (G) revealing undulating morphology and microcracks. (I) Optical properties of film in (G) reveal presence of diffuse transmission and reflection, and absorption at specific frequencies due to formation of SPPs. Insets in (E) and (H) show photos of the film in the unstrained (transparent) and strained (translucent) states.
We now present a detailed explanation of the theoretical origins of the various phenomena observed from the perspectives of mechanical structure, electrical properties and optical properties of the strained metallic thin films as a function of strain and metal film thickness. We then examine the application of a strained metallic film within the framework of a multilayer elastomeric-dielectric/metal/elastomeric-dielectric tunable transparent heat mirror, and conclude with a discussion of the potential of a manifold of structures, phenomena and applications possible.

### 4.1 Mechanical Structure

The origin of the various optical resonances in strained metallo-dielectric films is a function of the physical structure of the films under strain. The collection of SEM images in Fig. 13 show the changes in the physical structure of a series of thin silver films (10, 20, and 30 nm in thickness) deposited on a 3nm AlN seeding layer on a 1mm thick polydimethylsiloxane substrate that are subjected to mechanical strain ranging from 0 to 15%. Observation of the images reveals three principal features.
Figure 13: Surface structure of strained metal thin-films. SEM images show surface morphology of post-fractured metal thin-films of different thicknesses (10, 20 and 30nm Ag) under a range of strains (0, 5, 10 and 15%). Insets show higher magnification images focusing on the periodic undulations parallel to the direction of strain.
First, the unstrained silver films exhibit a fully closed structure despite having been previously strained beyond the tensile strength of the metal. While cracks from prior straining remain, relaxation of the PDMS after strain closes the cracks. The low amplitude random roughness patterns visible in the SEM images are attributed to the underlying PDMS substrate roughness. The continuous network of electrical conducting segments comprising the closed metal film would suggest optical properties similar to a closed thin metallic film deposited on a non-elastomeric film albeit with a slight increase in optical scattering and absorption caused by the increased roughness of the film at the crack edges.

Second, the silver film structure arising upon straining beyond the tensile strength of the film indicates the crack formation mechanism. Multiple linear cracks are formed in the film at different locations with a crack orientation which is perpendicular to the direction of the applied strain; further, these cracks propagate with increasing strain. When misaligned cracks meet, a torsional force in the film leads to crack formation parallel to the direction of strain. These parallel cracks allow the perpendicular cracks to slide past each other. These parallel cracks prevent further propagation of the perpendicular cracks and thus ensure that a continuous conduction path exists over the entire film. The exact conditions governing the distances between these cracks and whether the crack properties depend on the seeding layer, film quality, or a combination of both has yet to be determined, however a variety of crack dimensions including those shown in Fig. 13 as well as cracks on the order of 10s of μm (see Fig. 14) have been demonstrated. Despite these differences in the crack dimensions, the optical properties of the two films in the visible and NIR are very similar. They are expected to vary greatly in the MIR however.
Third, and most importantly, the film structure reveals the formation of undulations in height in the Ag film that are parallel to the direction of strain. Variations in the height of the film are observed as periodic bright and dark regions parallel to the direction of strain in addition to the cracks parallel to the strain direction. Further, it is seen that the period between adjacent undulations, which are semiperiodic, approximately increase with increasing film thickness.

The basis of these undulations in height lie in the mechanics of the underlying elastomeric substrate. An elastomer, and generally many materials, when strained in one direction experiences a simultaneous compression in the transverse directions perpendicular to the applied strain wherein the ratio of the negative of the differential transverse compressive strain $\partial \varepsilon_{\text{trans}}$ to the differential longitudinal tensile strain $\partial \varepsilon_{\text{axial}}$ is its material property given by Poisson’s ratio $\nu$[47]

$$
\nu = -\frac{\partial \varepsilon_{\text{trans}}}{\partial \varepsilon_{\text{axial}}} \quad (4-1)
$$
For PDMS, volume is approximately conserved upon straining and Poisson’s ratio is nearly 0.5[48], therefore the thickness and width of the PDMS substrate will shrink significantly as it is elongated. In tension, the Ag film tears easily and results in the observed cracks. Considering that the metal film is well adhered to the PDMS substrate, it must also compress in the direction perpendicular to the direction of strain. However, silver has a very high Young’s modulus (76 GPa)[49] relative to that of PDMS (2.61 MPa)[50] and as a result will not compress, but rather due to the flexibility of thin silver films and the pliability of the underlying PDMS substrate the Ag film will crumple in the direction of compression. For the three film thicknesses examined, it was observed that the average period of the undulations and its variance increased with film thickness, and that these parameters did not vary by a statistically significant amount with variation in the applied strain. For the 10nm, 20nm and 30nm films, the average periods were 2.2 (σ: 0.1 μm), 2.6 (σ: 0.2 μm) and 4.2 (σ: 0.3 μm), respectively. The height of these undulations is estimated by assuming a sinusoidal profile and using Poisson’s ratio to calculate the change in the width of the PDMS. For a 15% strain, the transverse strain on the PDMS is 6.75%, and the resulting amplitude of the sinusoidal undulations are 187 nm, 225 nm and 362 nm for the 10nm, 20nm and 30nm films, respectively, resulting in a peak-peak height of 374 nm, 450 nm, 724 nm, respectively. These results are summarized in Table 1.

Table 1: Summary of undulation dimensions for 10nm, 20nm, and 30nm thick Ag thin films seeded by AlN and deposited on PDMS

<table>
<thead>
<tr>
<th>Ag Film Thickness (nm)</th>
<th>Undulation Period</th>
<th>Undulation Peak-Peak Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.2 μm (σ: 0.1 μm)</td>
<td>374 nm</td>
</tr>
<tr>
<td>20</td>
<td>2.6 μm (σ: 0.2 μm)</td>
<td>450 nm</td>
</tr>
<tr>
<td>30</td>
<td>4.2 μm (σ: 0.3 μm)</td>
<td>724 nm</td>
</tr>
</tbody>
</table>
4.2 Electrical Properties

The electrical conductivity of metallic films is a major factor in determining their optical properties. The Drude model that describes the optical properties of ideal metals (that do not exhibit inter-band optical absorptions) provides two important characteristic material properties that govern the refractive index $n$ of the material (as a function of frequency $\omega$), which are the plasmon frequency $\omega_p$ and the damping frequency $\gamma$[51]:

$$n^2 = 1 - \frac{\omega_p^2}{\omega^2 - j\omega \gamma} \quad (4-2)$$

For wavelengths of light large in comparison to the size of the film features, the strained films can be treated as a single homogeneous effective film[51]. In this context, the plasmon frequency $\omega_p$ ($\omega_p^2 = e^2 N / (\varepsilon_0 n_e)$ where $e$ is the electronic charge and $\varepsilon_0$ is the permittivity) and the damping frequency $\gamma$ are both modified by the formation of the microscale cracking pattern[51]. The large change in the resistance and hence effective film resistivity (Fig. 15) suggest that a significant change in the effective plasmon frequency and damping factor for the film can be expected.
Figure 15: Electrical properties of strained films. (A) Measured resistance of the strained Ag films. (B) Inferred effective resistivity of the Ag films under strain. Red squares, blue diamonds, and green triangles correspond to 10, 20, and 30nm Ag films, respectively.

4.3 Optical Properties

The observed mechanical structure of the films is expected to create several unique optical phenomena across the electromagnetic spectrum. In the visible region, the large micron scale undulations will act as sources of scattering. In the infrared, the semi-periodicity of the undulations will diffract infrared light strongly and likely result in the creation of travelling SPPs on the surface of the metal films. In the mid-infrared (MIR) region, where the undulations are extremely sub-wavelength, the microscale cracking pattern will diffract light and can allow for the propagation and absorption of SPPs. Finally, in the communication bands (microwave and radiowave) we expect the increased effective resistivity of the film to reduce its reflectivity.

In the visible wavelength range, the two principle features of cracks with periods on the order of 5-20 μm and undulations with periods of 2-4 μm are too large for visible light to exhibit strong
surface plasmon resonances. However, the pseudo-periodicity of the undulations is expected to create a weak diffraction pattern that should be visible as angle dependent scattering of different wavelengths of the reflected and transmitted light from the film (insets in Fig. 12 E, H). Due to the decreased uniformity in the undulation period as the film thickness increases, the diffraction pattern is expected to be weaker for thicker metal films, resulting in a more whitish appearance due to random diffuse scattering of the visible light (Fig. 16).

![Image](image1.png)

Figure 16: Optical appearance of a 30nm Ag thin-film on PDMS (A) when unstrained showing a large amount of specular reflection, and (B) when strained where most of the reflected light is scattered, and no reflected images are visible. Comparison of the two films clearly shows an increase in diffuse scattering of transmitted light and reflected light after being strained.

The foregoing predictions are evident in the optical transmittance and reflectance measurements (Fig. 17) obtained for films of various thicknesses (10, 20 and 30 nm) under a range of applied strains (5, 10 and 15%). The specular and total transmittance curves for each film thickness indicate a drastic increase in the amount of scattered light by the film in the visible range with the applied strain. Specifically, a drop in the peak transmittance over the visible region is observed in the specular transmittance profiles for the three film thicknesses. The minimal change in the total transmittance over the visible suggests that the decrease in specular transmittance is a result of the light being scattered rather than being redistributed to absorbed or reflected modes. A slight
decrease in transmission for the 10nm sample is observed and is attributed to a failure to collect all angles of scattered light. This is discussed further in the supplementary information.
Figure 17: Optical transmittance and reflectance of 10nm, 20nm and 30 nm Ag films under strain. (A), (B) and (C) show specular transmittance, specular reflectance and total transmittance of 10nm Ag films under strain, respectively. The black, red, green and blue curves correspond to 0, 5%, 10% and 15% strain, respectively. Similarly, (D), (E) and (F) show the spectra for 20nm Ag films under strain, and (G), (H) and (I) show the spectra for 30nm Ag films under strain.
In the near-infrared range, the pseudo-periodic undulations of the metal film display a period which permits coupling of incident radiation to travelling surface plasmon polaritons. As SPPs travel along the surface of the metal they would be absorbed by the metal and correspondingly result in a drop in the total reflectivity of the film about a certain wavelength[1]. We model a corrugated 10 nm Ag film on PDMS with a sinusoidal profile of peak-to-peak height of 374 nm and periodicity of 2.2 μm (Fig. 18) in order to predict the properties of the 15% strained 10 nm sample. The specular and total reflectance and transmittance profiles are shown in Fig. 19A below. The results of the simulation reveal two strong dips in the reflectivity of the film at 1100 nm and 2200 nm as a result of the coupling of incident radiation to SPPs. If this SPP phenomenon is also observed in the experimental measurements, due to the variability in the period of the undulations of the fabricated film, it is expected that SPPs will be excited over a broad range of wavelengths about a certain median. Evidently this is observed in the two significant drops in the total reflectance spectrum at ~1100 nm and ~2000 nm (Fig. 12) for 10 nm Ag film under 15% strain. The specular reflectance also shows evidence of SPP coupling at ~1100 nm wavelength. The correspondence between the dip in the simulated total reflectance, which are a result of incident light coupling to SPP modes, and the dips in the experimental measurements suggest that the broad infrared dips observed in the experimental measurements are a result of the incident light coupling to SPP modes along the undulations of the strained metal thin-films. A slight increase in the transmittance around these SPP wavelengths is also expected due to SPP tunneling[1] as seen in the simulated total transmittance (Fig. 19A), however there is no strong experimental evidence of this in the films examined. A slight increase in the transmission of infrared light is also expected based on the simulations and observed in experiment.
To further illustrate the qualitative agreement between the agreement between experimental and simulated optical spectra of the strain 10nm thin-film, we have shown these spectra overlaid with their partners in Fig. 20.

![Figure 18: Structure of the undulated 10nm Ag thin-film simulated in COMSOL](image)

Exchanging changes in the specular transmittance, total transmittance and specular reflection spectra with increasing film thickness (Fig. 17), the variations in absorption intensity with wavelength and spectral broadening can also be explained. SPPs are known to be coupled from incident light slightly after a diffracted order would be diffracted at 90°, known as the passing
off[52]. For the 10nm film, where the undulation period is 2.2 μm, the 1\textsuperscript{st} order would have a passing off at 2200 nm, and as such the absorption peak observed at 2000nm can be attributed to the 1\textsuperscript{st} diffraction coupling into SPPs. Similarly, the 2\textsuperscript{nd} order would have a passing off at 1100 nm. Considering that the 2\textsuperscript{nd} order carries less power, the coupling of this mode to an SPP results in less absorption. At approximately 860nm, one third of the undulation period 2.6 μm, the 20nm sample’s 3\textsuperscript{rd} order diffraction couples into SPPs and thus we see a dip in the specular reflectance around this point, (Fig. 17E), which is noticeably weaker than both the 1100nm and 2000nm dips of the 10nm film. For the 30nm film, where the undulation period is 4.17 μm, the SPPs being coupled around 1000nm are due to a 4\textsuperscript{th} order diffraction. The spectral broadening in the 30nm film’s dip is also greatest due to the increase in the variance of the undulation period, resulting in a greater range of wavelengths about the 1000nm average that can be coupled.
Figure 20: Comparison of experimental and simulated optical spectra for a 10nm Ag thin-film seeded by AlN and deposited on PDMS. Good qualitative agreement between the experimental and simulated results as to the wavelengths at which various changes occur in the spectra can be observed.

In the MIR, the undulations which are on the scale of several micrometers are too small for the incident radiation to interact and thus cannot scatter light in the MIR. The distance between the cracks in the metal films however are on the order of 5-20 μm, and thus the MIR radiation interacts strongly with these features. The measured emissivity of a 10nm Ag thin-film on PDMS under 0% strain and 15% strain are 5.9% and 28.7%, respectively. Two factors are believed to be
responsible for this large change in emissivity. First, although the undulations are sub-wavelength features, the undulated film forms an effective medium with a higher resistivity than the initial unstrained 10nm film, and accordingly the reflectivity is expected to decrease slightly. Another potential source of the decreased reflectance, and hence increased absorption of the film, is the ability of the crack features to couple SPPs on the order of the distance between the cracks. These SPPs could be absorbed by the film similar to the NIR SPPs and hence increase the absorption of the film in the MIR.

With increasing wavelength, the small width of the cracks and the interconnectivity of the metal film as a whole represents a material that behaves as an effectively continuous medium described by the Drude model[51]. Considering that the distance between adjacent cracks is at most several hundred µm, at wavelengths above 1mm the material is expected to behave as a single homogeneous medium to incident radiation – corresponding to the microwave and radiowave bands of radiation. Modelling the GHz behavior of the film however requires an in depth knowledge of the change in the effective electron concentration, electron effective mass and electron mean free path[51] and as such is left for a future study. The large variation in the effective resistivity of the films (Fig. 15B) however suggest that large changes in the dielectric properties of the film in the GHz range should be expected.

4.4 Multilayer Coatings

The foregoing experiments with single Ag thin-films on PDMS illustrate the tunability of the visible, NIR, MIR and long wavelength properties of strained metal thin-films. We will now address how the local environment affects the resonances observed in the strained metal thin-films. We integrated the strained metal thin-film into a multilayer device with a PDMS/Ag/PDMS
structure. The measured specular transmittance, specular reflectance, total transmittance, and total reflectance of the device for 0% and 15% strain (Fig. 21) exhibit an increase in the amount of scattered light, an increase in the infrared transmittance and absorbance, and a decrease in the infrared light reflection with the applied strain. Additionally, the emissivity changes from 0.14 to 0.30 upon changing the strain from 0% to 15%, respectively. The effect of the dielectric layer on top of the metal thin-film is also observed in the total reflectance profile where the wavelengths of the SPP absorptions shift to longer wavelengths.

Figure 21: Optical spectra of a multilayer thin-film structure with a 1mm PDMS substrate, a 3nm AlN seeding layer, a 10nm Ag thin-film and a PDMS capping layer of an unknown exact thickness. Unstrained samples are shown in blue, and 15% strained samples are shown in black. (A) specular transmittance, (B) total transmittance, (C) specular reflectance, (D) total reflectance.
This device demonstrates the ability to tailor the exact plasmonic properties of the device through proper choice of the dielectric index of the layer on top of the strained metal thin-film. It also demonstrated that even with the introduction of a second elastomeric layer on top of the metal thin-film, the metal thin-film still has the same cracking behaviour.

4.5 Conclusion

In this chapter, we have investigated several aspects of AlN seeded Ag thin-films, and we summarize the emerging conclusions here. Primarily, we have demonstrated that AlN seeded Ag thin-films on PDMS represent an example of a poorly seeded metal thin-film that has a microscale cracking pattern similar to that observed in the literature. We have also demonstrated that like other poorly adhered metal thin-films, these films are poor examples of strain resistant electrical conductors and lose electrical conductivity very rapidly with strain.

With respect to the optical properties of AlN seeded Ag thin-films on PDMS substrates, we have shown several novel and previously unreported properties of the strained films. The first and most significant observation is that under strain, a normally reflective metal thin-film will have a periodic undulation pattern induced on the surface of the film, with a period dependent on the thickness of the metal thin-film. The undulation appear to result in the coupling of incident light into SPPs on the surface of the metal at a specific wavelength of light and results in an absorbance enhancement at the wavelength of light. The strength of the absorbance enhancement is dependent on the magnitude of the strain as additional strain increases the amplitude of the undulations in the film. Additionally, the wavelength at which SPPs are coupled can be shifted by altering the refractive index at the surface of the metal.
Another observation made was that there is a significant change in the MIR reflectance of the metal thin-films as a result of the microscale cracks formed in the metal thin-films. These MIR reflectance changes are broadband however and are not in a specific range of wavelengths as seen for the NIR reflectance decreases. This is likely due to the broad range of inter-crack dimensions observed in the metal thin-film samples. Patterned substrates should be examined to see if specific resonances can be created in the MIR.
Chapter V: Nanoscale Fracturing of Strained Silver Thin-Films

When metal thin-films are poorly adhered to an elastomeric substrate and strained, as shown in the previous chapter microscale cracks are observed. These microscale cracks result in microscale changes in the morphology of the film and produce a wide range of optical effects in the visible and infrared. Due to the size of the features however, incident light interacts with the individual features rather than interacting with the film as a whole, resulting in a large amount of scattering effects. Though these effects have a large range of applications in strain sensitive sensors and tunable resonators, for use as tunable metallic layers in applications such as metamaterials, they are less useful.

Fortunately, it has been demonstrated that the cracking patterns formed by strained metal thin-films strongly depend on the adhesion between the substrate and the metal thin-film[23]. When a seeding layer that strongly adheres to the substrate and the metal layer is placed between the substrate and the metal thin-film, the stress within the film is delocalized and many small and non-linear cracks form within the film[23]. For chromium seeded gold thin-films the size of the cracks have been shown to be below 400nm[21]. Given that the feature size is less than the wavelength of light, strained metal thin-films with cracks of these dimensions should not strongly scatter light, and it is expected to behave as an effective medium.

5.1 Mechanical Properties

In order to examine the optical properties of metal thin-films with nanoscale cracking patterns, we have utilized Ag as our metal thin-film material and used a Cr seeding layer to improve the adhesion to a PDMS substrate. The choice of Ag was made so that comparisons between the
properties of nanoscale cracked and microscale cracked films analyzed in the previous chapter could be made.

We began by fabricating a set of Ag thin-films. They were deposited on a 1mm thick PDMS substrate with a 5nm Cr seeding layer and a 25nm Ag layer both deposited using e-beam evaporation. The mechanical structure and cracking behaviour of the samples were then examined in an environmental SEM to allow the surface structure to be examined while the samples were in a strained state. The morphology of the Ag thin-films with strain varying from 0-15% in 5% intervals are shown in Fig. 22 below.

Figure 22: SEM image of a 25nm thick Ag thin-film with a 5nm Cr seeding layer deposited on PDMS. Inset show a higher magnification of the same strained film.
With the e-beam deposited Ag thin-film, we note that there is a large amount of surface roughness even in the unstrained state, and the outline of the cracks are already visible. This is likely due to the fact that silver deposits in a Volmer-Weber growth mode[42] when deposited on chrome, forming large islands as opposed to a single smooth film. In the initial unstrained state, the crack lines are still visible, however they are very small and oriented randomly overall. When strain is applied, cracks approximately perpendicular to the direction of strain open up. Individual crack branches link together to form extended zig-zag shaped cracks. As strain is increased, though the length of the crack branches and the number of branches in a zig-zag do not increase, the width of the cracks increases. The crack lines parallel to the strain direction appear to be compressed and closed when in a strained state. This is likely caused by the transverse compression discussed in the previous chapter. This initial width of the cracks appears to provide the metal thin-film with enough room to accommodate the transverse compression and therefore unlike the microcracked films, no undulations form initially.

As the strain is increased above 15% however, we notice the appearance of large micron sized undulations perpendicular to the strain direction at the edges of the film where strain is highest as shown in Fig. 23. These undulations cause visible light scattering similar to the undulations observed in the microscale cracked films. In this case the average period of the undulations was found to be ~10 μm.
Based on the SEM images of the unstrained films and the assumption that the cracks do not change in length during straining, we can extract several aspects of the films in their unstrained conditions. The average length of the branches of the tri-branch cracks were found to be 108nm, the average width 13nm, and the average distance between adjacent cracks was 130nm.

5.2 Electrical Properties

Given that the material is assumed to be behaving as an effective medium, the resistivity is an important property in determining the optical properties of the material. As in Chapter 4, we have measured the resistance of the Ag thin-films under strain and utilized the resistivity measured for
the unstrained film to approximate the resistivity of the strained film. Both are shown below in Fig. 24.

![Figure 24: Resistance (left) and approximate resistivity (right) of the film under varying amounts of strain. Clearly illustrating the maintaining of conductivity even as large amounts of strain (up to ~20%) are applied.](image)

We evidently observe that the resistance and resistivity steadily increase as strain is applied until approximately 12% strain where the resistance decreases shortly before increasing again. This was originally thought to be a fluke, however when the resistance was re-measured the same trend of the resistance decreasing beyond ~12% before increasing again was observed. This may be a result of a change in the morphology of the cracks at around 12%.

### 5.3 Optical Properties

Following the mechanical and electrical measurements of the samples and the confirmation that we obtained highly strainable nano-cracked metal thin-films, we analyzed the optical properties of the films. Similar to the analysis in Chapter 4, we measured 4 different optical properties, the
specular transmittance and reflectance and the total transmittance and reflectance for four different amounts of strain, 0%, 5%, 10% and 15% from 350 nm to 2000 nm as shown in Fig. 25. We additionally calculated the absorption of the sample and show this in Fig. 26.

Figure 25: Optical transmittance and reflectance of 25 nm Ag films under strain. (A), (B), (C), and (D) show UV-Vis specular reflectance, total reflectance, specular transmittance, and total transmittance under strain, respectively. The black, red, green and blue curves correspond to 0, 5%, 10% and 15% strain, respectively.
Even in the initial unstrained film, we note a strong deviation from the behaviour of a continuous smooth metal film. As in the case of a smooth film, the reflectance begins at a low value of \(~30\%\) for 400 nm and gradually increases as the wavelength increases; unlike an ordinary 25nm Ag film however, the reflectance does not increase as rapidly and reaches a peak value of 62\% at \(~720\) nm and then proceeds to decrease instead of increasing. A small amount of scattering of the reflected light is also observed and this scattering is highest near the 720 nm peak. This peak is clearly evidence of a LSP resonant behaviour in the metal film, however it is unclear without further investigation whether the cause of this resonances is the resonances of individual segments of the metal film, or the cracks between the films.

![Absorbance graph](image)

*Figure 26: Absorbance of the 25nm Ag thin film, the optical properties of which are shown in Figure 24.*

When looking at the transmittance, we observe similar abnormal behaviour. The transmittance decreases until a minimum of 5\% at \(~720\) nm and then increases again. Unlike the reflectance, the scattering observed for 0\% strain is extremely minimal.
As strain is applied, examining both the specular and total reflectance spectra, the reflectance drops by nearly the same amount as the strain applied across the entire visible-NIR spectrum. The transmittance similarly increases across the spectrum as well. In the case of the reflectance, we also note that the peak reflectance decreases by a greater amount than the decrease at longer wavelengths. This decreases the prominence of the resonance at 720 nm, however it is important to note that the peak position does not change.

From observing these plots, it is clear that the transmission enhancement feature continues on until longer wavelengths, and therefore it was essential to do MIR reflectance measurements in order to fully understand this phenomenon. For this reason, we once again did MIR measurements using a reflectance FTIR and determined both the reflectance across the MIR spectrum as well as the emittance of the sample.

![Image of MIR Reflectance of a 25nm thick Cr Seeded Ag thin-film on PDMS. Illustrating how in the long wavelength limit, the nanocracked Ag thin-film has metallic reflection and behaves as a homogenous conductive film.](image)

Figure 27: MIR Reflectance of a 25nm thick Cr Seeded Ag thin-film on PDMS. Illustrating how in the long wavelength limit, the nanocracked Ag thin-film has metallic reflection and behaves as a homogenous conductive film.
In the MIR range from 2μm to 25μm, we clearly see (Fig. 27) the reflectance increasing from a minimum of ~50% to a maximum of almost ~90%. The long wavelength reflection is characteristic of a continuous electrical medium, and this both confirms the electrical connectivity that we showed with the resistance measurements, as well as demonstrates that the size of the nanoscale crack features is insignificant in the MIR range, and the film simply behaves as if it were a single homogeneous medium with the electrical properties of the cracked film. From these reflectance measurements, it was possible to determine the emissivity of the unstrained film. We found this to be 13.2%, which is significantly higher than the theoretical emissivity of bulk silver of 3%, however the deviation can be explained by the reduced conductivity increasing the resistive losses in the material and therefore increasing the absorbance and emissivity of the film.

MIR reflectance measurements were also taken under strain, however the accuracy of these measurements is uncertain due to the complexity of taking measurements under strain. See Appendix C for a detailed explanation of the difficulties, and see Appendix E for reflectance measurements of strained samples. At 15% strain the emissivity was measured to be 38.6%.

5.4 Electromagnetic Simulations

In order to obtain a better understanding of the physical origins of the resonances observed, we modelled the electromagnetic behaviour of the film. In the literature pertaining to nanoscale crack formation, mechanical simulations aimed at explaining how strain is delocalized and distributed throughout the cracked film, the crack geometry is described as a hexagonal array of tri-branched cracks[21], as demonstrated by the unit cell in Fig. 28 below. In creating an electromagnetic model
to approximate the optical properties of the film, we use the same structure, albeit with the crack dimensions extracted from the unstrained film structure as detailed in section 5.1.

![Figure 28: Unit Cell Proposed in Lacour et. al.[28]](image)

The use of the hexagonal tri-branched crack structure as opposed to the actual zig-zag shaped crack structure is a simplification and therefore we are not simulating an identical structure to that which produced the measured optical spectra, however we postulate that the source of the optical resonances observed in the spectra are a result of the dimensions of the individual crack segments. This will be demonstrated subsequently by showing that only the dimensions of the individual crack segments significantly alter the reflectance and transmittance spectra of the metal thin-film and therefore any model that can accurately describe these should produce the same optical properties that we observed in the real metal thin-films.
Using COMSOL Multiphysics, a wave-optics electromagnetic frequency domain simulation was performed. In the simulation, the refractive index of PDMS substrate, included in Appendix E, was assigned to the substrate, and the refractive index of air was assigned to the medium above the metal thin-film. A lower 5nm thick Cr layer and upper 25 nm Ag layer with the geometry of the unit cell shown in Fig. 28 were used to describe the metal thin-film structure. The six sides of the hexagonal unit-cell were made periodic boundaries in order to simulate a continuous period structure, and a periodic inlet port above the metal thin-film and periodic outlet port below the film were also assigned. After running the simulation, the relative reflected intensity (R) and relative transmitted intensity (T) through the film were extracted from the simulation, as shown in Fig. 29.
In the results of these simulations, we notice three key features. The first is the presence of a reflectance peak at ~420 nm, the second is another reflectance peak at ~700 nm, and the last is a transmittance peak in the IR. In order to understand the source of the resonance, we modified three aspects of the structure in order to attempt to elicit the source of the resonance. The first was the length of the individual branches in the zig-zag cracks. When we did this, we saw that as the crack length increased, the peak at 700 nm position shifted to longer wavelengths. Following this, we altered the width of the crack. Decreasing the width of the crack results in a shift in the peak at 420 nm to shorter wavelengths, and a minor change in the peak at 700 nm to longer wavelengths.
The final feature we modified was the distance between adjacent cracks (i.e., the periodicity of the unit cell). We found that as the inter-crack distance was increased, only the transmittance peak was affected.

The above observations suggest three different explanations for the three features. The first peak at 420nm can be explained by a resonance in the short side of the rectangular cracks. This explains why the feature was seen in simulations and not in our experimental measurements, as in reality the cracks would not terminate in an abrupt straight end, but would instead have a tapered shape. The source of the second reflectance peak at 700nm is the resonances of cracks in the long direction. When the length of the crack is increased, the resonance increases to longer wavelengths as expected. The reason that the resonance also experiences a shift to longer wavelengths when the width of the crack is decreased, is that the distance between the two surfaces of the crack is decreased, and the two LSPR modes begin to couple, causing a decrease in their energy and a red-shift in their resonant wavelength, as would be expected for coupling of two LSP modes. This is similar to a phenomenon where the wavelength of trapping in a sub-wavelength metal groove is shifted through coupling between LSP modes of the sidewalls in the groove[53]. The wavelength observed for this peak corresponds strongly with the 720nm peak observed in our actual measurements, and therefore we can be fairly confident that the physical origin of the peak in simulation and in actual films are the same. A comparison of the peak positions of the experimental and theoretical spectra is shown in Fig. 30 below. We see in this figure that although the peak amplitudes and broadness vary, the peak positions correspond very strongly to each other.
The third feature, transmittance peak, is another example of an artefact of the simulation resulting from oversimplification. In this simulation, we have treated the pseudo-random structure of the actual metal thin-film cracks as a periodic structure. This oversimplification results in a common phenomenon observed in periodic hole arrays known as extraordinary optical transmission (EOT). This phenomenon is a result of constructive interference between surface modes enhancing the coupling of light to modes through the film, and therefore as the true films do not have periodic spacings between the holes, we do not see the phenomenon of EOT[1].

When we extend the simulation to longer wavelengths, where the phenomenon of EOT will not be observed in the simulation, we see a slight increase in the transmission and decrease in the reflection as was observed in the experimental measurements. This is a broadband phenomenon and is caused by any increase in the relative size of the crack to the size of the unit cell. This can be explained based on the concept of an effective medium. As the crack features are much smaller, both in length, width and periodicity than the wavelength of light, the film behaves as a single
effective conductive medium with a higher resistivity than the perfectly smooth metal film. This enhanced resistivity makes the material a poorer reflector, thus decreasing the reflectance and increasing the transmittance across the entire spectrum. This can be predicted by taking the long-wavelength approximation of the Drude model, $\varepsilon_r = 1 - \frac{j\sigma}{\varepsilon_0 \omega}$, and simply observing that a decrease in the overall conductivity of the film will result in a decrease in the imaginary component of the permittivity and thus a decrease in the reflectance of the air-metal interface.

From these first simulations of the unstrained film, we found that we were capable of accurately predicting the LSPR reflectance peak wavelength of the film, however the simulation falls apart at shorter and longer wavelengths. For this reason, in the strained simulation, we could only draw qualitative conclusions in the visible region of the electromagnetic spectrum.

A major curiosity in the optical spectra of the real strained metal thin-films was why the position of the reflectance peak did not shift as strain was applied. Based on the observation from our simulations of the unstrained films where the crack length is the major factor in determining the peak position and that the crack width and not the crack length changes during straining, the lack of a change could be partially understood, as changing the crack width only minimally changed the resonance at 700nm. In order to confirm that the magnitude of the change in the crack width with strain would not cause a significant change in the reflectance of the metal thin-film, we simulated the strained metal thin-film as well.

In simulating the strained metal thin-film we began with the unit cell of the unstrained metal thin-film. We then expanded the size of the film by creating an array of cracks. Using the solid
mechanics module of COMSOL Multiphysics, we applied a tensile strain of 10% to the sides of the film and produced the post-strain structure as shown in Fig. 31.

![Structure of the Strained Nanoscale Cracked Metal Thin-film.](image)

Figure 31: Structure of the Strained Nanoscale Cracked Metal Thin-film.

The new dimensions of unit cell in the centre of the film were then extracted and imported into a Wave Optics simulation. From this Wave Optics simulation, the reflected and transmitted intensities, shown in Fig. 32, were extracted.
Figure 32: Simulated change in VIS-NIR transmittance and reflectance of Ag-Cr thin-film under 10% strain (unstrained structure shown in Fig. 28, strained structure shown in Fig. 31.

From Fig. 32 we can see that the transmittance and reflectance spectra are extremely similar to the unstrained simulation, except that the reflectance peak intensity has been reduced. These changes are in agreement with the optical measurements shown in section 5.3. A very slight change in the peak positions are noted due to a change in the coupling between crack sidewalls, however in the real films, there are a distribution of crack lengths and widths, thus broadening the resonant peaks. This broadening makes it difficult to distinguish extremely small shifts in the peak position such as that expected from the change in coupling intensity.
5.5 Effect of Film Thickness

Following our work on understanding the optical properties of the chromium seeded silver thin-films, we sought to develop a better understanding of how we could manipulate these properties to achieve more tailored responses. For this our final study was into the effect of film thickness on the structural properties of the thin-films as well as their resulting optical properties.

Once again, we began by examining them under the SEM. Two unstrained films, the first with a 20nm thickness, and the second with a 30nm thickness are shown in Fig. 33.

![SEM image of the surface of a 20nm (right) and 30nm (right) thick Ag thin-film seeded by Cr and deposited on PDMS.](image)

From these two figures we can instantly see a trend. In the case of the 20nm film, we have a far greater number of nanoscale cracks, and their lengths are much smaller, with their average length being 122nm. In the case of the 30nm film, the distance between the cracks has increased, and the average length is now 184nm. We further fabricated a 10nm sample, however it was found that the metallic layer was discontinuous in this film, and so the film was non-conductive and an SEM image could not be retrieved. Based on this structure, we would expect that if reflectance peak in the prior film measurements are truly a result of LSPR modes of the cracks, then an increase in
the resonance wavelength should be seen with increasing film thickness. To verify this, we performed specular reflectance and transmittance measurements, Fig. 34, of three the samples.

![Figure 34: (A) reflectance, and (B) transmittance, of Ag thin-films of varying thickness seeded with Cr and deposited on PDMS.](image)

The reflectance peak evidently shifts from a longer wavelength for the 30nm film to the shortest wavelength for the 10nm film. This is in agreement with the decreasing length of the cracks as well. We further note that in the case of the 10nm film, the reflectance drops in the NIR and transmittance increases. This is as a result of the film becoming discontinuous and thus electrons no longer being able to oscillate with incoming electromagnetic radiation. We confirmed this by measuring the resistance of the film and finding that it was beyond 10MΩ.

When we applied strain to the 30nm film, we also observed a very interesting phenomenon. Unlike the 25nm films shown previously, when the 30nm films were strained, much larger cracks formed and linked together, shown in Fig. 35. Further, the room that the cracks parallel to the strain had provided for transverse compression were no longer enough, and so undulations similar to those in the microscale cracked films were observed.
Figure 35: SEM of the surface of 30nm Ag thin-film seeded by Cr under 15% tensile strain. A transition between micro-cracking and nano-cracking behaviour is observed, including the formation of undulations aligned parallel to the applied strain.

Though these results seem relatively straightforward, they suggest a completely different explanation for the mechanism of crack formation from that agreed upon in the literature. As discussed in Chapter 3, the literature is in consensus that nanoscale cracks form in the films when there is strong adhesion between the substrate and the metal thin-film, thus resulting in the film forming many smaller tears as opposed to fewer large linear tears. What these results show however is that when we deposit a very thin-film, we obtain isolated islands, illustrated by the lack of connectivity in the 10nm film. As we increase the film thickness, the film becomes fully connected, but with many small cracks, and as the film becomes thicker further, the smaller of these cracks are filled in. This kind of behaviour is reminiscent of the Volmer-Weber growth of the silver films, and suggests that rather than the cracks being actual cracks in the films, they are simply voids where silver clusters have yet to be deposited, and the formation of nanocracks is simply a result of the film being extremely rough and discontinuous. If this explanation is correct, then the 30nm film represents the transitional period between the microscale and nanoscale cracking behaviour. In order to confirm or disprove whether or not this is the true cause of the nanocracking behaviour however, further studies will be required.
5.6 Conclusion

In this chapter, we have demonstrated the optical properties of well-adhered metal thin-films. We have shown how the films exhibit nanoscale cracking patterns, and that these nanoscale cracking patterns result the plasmonic phenomenon of LSPR within a specific wavelength range dependent on the dimensions of the cracks. When strain is applied, the resonant phenomenon is preserved albeit with a decrease in the intensity of LSPR induced reflection enhancement. In addition, the IR transmittance of the film increased and reflectance decreased with increasing strain, explicable by the effective resistance of the film as a whole increasing. We also demonstrated that it is adequate to model the optical properties of these nanoscale cracked strained metal thin-films as an array of tri-branch cracks. Lastly we demonstrated how the average length of the cracks increases with film thickness, and the density of the cracks decreases with increasing film thickness. It was further hypothesized that growth mechanics of the thin-films as opposed to the adhesion strength of the film to the substrate is the determining factor in whether micro or nanocracks will form in the strained film. Further investigations into the properties of these films should attempt to verify or disprove this hypothesis and improve our understanding of the transition between nanoscale cracks and microscale cracks.
Chapter VI: Applications

We have dedicated a large amount of discussion to the properties of strained metal thin-films, however at the heart of any engineering research project are the potential applications. We will discuss briefly several potential applications for strained metal thin-films in optical devices. An introduction to each type of device as well as an explanation of how tunable metal thin-film layers could potentially be implemented will be given.

6.1 Tunable SPP Sensors

One very common plasmonic device is the SPP sensor. The sensor is a refractometric sensor whereby the change in the local refractive index at the surface of the metal can be detected. A SPP in a metal film is excited using one of the coupling mechanisms discussed in Chapter 2. In the prism coupling mechanism, Fig. 36, the incident light is shone at the specific angle necessary to excite a SPP in the metal film. Due to the sensitivity of the surface plasmon wavevector to the local refractive index of the dielectric at the metal interface, very small changes in the refractive index of the local dielectric result in large changes in the coupling efficiency to the SPP. This reduction in the coupling efficiency is ultimately detected as an increase in the reflected light intensity from the prism.
Figure 36: Schematic of a simplified SPP prism coupled sensor. The shift in refractive index caused by the binding of the green molecules changes the SPP wavelength and results in the light being reflected at the prism interface instead of coupled to the SPP.

Often the surface of a metal film is functionalized with biological aptamers that can trap specific biological molecules. This allows the biological molecules to be detected, as the binding of the molecules to the aptamers results in a change in the local refractive index at the surface of the metal.

A major limitation of the refractometric SPP sensor is that the wavelengths of light that can be probed are limited. As the wavelength of light is increased, the confinement of the SPPs to the surface of the metal-dielectric interface is decreased, and the surface sensitivity is decreased. We have demonstrated that the nanoscale cracked strained metal thin-films behave in the far NIR and MIR as an effective material with a higher resistivity. The change in resistivity suggests that the effective plasma frequency will also shift to a lower frequency, this will allow the film to have a larger SPP wavevector at long wavelengths when compared to the unstrained film. Thus, the same metal thin-film can be used for effectively probing SPPs at a short and long wavelength, simply with strain being applied when measuring the longer wavelength.
6.2 Flexible and Strainable Plasmonic Devices

An additional benefit of our demonstration of strained metal thin-films is that they illustrate how it is possible to implement metal thin-film layers in flexible and strainable devices without risking the failure of the device. In the case of the nanoscale cracked films in the NIR and MIR we have shown that the film still exhibits metal-like properties despite the presence of sub-wavelength cracks in the film. This suggests that even when strain up to 15% is applied to a well adhered metal thin-film on an elastomeric substrate, whether the strain be caused by intentional straining or tension from flexing of the substrate, the layer will continue to be plasmonically active in the NIR and MIR.

This concept can be further extended to allow the use of strain to tune the properties of plasmonic gratings. With the demonstration that metal thin-films can be strained up to 15% and maintain their metallic optical properties in the NIR and MIR, we can now use metal thin-films on grated elastomeric substrates to provide a mechanically tunable plasmonic grating (Fig. 37). This idea may be especially useful in the field of plasmonic lenses[54], where the focal point of the lens could be altered by applying strain and altering the far-field diffraction pattern of the lens.

![Figure 37: Illustration of how a strain based tunable SPP grating can operate. Initially the period is short and green light can be coupled to SPPs on the grating surface. As strain is applied, the period of the grating increases and the grating can now couple red, instead of green, normally incident light.](image-url)
6.3 Tunable Metallo-Dielectrics

Metallo-dielectrics are a class of material that is comprised of multilayers of metal and dielectric thin-films. They are employed in a variety of devices, including solar control coatings that reflect NIR and MIR radiation while being transparent to visible light in order to provide heat reflecting properties to windows, as well as metamaterial devices that utilize the plasmonic properties of metal thin-films to create optical devices with exotic properties. Due to the utilization of metal thin-films in these devices, the development of strainable metal thin-films are highly relevant to this class of devices.

6.3.1 Metamaterials

Metamaterials are materials that exhibit optical properties not observed in nature. A large portion of such materials are so called left-handed materials that have both a negative permittivity ($\varepsilon_r$) and a negative permeability ($\mu_r$), and therefore a negative refractive index ($n$)[55]. Recent work has shown that it is possible to create a left-handed material using a multilayer of metal thin-films and dielectric materials[16]. One of the most important properties of these devices in determining the wavelength of operation is the thickness of the dielectric layers. Using elastomeric dielectrics, it is possible to tune this thickness by applying strain, similar to how elastomeric photonic crystals have been tuned in the past[56]. An issue with applying this same principle to tuning the thickness of the dielectric layers in a metallo-dielectric device however is the inability of the metal layer to undergo large amounts of strain. We have shown however that using a nanoscale cracked film it is possible to maintain the metallic properties of the film up to 15% strain and thus a tunable metallo-dielectric superlens could potentially be developed.
6.3.2 Solar Control Coatings

Another application of metallo-dielectric multilayers is as transparent heat-mirrors. In these devices, a high NIR reflectance is desired while maintaining a high visible transparency[57]. They are applied to windows, and in hot-climates, where they function by rejecting the infrared portion of the solar spectrum, that otherwise would contribute to heating the interior of a building, while allowing the desired visible light through the window. This can drastically improve the energy efficiency of the building.

In cold climates however, the energy savings achieved by rejecting the infrared energy in the summer can be small compared to the energy loss in the winter through not accepting the infrared radiation. For this reason, cold-climate windows are currently designed to have maximal transmissivity in the NIR. Over the last decade research progress in smart windows have led to dynamic control over the transmission of solar irradiation, opening the potential of realizing additional energy savings through reduction of heating loads, cooling loads and electric daylighting demands. Some of these smart switchable coatings include chromogenic (electrochromic, gasochromic, photochromic, thermochromic)[58], liquid crystal, electrophoretic (suspended-particle), micro-blind and nanocystal devices[59]. While some of the smart coatings, namely electrochromic and electrophoretic devices, have been commercialized their adoption in the built environment has been limited owing to the material complexity and cost of the devices, electrical power requirements and associated installation costs, limited degree of transparency and switching speeds, and durability concerns.

Strained metal-thin films provide a simple low-cost mechanically tunable method of modulating the heat-reflective properties of the metallo-dielectric heat-mirrors. In a simple implementation, a
nаноскопические трещиноватые металлические пленки могут быть использованы в ненатянутом состоянии во время летних месяцев, и чтобы уменьшить отражение в инфракрасном диапазоне в зимние месяцы, требуется небольшое натяжение. Дополнительные сложные покрытия также могут быть разработаны при использовании многослойной архитектуры, где фотонные резонансы также используются для улучшения видимой прозрачности и приспособляемости.

6.4 Сенсоры активированные напряжением

Фокус вышеописанной дискуссии был на наноскопических трещиноватых металлических пленках, однако микротрешиноватые пленки также имеют потенциальные применения. Основное преимущество микроскопических трещиноватых металлических пленок заключается в том, что в их первоначальном ненатянутом состоянии они имеют оптическое поведение очень схожее с идеальной металлической пленкой, однако при натяжении они начинают показывать признаки возбуждения поверхностных волн. Восстановление SPP приводит к уменьшению отраженной мощности при определенной длине волны света, зависящей от периода гравитации. Основные аспекты возбуждения SPP в микроскопических трещиноватых пленках — это зависимость снижения интенсивности от высоты волн, которую можно контролировать при помощи натяжения пленки. Это можно использовать для создания высоко чувствительного оптического датчика напряжения. В дополнение, пик позиции может контролироваться как периодом волны, который можно настроить на основе толщины пленки, так и местным показателем преломления диэлектрика над металлической пленкой. Используя этот свойство, изменение местного показателя преломления можно измерить, основываясь на сдвиге частоты SPP. Если апаптеры или другие объекты для захвата биомолекул используются, то можно создать простой, самоассимилирующийся биомолекулярный датчик.
Chapter VII: Conclusion and Future Work

The objective of this research project was to study the optical properties of strained metal thin-films on elastomeric substrates. A historical survey of the field of strained metal thin-films on elastomeric substrates shows that there is a large amount of prior work relevant to their use in electronic devices, however there is a need for studies into their optical properties. As part of this research we also present how the unique mechanical structures of these strained metal thin-films presuppose that they would behave as plasmonically active materials with very unique and tunable plasmonic properties.

In this research we investigated the optical properties of two examples of strained metal thin-films on elastomeric substrates that embody the two regimes of mechanical cracking structures observed in strained metal thin-films on elastomeric substrates. The first were Ag thin-films seeded on a PDMS substrate by AlN, which exhibit a microscale cracking pattern. The other thin-films that we studied were Ag thin-films seeded by Cr on PDMS substrates. This second set of thin-films exhibits the nanoscale cracking patterns which have been discussed in the literature.

The AlN seeded Ag thin-films deposited by sputtering were the first set of metal thin-films we studied under mechanical strain. By examining the mechanical structure of the thin-films under strain, we show that they exhibit a large linear microscale cracking pattern characteristic of a metal thin-film poorly adhered to the elastomeric substrate. This led to the conclusion that although AlN seeding layers provide a smooth Ag thin-film after deposition, they do not adhere well to the PDMS substrate and thus microscale cracks are formed under strain. We also observed that transverse compression of the substrate results in periodic undulations in the metal thin-film when a microscale cracking pattern is present. Through comparison to optical simulations, the
ability of these periodic undulations to couple incident radiation to SPPs was demonstrated. This suggested that the coupling of incident light to SPP modes in the undulated film may be responsible for the wavelength dependent drops in the total reflectance of the metal thin-films in the NIR. The thickness of the metal thin-film was demonstrated to be proportional to the average period of the undulations, with 10nm, 20nm and 30nm thick Ag films having a period of 2.2\(\mu\)m, 2.6\(\mu\)m and 4.2\(\mu\)m, respectively. Though we demonstrated control over the period of the undulations formed, we noted that the factors affecting the size of the microscale cracking pattern were still not discernable, and need further investigation.

Subsequently we investigated the optical properties of Cr seeded Ag thin-films deposited by electron beam evaporation on PDMS under strain. These films demonstrated branched nanoscale cracking patterns even before strain had been applied. Under strain the film was observed to deform by the opening and closing of crack branches depending on their orientation. The electrical resistance of the film was measured and we demonstrated that the film was electrically conductive even under strains as high as 20\%, suggesting that the film has electrical connectivity overall despite the nanoscale cracks. In the optical spectra we observed three key features, a broad reflectance peak in the visible, a broad enhancement of the transmissivity in the NIR, and a Drude reflectance tail in the MIR. Through simulations, we showed that the reflectance peak in the visible could be explained by the LSP modes of the nanoscale cracks resonating under visible light and reflecting the incident radiation. In the NIR and MIR the film could be explained as acting as a continuous effective electrical medium, however with an increased resistivity, and therefore reduced reflectance relative to a smooth metal thin-film. As strain in the film was increased, an overall drop in the reflectance of the film across all wavelengths, and an increase in the transmittance across all wavelengths were observed. This was similarly explained by the
plasmonic phenomena described. We additionally demonstrated that as the thickness of the film is increased, the size of the nanoscale cracks increases while their density decreases. This was understood as a result of smaller voids in the film being filled in, and the film becoming more continuous. This explanation however is at odds with the generally accepted mechanism of nanocrack formation and suggests that nanoac cracks are a result of the Volmer-Weber growth mechanism of the silver films. Despite these major advances in understanding both the optical properties of these nanoscale cracked strained metal thin-films and their theoretical origins, there are still aspects of the films that require detailed study. Further study of the cracking mechanism, and importantly the factors determining whether a film will exhibit nano or microscale cracks, must be undertaken.

In addition to the future work discussed with respect to the two types of thin-films deposited, there are several other interesting and important investigations that needs to be done to further advance this work.

The first avenue pertains to investigating more thoroughly the effect of the seeding layer on the cracking geometry. Although some research has been done and a rough consensus on the factors affecting the cracking geometry are agreed upon within the literature, in order to design films with specific optical properties, it is necessary to fully understand the various aspects of the seeding layers that affect the cracking geometry. This will necessitate inclusion of other seeding layer materials. Among the potential candidates are TiN, Ti, Ni and Cu, as these are all common seeding layers used for the deposition of smooth and continuous metal thin-films. In addition to this, we would like to study the morphology of the seeding layers themselves and determine if this has any bearing on the ultimate cracking behaviour of the metal thin-films.
Another factor that has been discussed which affects the cracking behaviour of metal thin-films on amorphous substrates is the Young’s modulus of the substrate, as discussed in Chapter 3. A benefit of the use of PDMS as an elastomeric substrate is that we can continuously alter the young’s modulus of the PDMS when curing the PDMS substrate. This allows us to characterize the cracking behaviour of metal thin-films deposited in the same manner for a variety of substrate elasticities; it is worth noting that this has not as yet been reported even in the mechanical and electrical literature on strained metal thin-films on elastomeric substrates.

Considering that functional groups on the surface of the PDMS also affect the adhesion of the seeding layer to the substrate and the growth of the silver thin-films, additionally it is important to examine how manipulating the surface properties of the PDMS substrate through procedures such as oxygen plasma treatment or UV ozone cleaning can alter the adhesion of the film and thus change the cracking behaviour of a metal thin-film deposited on the substrate.

In addition to studying the factors that affect cracking behaviour, we would also like to investigate the actual morphology of the cracks in greater detail. This should include studying the fractional area of the surface that the cracks cover, and how this changes as strain is applied. In the nanocracking regime, this is especially interesting as there is an initial void fraction even when no strain is applied, and it may help to elucidate aspects of the film growth mechanism if we are to study this in more detail.

A final avenue that warrants exploration is the study of the optical properties of strained thin-films of other metals. The most interesting metals to investigate would be other metals commonly used in plasmonics, such as gold and aluminum. The different plasma frequency and interband
transitions of these materials are expected to alter the optical resonances observed in the strained metal thin-films and may exhibit other useful phenomena.

Finally, in addition to furthering the study of the optical properties of strained metal thin-films, it is necessary that these new tunable materials are harnessed and utilized in novel applications. As discussed in Chapter 6, we see a variety of tunable devices that could be developed based on the properties of the strained metal thin-films that we have investigated. Among these are tunable SPP sensors, flexible plasmonic devices, tunable metamaterials, tunable solar control coatings and strain-activated SPP sensors.

In closing, it is believed that our investigation of the optical properties of strained metal thin-films will potentially open up an entirely new avenue of tunable plasmonic materials that can be harnessed and utilized in a wide variety of new applications that have yet to be considered.
References


Appendix A: Derivation of the Drude Model

In deriving the dielectric constant for an ideal metal using the Drude model, we will seek to find a formula for $\chi_e$. Based on Newton’s second law of motion we can write the equation of motion for the electron[6].

$$m \frac{\partial^2 x}{\partial t^2} = -qE - f \frac{\partial x}{\partial t} \quad (A-1)$$

where $m$ is the effective mass of the electron, $q$ is the charge of the electron, and $f$ is the coefficient of friction. If the applied field is a sinusoidal wave electric field of the form,

$$E = E_0 e^{j\omega t} \quad (A-2)$$

we can simply determine the particular solution to the ordinary differential equation (ODE) – which represents the steady-state solution – by assuming a sinusoidal solution. Doing this we find the position of the electron is given by,

$$x(t) = \frac{qE_0}{m} \frac{1}{\omega^2 - \frac{f}{m}\omega} e^{j\omega t} \quad (A-3)$$

As this is the position of the electron, the resulting dipole density created between the electron and the background field of the metal lattice is,

$$P = -Nq x(t) = -N \frac{q^2 E_0}{m} \frac{1}{\omega^2 - \frac{f}{m}\omega} e^{j\omega t} \quad (A-4)$$

where $N$ is the density of free electrons inside the metal. The electric susceptibility is thus,
\[ \chi_e = \frac{P}{\varepsilon_0 E} = \frac{\frac{Nq^2}{m\varepsilon_0}}{\omega^2 - \frac{f}{m}\omega} = \frac{-\omega_p^2}{\omega^2 - \gamma\omega} \quad (A-5) \]

where \( \omega_p = q\sqrt{\frac{N}{m\varepsilon_0}} \), is the plasma frequency, and \( \gamma = \frac{f}{m} \), is the damping frequency. This gives us the equation for the dielectric constant based on the Drude model[6].
Appendix B: Guided Wave Solution at an Interface and Surface Plasmon Frequency

The solution to the dispersion relation of a SPP is the solution to a guided wave along the interface of two media, where one of those media is a dielectric, and the other is a metal. For conciseness, we will only compute the solution for a TM polarized electromagnetic wave, as we know ahead of time that there will be no solution for TE polarization.

In this case, the problem is fully described by two electromagnetic waves. The wave in the dielectric that propagates upwards away from the interface, and the wave in the metal which propagates away downwards and away from the interface. This picture produces four equations describing the electric and magnetic fields in each medium.

\[ H_1 = H_{10} e^{j(\omega t - k_1 (\sin \theta_1 x + \cos \theta_1 y))} \]  \hspace{1cm} (B-1)

\[ H_2 = H_{20} e^{j(\omega t - k_2 (\sin \theta_2 x - \cos \theta_2 y))} \]  \hspace{1cm} (B-2)

\[ E_1 = -E_{10} e^{j(\omega t - k_1 (\sin \theta_1 x + \cos \theta_1 y))} (\cos \theta_1 \hat{x} + \sin \theta_1 \hat{y}) \]  \hspace{1cm} (B-3)

\[ E_2 = E_{20} e^{j(\omega t - k_2 (\sin \theta_2 x + \cos \theta_2 y))} (\cos \theta_2 \hat{x} - \sin \theta_2 \hat{y}) \]  \hspace{1cm} (B-4)

We then must make use of two of the boundary conditions for Maxwell’s equations, those being that under no-source conditions (no interfacial current densities or charge densities), the tangential electric field and tangential magnetic field must be continuous across the boundary. From this condition, we obtain,
\[ H_{10} e^{j(\omega t - k_1 \sin \theta_1 x)} = H_{20} e^{j(\omega t - k_2 \sin \theta_2 x)} \]  \hspace{1cm} (B-5)

\[-E_{10} e^{j(\omega t - k_1 \sin \theta_1 x)} \cos \theta_1 \hat{x} = E_{20} e^{j(\omega t - k_2 \sin \theta_2 x + \cos \theta_2 y)} \cos \theta_2 \hat{x} \]  \hspace{1cm} (B-6)

which reduces to,

\[ H_{10} e^{-jk_1 \sin \theta_1 x} = H_{20} e^{-jk_2 \sin \theta_2 x} \]  \hspace{1cm} (B-7)

\[-E_{10} e^{-jk_1 \sin \theta_1 x} \cos \theta_1 = E_{20} e^{-jk_2 \sin \theta_2 x} \cos \theta_2 \]  \hspace{1cm} (B-8)

From the first equation, we can deduce that \( H_{10} = H_{20} \), and \( k_1 \sin \theta_1 = k_2 \sin \theta_2 \). Further, assigning three variables \( \alpha = \sin \theta_1 \), \( \beta = \cos \theta_1 \), and \( \gamma = (n_2 k_1 / n_1) \cos \theta_2 \) allows us to represent the dispersion relation more simply. The variable \( \alpha \) represents the normalized propagation constant along the interface and is related to the surface plasmon wavevector \( \alpha k_0 = k_{sp} \).

The three variables can be related simply by applying the Pythagorean theorem to the wavevector in the two media. By doing this, we find,

\[ \beta = \pm \sqrt{1 - \alpha^2} \]  \hspace{1cm} (B-9) and \[ \gamma = \pm \sqrt{(n_2 / n_1)^2 - \alpha^2} \]  \hspace{1cm} (B-10)

Given that the relation between \( |E| \) and \( |H| \) for a plane wave in a non-magnetic medium is given by,

\[ |E| = \frac{|H| c_0}{n \varepsilon_0} \]  \hspace{1cm} (B-11)

we can solve for \( \alpha \) in the second equation, obtaining,
\[ \alpha = \pm \frac{n_2}{n_1} \sqrt{1 + \left( \frac{n_2}{n_1} \right)^2} \]  

\textit{(B-12)}

We must make one stipulation with this equation however, and that is that we can only accept the solution as a guided wave if \( \gamma \) and \( \beta \) produce electromagnetic waves that are propagating away from the interface, and decaying away from the interface. This condition is only possible for certain value of \( n_1 \) and \( n_2 \), and it happens that metals satisfy these required conditions. From a mathematical point of view, there is no requirement that the lower medium be a conducting material, however from a physical point of view, only materials with a conducting behaviour at the frequency of question will exhibit the mathematically required index values.
Appendix C: Fabrication Methods

Fabrication of PDMS Substrates

The PDMS substrate upon which the metal films are deposited is a 1mm thick planar substrate. Sylgard 184 PDMS was mixed in a 10:1 mass ratio of base to curing agent and drop-casted into a petri dish. The volume of PDMS used was calculated to provide a 1mm thick material should the PDMS spread evenly across the petri dish. The petri dish was then left overnight covered in a leveled shelf in order to allow the PDMS to distribute itself evenly. Finally, the remaining uncured PDMS was cured in an oven at 60 degrees for 2 hours. The finished PDMS was then cut into rectangular samples 1.5cm x 3cm in size.

Deposition of AlN Seeded Silver

The rectangular PDMS substrates of 1mm thickness were placed in a four-target RF/DC sputter deposition system by Kurt J. Lesker, wherein a thin seeding layer and silver layer were deposited.

The first layer deposited was an aluminum nitride (AlN) seeding layer to improve adhesion between the silver and PDMS substrate. An aluminum target was used with a nitrogen to argon partial pressure ratio of 60N₂:40Ar in order to create AlN by reactive sputtering. The deposition parameters were RF power of 150W, total chamber pressure of 2.5 mTorr, and total gas flow rate of 20ccm. The AlN layer was deposited for 4 minutes, producing a film of approximately 3nm in thickness.
Following the deposition of the AlN seeding layer, a thin silver film was deposited. For the silver film, a silver target was used with a nitrogen to argon partial pressure ratio of $60\text{N}_2:40\text{Ar}$, as a partial nitrogen pressure has been shown to improve silver film quality when sputtering (25). A deposition power of 300W, gas pressure of 5 mTorr, and total gas flow rate of 20ccm was used. The deposition rate measured for silver was 0.35 nm/s as measured by a Quartz Crystal Microbalance sensor within the sputtering system.

**Deposition of Cr Seeded Silver**

The rectangular PDMS substrates of 1mm were placed inside an electron-beam evaporation chamber designed and built by Kurt J. Lesker. A 5nm thick Chromium layer was deposited by evaporation onto the substrate using a deposition power of 3.7% (3.1V and 0.19 A on Telemark TT-6 Power Supply for E-beam) from a Graphite crucible. Following the chromium layer, a 25nm thick Ag layer was deposited also using electron-beam evaporation. A deposition power of 7.8% was used. A Quartz Crystal Microbalance was used to monitor the film thickness.

**Spin Coating of PDMS Antireflective Layer**

A solution of 3%wt PDMS in heptane was prepared by mixing uncured PDMS in a ratio of 10:1 base to curing agent with 97%wt heptane, giving heptane sufficient time to dissolve the PDMS. Following this the 3%wt solution was spin-coated at 2000rpm for 1min10s onto a 10nm silver coated PDMS substrate. The resulting structure was then cured in an oven at 60 °C in order to cure the PDMS layer.
UV-Vis Measurements

UV-Vis measurements were performed using a Perkin Elmer Lambda 1050 comprising a 3-detector module, a universal reflectance module, and a 150mm integrating sphere module. Strain was applied to the PDMS mounted silver films using a modified PELCO® Large Universal Vise Clamp sold by Ted Pella. An image of the modified stage is shown in Fig. S4. During total transmittance and total reflectance measurements, as a result of the stage design, the sample is distanced several mm from the integrating sphere inlet, resulting in some of the large angle scattered light not being collected. For the 10nm Ag film samples where visible light transmission is high, some of the transmitted visible light was believed to have been lost due to large scattering in strained samples, thus decreasing the total transmittance slightly.

SEM Measurements

SEM measurements were performed using a FEI Quanta FEG 250 Environmental SEM/STEM provided by the University of Toronto Centre for Nanostructure Imaging and the modified PELCO® Large Universal Vise Clamp which was also used for the UV-Vis measurements. The straining stage was designed to fit into a pin slot for SEM stubs of the SEM instrument. Samples were removed each time a strain needed to be applied and then reinserted into the chamber.

Resistivity Measurements
Resistivity measurements were performed in two stages and only represent approximate resistivities in the case of the strained samples. Initially, the unstrained samples were placed into a Hall effect measurement system and their resistivities were directly measured. Following this, the samples were mounted in the straining stage used for UV-Vis and SEM measurements, and an electrical lead was attached to each side of the film. The resistance of the film was measured for various amounts of strain, and the relative change in resistance was used to determine the approximate resistivity corresponding to each level of strain.

Emissivity Measurements

Emissivity was measured using a Fourier Transform Infrared Spectrometer in reflectance. Strained metal thin film reflectance was measured, and under the assumption of no transmission through the PDMS substrate, the weighted average emissivity was calculated for the sample being at 300 K. These measurements were done at the University of Waterloo in the Solar Thermal Research Laboratory of Prof. Michael Collins.

Modified PELCO® Large Universal Vise Clamp

A PELCO® Large Universal Vise Clamp was purchased from TED Pella. In order to allow for strain to be applied to the elastic films, a spring was placed over top of the central screw, thus always forcing the stage to extend to its maximum. To fit inside the QUANTA FEG 250 ESEM used for SEM measurements, we created short clamps with screw holes drilled through them to
allow the sample to be held tightly when strained. Finally, in order to be able to do transmission measurements through the films, we drilled a hole through the stage. A picture of the modified device is shown in Fig. C1.

Fig. C1: Modified PELCO® Large Universal Vise Clamp by TED Pella. The vise clamp was modified (i) to include fasteners so as to firmly secure the two sides of a strainable rectangular metal-dielectric film sample, (ii) to include a spring on the drive shaft to ensure reproducible separation of the two half stages, and (iii) to include a large hole to facilitate optical characterization.
Appendix D: Microscale Fracturing of Strained Silver Thin-Films - Supplemental Information

Calculation of Undulation Height

The approximate height of the undulations was calculated by assuming a sinusoidal profile and using a line integral to estimate the height. As a first step, the expected fractional change in the transverse direction of the PDMS substrate width is determined. To do this, Poisson’s ratio is utilized, however to get an accurate measurement, the formula must be applied for small incremental steps until we reach 0.15 axial strain.

\[
\nu = -\frac{\partial \epsilon_{\text{trans}}}{\partial \epsilon_{\text{axial}}} \quad (D-1)
\]

\[
\partial \epsilon_{\text{trans}} = -0.5 \partial \epsilon_{\text{axial}} \quad (D-2)
\]

\[
(1 + \partial \epsilon_{\text{axial}})^n = 1.15 = 1 + \Delta \epsilon_{\text{axial}} \quad (D-3)
\]

\[
1 - \Delta \epsilon_{\text{trans}} = (1 - \partial \epsilon_{\text{trans}})^n \quad (D-4)
\]

Doing this to the limit of \( n=\infty \) we obtain,

\[
\Delta \epsilon_{\text{trans}} = -0.45 \Delta \epsilon_{\text{axial}} \quad (\text{For } \Delta \epsilon_{\text{axial}} = 0.15) \quad (D-5)
\]

We then take the period measured for a given undulation, and determine the original flat length of the film that created this undulation by inverting the above equation. This becomes our total length \( L \) for the film. By calculating the line integral of this sinusoidal undulation, we can show that,
where \( P \) is the undulation period, \( h \) is the undulation height, and \( L \) is the length calculated as described above. By factoring \( h \) out of the integral, we can then iteratively find \( h \) by providing an initial guess and then numerically solving the integral.

**MIR Reflectance of 10nm Ag on PDMS at 0 and 15\% Strain**

The reflectance measured for a 10nm Ag-PDMS multilayer sample is shown in Fig. D1.

**MIR Reflectance of Multilayer PDMS-AG-PDMS Structure at 0 and 15\% Strain**

The reflectance for the PDMS-Ag-PDMS multilayer sample is shown in Fig. D2.
Fig. D1: Reflectance of 0% strained and 15% strained 10nm Ag on PDMS sample.

Fig. D2: Reflectance of 0% strained and 15% strained PDMS-Ag-PDMS multilayer sample.
Appendix E: Refractive Indices used in Simulation

The refractive index of silver used in the simulations discussed in this thesis were taken from Rakic[60], and are included below.
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The refractive index of Chromium used in the simulations discussed in this thesis were taken from Rakic[60], and are included below.
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The refractive index of PDMS used in the simulations was approximated to be 1.4 for all wavelengths of light. This assumption is relatively accurate for visible frequencies as shown by the PDMS refractive index data in the Master’s thesis of Weiping Qiu from the University of Louisiana[61].
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