Colour tunable plasmonic devices

by

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Abstract

Localized Surface Plasmon Resonance (LSPR) is a resonant optical phenomenon arising within nanoscale metallic particles and is capable of generating vibrant, high resolution and enduring colour. Coupled with their high sensitivity to nearby changes, such structures have been the focus of significant research over the past couple decades. At present, much of the investigation has been focused towards developing novel nanomaterials along with new processes for their realization. While such efforts have yielded an array of impressive static colour features, progress towards realizing dynamic devices has only recently gained significant traction. In recent years, several researchers have reported upon dynamic plasmonic response primarily based on mechanically tunable or electro-chromic responses.

This document focuses on the development of novel mechanically and electrically responsive plasmonic features. Dynamic colour was achieved by embedding metal nanoparticles within a deformable gap. The gap serves to control the optical coupling between the nanoparticles and an opposing reflector film; as the gap changes, so too does the colour. The intent of this work is to develop a structure that is amenable to volume manufacturing and that has the potential for broad colour response.
Acknowledgments

As is the case with most things, a thesis is not a solitary endeavour. I would like to take the opportunity to thank all those that have helped along the way.

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For any friends or family reading...your consistent requests to know whether I was done yet provided ample and continual motivation. With the conclusion of this document, I hope that we can broaden our discussions to weather and local sports.

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## Nomenclature

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<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>CV</td>
<td>High Frequency Capacitance vs Voltage measurement</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Method</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide; transparent conductor</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localized Surface Plasmon Resonance</td>
</tr>
<tr>
<td>MIM</td>
<td>Metal Insulator Metal structure</td>
</tr>
<tr>
<td>MEMs</td>
<td>Microelectromechanical systems</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane Elastomer</td>
</tr>
<tr>
<td>PEC</td>
<td>Perfect Electric Conductor</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate; commercial plastic</td>
</tr>
<tr>
<td>PMC</td>
<td>Perfect Magnetic Conductor</td>
</tr>
<tr>
<td>PML</td>
<td>Perfectly Matched Layer</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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Chapter 1

Introduction

Although colloidal gold mixtures such as those found in stained glass have a long history, a rigorous scientific treatment of the phenomenon proved elusive until comparatively recent developments in electromagnetic theory. Their vibrant colours are due to localized surface plasmon resonances, an oscillation in electron density, often observed at the interface of a dielectric material and metallic nanoparticles.

Over the past two decades, the field of plasmonics has benefited from sustained academic attention. A number of factors have contributed to the field’s endurance:

- Continual improvement in the synthesis and assembly of nano-materials, enabling new applications along with more control over the fabricated structure;

- Their unique optical properties are well suited for use as highly sensitive sensor platforms;

- Their intense near field is an enabling technology for a wide range of optical devices; and

- Metal nanoparticles provide an alternative colour source that is less likely to fade over time compared to conventional chromophores and their response can be tuned across the visible spectrum without chemical change.
Applications for plasmonic devices are widespread. Recently, they have been considered for improvements to solar cell efficiency, for telecommunications, as biological sensors, and as colour feature technologies. Metallic nanoparticles have even found applications in cancer research due to their ability to amplify the local intensity of incident infrared energy and destroy cells to which they have been attached.

1.1 Motivation

Despite an increasing number of striking colour features that have been reported upon over the past several years, much of this work has focused on realizing static images and further developing the nano-fabrication processes necessary to realize them. Comparatively few works have focused on developing the dynamically tunable platforms into which such structures can be integrated.

In parallel, there is an insatiable demand to provide increased functionality into commercial products. A mechanically responsive structure, for example, would be an appealing authentication feature for a wide range of documents; from currency, to government issued identification, to event tickets. Already, such items have begun to integrate nano-materials in order to enhance their security.

For mobile products, meanwhile, there is continual pressure to increase battery lifetime and reduce device thickness. Both could potentially be achieved with an electrically/mechanically tunable plasmon-based reflective display technology. While conventional LCD displays require LED backlights, polarizers, and colour filters; reflective displays function as tunable colour filters and require only ambient light. Despite their limitations, e-reader technologies based on electrophoretic ink remain popular primarily due to their long battery lifetimes. A plasmon based reflective technology should significantly outperform conventional e-readers in both colour rendering and
CHAPTER 1. INTRODUCTION

speed.

One limitation of existing reflective display technologies is that they typically rely on RGB sub-pixels for colour. With each sub-pixel only capable of generating a single colour, much of the incident light is absorbed and the resulting image appears muted. If, instead, each pixel were capable of rendering many colours, the resulting image should be significantly improved. The absorbance of plasmonic nanoparticles is responsive to any change within its proximity and can therefore be anticipated to provide a variable colour pixel.

1.2 Research Objectives

The intent of this work is to explore a pair of responsive structures that leverage metal nanoparticles as a source for colour. The primary goals for the structures developed were:

- That fabrication would be compatible with existing volume production capabilities; and

- That fabricated structures produces a visually apparent colour shift upon the application of stimulus (mechanical and electrical in this case).

1.3 Thesis Overview

This document provides a summary of two responsive colour tunable structures that have been produced along with sufficient detail to understand the physical principles of operation and some of the fabrication challenges that were addressed as part of this work. A brief overview of subsequent chapters follows:
• Chapter 2 Background: Summarizes the physics of localized surface plasmon resonances and their interaction within neighbouring particles or substrates. Summarizes recent work in the field of colour tunable plasmonic materials.

• Chapter 3 Fabrication Challenges: Identifies the key challenges encountered in realizing stimuli-responsive plasmon structures along with the process sequences developed in the course of this work to address them.

• Chapter 4 Mechanically tunable plasmonic colour: Presents the design, fabrication and testing of a novel pressure sensitive plasmon structure. The realized device is flexible and visually apparent colour change can be activated by hand. Compared to previously demonstrated structures, this device represents an improvement in terms of potential for integration on commercial plastics.

• Chapter 5 Electro-mechanically tunable plasmonic colour: Provides an overview of the principle of operation and fabrication of an electro-mechanically actuated plasmon structure. The proposed structure is based upon a MEMs-style bridge structure.

• Chapter 6 Summary: Provides an overview of what has been accomplished in this work
Chapter 2

Background

2.1 Surface Plasmons and their interactions

2.1.1 Localized Surface Plasmon Resonance of an isolated particle

The term, Localized Surface Plasmon Resonance (LSPR), refers to the collective motion of many electrons within nano-sized objects in response to incident light. As such, the behaviour is typically well described by classical electrodynamics\(^1\). The phenomenon has therefore been quite well understood since the early 20th century. It is only recently with improved metrology and synthesis techniques for nanoscale structures that the field has attracted widespread interest.

Nanostructures of sufficient complexity are often most conveniently treated using one of many popular numerical methods. However, a familiarity with the underlying principles can be useful in connecting seemingly disparate phenomena and motivating new avenues for exploration. With this in mind, a brief overview of the theory of plasmonic nanoparticles will be presented.

\(^1\)Quantum mechanical descriptions do become necessary where the effects of lower carrier densities or tunnelling become non-negligible.
In the electrostatic limit

Plasmonic nanoparticles whose resonances are located within the visible spectrum are, in general, much smaller than the incident wavelength. As such, it is often convenient to disregard the finite speed of light and assume that the incident field is applied instantaneously across the region of interest. Such simplifying assumptions are often used to produce compact closed form solutions and have proven to accurately describe the response of very small particles or nanostructures.

One conceptually satisfying model treats free electrons within a metallic nanoparticle as an incompressible, irrotational charged fluid \[ \mathbf{j} \]. In what is often referred to as a hydrodynamic model, the electron fluid redistributes in response to applied electric fields while a fixed background charge due to the ion cores, \( \rho_0 \), produces a restoring force. Mathematically, the behaviour is described by:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0, \quad (2.1) \\
\nabla \times \mathbf{j} = 0, \quad (2.2) \\
\mathbf{j} = \rho \mathbf{v} = n_e e \mathbf{v}, \quad (2.3)
\]

**Figure 2.1:** Illustration of a plasmonic nanoparticle within the electrostatic regime.

where \( \rho \) is the electron charge density, \( \mathbf{j} \) is the electron current density, and \( \mathbf{v} \) is their velocity as a function of space. Because the fluid is irrotational (as stated in equation 2.2), we can use equation 2.2 to further conclude that \( \nabla \times \mathbf{v} = \nabla \times (\nabla \eta) \). In other words, velocity can always be described by the gradient of a scalar field, \( \eta \).

If we also limit displacement of the fluid to small perturbations, uncompensated
CHAPTER 2. BACKGROUND

charge is constrained to an infinitely thin spherical shell at the nanoparticle boundary with the remaining volume being neutral. In such conditions, equation 2.1 simplifies to Laplace’s equation:

\[ n_e \varepsilon \nabla^2 \eta = 0 \]  \hspace{1cm} (2.4)

where all solutions for \( \eta \) must satisfy the Laplace equation throughout the domain with the following boundary conditions at the surface:

\[ \frac{\partial \sigma}{\partial t} = n_e \varepsilon \frac{\partial \eta}{\partial n} \bigg|_{S}, \]  \hspace{1cm} (2.5)

where \( \sigma \) is the induced spill-out charge and \( n \) is the surface normal vector. The dynamic response of the system can now be explored by constructing a Lagrangian.

Lagrangian dynamics, or the principle of stationary action, rests upon the underlying link between the energy of a physical system and its equations of motion 13. If the relationships for potential and kinetic energy can be calculated for a given system, so too can its resulting dynamic behaviour.

Assuming that, for each electron, the kinetic and potential energies can be expressed as:

\[ T_i = \frac{1}{2} m_e v_i^2, \]  \hspace{1cm} (2.6)

\[ V_i = \frac{e^2}{8\pi \varepsilon_0} \sum_{j=1}^{n-1} \frac{1}{|r_j - r_i|}, \]  \hspace{1cm} (2.7)
the Lagrangian for this system can be defined in spherical coordinates, as:

\[
\mathcal{L} = \sum_i T_i - \sum_i V_i
\]

(2.8)

\[
\mathcal{L} = \frac{m_e}{2e} \int \eta \dot{\sigma} dS - \frac{1}{8\pi\epsilon_0} \int \frac{\sigma(r)\sigma(r')}{|r - r'|} dS_r dS_r.
\]

(2.9)

where the above transformation from discrete sums to integrals over continuous charge distributions relies on the application of divergence theorem and has been described in detail elsewhere [12].

For a spherical particle of radius \(a\), using \(\nabla^2 \eta = 0\) and equation (2.3), we can conclude that the surface charge density can be expressed in the form:

\[
\sigma_s(t, \Omega) = n_e m_e \sum_{l,m} \sqrt{\frac{l}{a^3}} S_{lm}(t) Y_{lm}(\Omega),
\]

(2.10)

where \(S_{lm}(t)\) are time-dependent variables, that are characteristic of the specific system, and \(Y_{lm}(\Omega)\) are the orthogonal solutions to Laplace’s equation in spherical coordinates. By substituting (2.10) into (2.9) and taking advantage of orthogonality of \(Y_{lm}\) the Lagrangian simplifies to:

\[
\mathcal{L}_s = \frac{n_0 m_e}{2} \sum_{l,m} \left[ \dot{S}_{lm}^2 - \omega_l^2 S_{lm}^2 \right]
\]

(2.11)

\[
\omega_l = \sqrt{\frac{e^2 n_e}{\epsilon_0 m_e} \frac{l}{2l + 1}}
\]

(2.12)

The resulting Lagrangian describes the collective response of free electrons as a set of independent harmonic oscillators which resonantly couple to excitations at \(\omega_l\). Of
these, the most relevant to the colourful properties of isolated metallic nanospheres is the \( l = 1 \), or so-called dipole mode. For very small particles, the exciting field can often be approximated with a uniform one. In such scenarios, the dipole is most strongly excited. In fact, such particles can often be accurately regarded as a point-like dipole.

Interaction between a particle and an incident field can also be incorporated into equation 2.11 to quantify its optical response. The absorption cross-section, which provides a measure of an objects ability to capture and absorb power, can be described as:

\[
C_{\text{abs}}(\omega) = \frac{\omega}{c} Im[\alpha(\omega)] ,
\]

\[
= 4\pi k \frac{n_e e^2 a^3}{m_e} Im \left[ \frac{1}{\omega^2 - \omega_1^2 + i\delta} \right] ,
\]

where \( \delta \) is an arbitrary factor which could approximate damping processes that were not considered in the model. The above model treats electrons as being lossless and would result in resonance peaks having infinite finesse. In reality, losses due to inelastic scattering or inter-band transitions serve to dampen such a response.

Inspecting equation 2.14 we note immediately that a tunable response could potentially be achieved by modulating the electron carrier concentration of the system. As illustrated in Figure 2.2 an increase in electron concentration shifts the resonance peak to shorter wavelengths. The plot demonstrates optical response for a material with carrier concentration of \( 5 \times 10^{26} \) cm\(^{-3} \) and an electron mass equal to it’s rest mass.

Experimentally, this effect has been observed using indium tin oxide (ITO)
Figure 2.2: Normalized cross-section of a spherical nanoparticle as a function of incident wavelength in the electrostatic limit. The localized surface plasmon resonance peak is a function of electron carrier concentration, \(n_e\). An arbitrary damping factor has been added to broaden the response. In practice, the damping factor would represent losses due to scattering or absorption within the material.

nanoparticles within an electrolytic capacitor structure \cite{14}. Strong electric fields, maintained across the electrolyte’s double layer, induce appreciable changes in the carrier density. For particles whose resonant behaviour lies within the visible spectrum, however, meaningful modulation of the peak wavelength is difficult to achieve due to the very large electron concentrations of gold, silver, and copper. A colour tunable response will require a different approach, which will be considered more fully in Section 2.1.2.
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The hydrodynamic model has proven surprisingly versatile in describing a variety of surface plasmon phenomena\textsuperscript{[12][15][16]}. Nevertheless, as particle sizes or interaction distances increase, the wave-like nature of light is no longer negligible. Furthermore, in order to design a fabricated device, the polarization and damping processes that are embedded within measured dielectric properties must be considered.

**Full-wave treatment - Mie Theory**

For a complete description of the behaviour of metallic nanoparticles of all shapes and sizes, we turn to Maxwell’s equations,

\[
\nabla \cdot \mathbf{D} = \rho_f, \quad \nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0, \\
\nabla \cdot \mathbf{B} = 0, \quad \nabla \times \mathbf{H} = \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t} .
\]

More specifically, we turn to a particular solution for Maxwell’s equations which describes scattering by a particle in response to a time harmonic source. In an approach that is similar to the decomposition of a signal’s spectral content by Fourier analysis, a particle’s response to an arbitrary incident field can be uniquely expanded into a series of orthogonal modes known as Vector Spherical Harmonics (VSH)\textsuperscript{[17]}. With this technique, scattering by a spherical particle can be expressed as

\[
\mathbf{E}_s = \sum_{n=1}^{\infty} E_n[i a_n \mathbf{N}_n(r, \phi, \theta) - b_n \mathbf{M}_n(r, \phi, \theta)]
\]

(2.15)

where \(a_n\) and \(b_n\) are scattering coefficients specific to particle geometry, as calculated using Mie theory\textsuperscript{[17]}, and \(E_n\) represents the contribution of the incident field to a
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given multipole mode.

Vector spherical harmonics form an orthonormal basis set and can be used to describe any field distribution. An incident plane wave, for instance, can be decomposed into a series of multipole field distributions such that $E_n = \frac{i^n E_0 (2n + 1)}{n(n + 1)}$. Once the scattering coefficients for a given particle are calculated, its response to an arbitrary light source can be easily obtained by decomposing the incident field into VSH modes. This approach forms the basis for calculating the scattering properties of particles by the T-Matrix method \[18\]. Although the method is very efficient for axisymmetric particles, the matrices become quite large for other shapes.

Following from the above, Figure 2.3 illustrates the near field responses of two individual silver nanospheres due to an incident plane wave with a wavelength of 400 nm. The response is unlike those derived using electrostatic approximations, whose resonances are size invariant. Furthermore, although the incident wave has significant dipolar and quadrupolar amplitudes, each particle preferentially responds to one mode and has a total effective extinction cross-section of:

$$C_{\text{ext}} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} \left| \frac{E_n}{E_0} \right|^2 \frac{n^2(n+1)^2}{2n+1} \text{Re}\{a_n + b_n\}. \quad (2.16)$$

While the scattering coefficients $a_n$ and $b_n$ are fixed for a given particle, total extinction can be controlled by altering the spatial distribution of the incident field. If, for example, the dipolar component in Figure 2.3 were to be attenuated, a much smaller extinction cross-section could be anticipated for the 50 nm sphere. By contrast, the total extinction cross-section of this particle is much less sensitive to changes in higher order modes. By selectively enhancing or attenuating specific multipole modes, tuning of the localized surface plasmon resonance peak or excitation of modes
Figure 2.3: Mie scattering calculation of multipole excitation for silver spheres having radii of 50 nm and 100 nm, excited by 400 nm plane wave propagating along the Z axis and polarized along the X-axis. The magnitude of the electrical near field has been plotted to depict the response to the dipole and quadrupole excitation for a pair of particles with different radii. a) Depicts the dipole contribution for an incident plane wave; orientation of incident plane wave is also depicted b) Dipole response by 50 nm sphere c) Dipole response by 100 nm sphere d) Quadrupole mode distribution from an incident plane wave e) Quadrupole response for a 50 nm sphere f) Quadrupole response for a 100 nm sphere

that are normally unexcited becomes possible. In practice, this can be accomplished by using highly focused light sources \[9,20\] or by introducing additional surfaces or nanostructures which modulate the local electric field distribution \[21,22\].

2.1.2 The influence of local field on plasmon response

In previous sections the response of an isolated plasmonic nanoparticle to incident field has been shown to be based on:
• material properties: density of electrons, damping processes, interband transitions (eg: the dielectric response, typically empirically quantified).

• geometric properties: shape, size, symmetry (eg: dictates how light is scattered)

The scattering parameters for a given particle are, essentially, immutable and depend only on the local field distribution. However, by positioning such a particle within an assembly or in proximity to other nano-structures, the local field can be altered. In so doing, the response (eg: the apparent colour), is also altered.

Resonant metal nanoparticles are essentially highly sensitive local field sensors, which is why they have enjoyed such enduring popularity over the past decade. Researchers investigating colour tunable response have, generally, relied upon interaction between neighbouring particles or with an underlying substrate.

**Particle-Particle interactions**

Optical coupling between closely-spaced nanoparticle dimers and clusters are amongst the simplest structures for achieving a tunable response. When separated at distances which are larger than their radii, the constituent particles can often be accurately regarded as isolated polarizable dipoles. For spherical particles, the dipole moment (in vacuum) for each scatterer is:

\[
p(\omega) = \alpha(\omega)E_{local}(\omega),
\]

\[
\alpha = 4\pi R^3 \frac{\epsilon_s - 1}{\epsilon_s + 2}.
\]

The above response is influenced not only by the incident field, but also by the fields of nearby particles. As particle-particle separation is reduced, the intensity of their interaction increases. Implicit to this treatment, however, is the assumption that
the local electric field is uniform across the particle volume. In fact, when particles are very close, this is no longer the case due to the presences of very large field gradients. As illustrated in Figures 2.4 & 2.5, the dipole approximation becomes insufficient when the gap is less than the particle radius. Contribution from higher order modes greatly enhance the interaction and must be considered for a complete description. Similarly, particles which are more responsive to higher order excitations will be more sensitive to near-field interactions. While typically, these effects are satisfactorily modeled by classical electrodynamics as the gap is reduced 1-2 nm, quantum mechanical effects must be treated to achieve a physically accurate mode. Figure 2.5 is intended to clearly demonstrate the role of higher order modes but would likely require modification below d/R values of 0.1.

A number of groups have reported on colour tunable devices based on modulating the inter-particle spacing of nanoparticle arrays [6, 23, 26]. Based on the results presented in Figure 2.4, such structures generally require a very dense network of particles and strains on the order of 10% are typically required to achieve an appreciable response. One alternative to this approach would be optical coupling to an underlying substrate which should mitigate some of the issues confronted by laterally coupled devices.

Particle-Substrate interactions

The coupled optical response of plasmonic particles with an underlying substrate has been explored using a commercial finite element analysis tool (COMSOL) for flexibility in the simulation of both spherical and non-spherical particles. The calculated results illustrate reflectance from an array of identical silver particles in close proximity to a Perfect Electric Conductor (PEC) substrate. The structure is an idealized
Figure 2.4: Localized surface plasmon resonance peak for a pair of coupled silver spheres as a function of particle spacing. The incident electric field is applied parallel to the interparticle axis. Contribution from higher order modes become increasingly important as the gap decreases. Treated in the electrostatic regime.

Figure 2.5: Polarizability as a function of wavelength for a pair of coupled silver nanospheres. Responses were calculated in the electrostatic limit for a) ideal dipoles $n = 1$, and b) where higher order modes are included $n = 20$. 
Figure 2.6: (a) Metal nanoparticle suspended over a conductive metal film at distance $d$ (b) Calculated reflectance from an array of 10 nm spherical silver particle in proximity to an underlying conductor at various distances $d$, with 20% surface coverage

model and is intended to illustrate some of the important design variables. Although incorporation of real substrate materials, such as aluminum, would alter the system response, the primary conclusions drawn from subsequent results will remain unchanged.

For the purposes of this investigation, an incident plane wave propagating normal to the surface was used as the source. Interpolation of tabulated material data was used for modelling silver permittivity. Air was selected as the ambient dielectric.

To focus on the behaviour of the particle-substrate interaction, the unit cell size was selected to minimize coupling between neighbours while simultaneously managing the domain size. By iteration, it was determined that these goals could be reasonably satisfied when the geometric cross-section of the particle occupies approximately 20% of the cell.
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Commonly exploited for anti-reflection coatings, standing waves occur due to interference between incident and reflected plane waves. For very small particles, such interference effects can be exploited using a deformable structure to modulate the optical density. In an unactuated state, the particles are separated from the substrate and have large optical density at resonance. In response to a stimulus – for instance, electrical or mechanical – a decreasing gap results in decreased optical density due to the reduced field strength experienced by the particles, as shown in Figure 2.6. Visual contrast between these two states is possible due to the significant absorbance generated, even by a single layer of nanoparticles. In Figure 2.6b, a surface concentration of only 20% imparts significant losses to the reflected signal when particles are separated from the film.

The absence of observed shifts in the resonance peak indicates that, for very small spheres (less than 10 nm in diameter), the contribution of near-field coupling is not significant even at 5 nm of separation. For larger or non-spherical particles, however, the optical absorption of the structure at these distances is dominated by near field interaction between the particle and reflected image field. In contrast to very small spheres, such particles are more responsive to changes in the spatial distribution of the exciting field. Furthermore, the near-field interaction is highly sensitive to changes in distance. It can therefore be nearly extinguished with minimal increase in separation between the structures. Such sensitivity is highly desirable for manufacturing a responsive device.

Illustrated in Figure 2.7 are the optical responses for a selection of spheroids in proximity to an underlying metallic film. Of particular note is the enhanced responsiveness of ellipsoidal particles compared to spherical particles. The explanation lies in their differing response to higher order multipole excitation. As distance decreases,
**Figure 2.7:** Reflectance changes due to near field interaction for (a) 40 nm spheres, (b) oblate spheroid (40 nm x 20 nm) and (c) oblate spheroid (40 nm x 10 nm). Surface concentration of 20% was used in all cases. (d) Relationship between primary resonance peak and distance to the underlying substrate.

The contribution of high order multipoles to the optical response is of increasing influence. Ellipsoids have a much larger response to high-order excitation than do spheres of similar size and can therefore be expected to produce larger shifts.

**Gap Plasmons**

In addition to the near-field interactions described above, gap controlled resonant colour can arise as metal nanoparticles interact with an optical mode supported between the particle and an underlying metal substrate. The mode, depicted in Figure 2.8a for a 1D metal-gap-metal structure, propagates parallel to the substrate.
Figure 2.8: a) Overview of metal-insulator-metal structure (MIM) and its associated transverse magnetic mode. b) The real part of the effective index for a 1-D MIM stack consisting of gold cladding separated by a variable air gap. c) Illustration of 2D structure simulated by finite element method. An infinitely long gold rod is suspended above an underlying gold substrate, allowing for the excitation of gap plasmons. d) Calculated reflectance from the structure in c for variable gaps. (inset) Magnetic field strength at resonance for a structure with 5 nm gap.

When such a mode is confined beneath the finite size of a nanoparticle, it will be reflected at either edge due to the large contrast between its effective index and the surrounding ambient. As in the case with conventional fabry-perot etalons, resonance occurs when the particle size is phase matched to the optical path of the cavity.

At this point, it is instructive to consider the properties of a metal-air gap-metal mode using a one dimensional analog. In practice, the modes of interest for colour
tunable applications tend to be transverse magnetic in nature; as a result we shall focus on those TM modes that are supported by this structure. The coordinate system is defined in Figure 2.8a. For simplicity, we shall further assume that the MIM structure is symmetric, as anti-symmetric modes tend to be cut-off for the gap thicknesses of interest.

Proceeding from Maxwell’s equations, it can be shown that a TM mode propagating along the MIM interface is governed by a set of equations in each of the surrounding media 28:

\[
\frac{\delta^2 H_y}{\delta z^2} + (k_0^2 - \beta^2) H_y = 0 \tag{2.19}
\]

\[
E_x = -i \frac{1}{\omega \epsilon_i} \frac{\delta H_y}{\delta z} \tag{2.20}
\]

\[
E_z = -\frac{\beta}{\omega \epsilon_i} H_y \tag{2.21}
\]

where \( \beta \) is the propagation constant for the mode and \( \epsilon_i \) is the permittivity in a given region.

The field within the gap region arises due to coupling between the two metal surfaces and can be assumed to take the form \( H_y = C_y e^{i \beta x} \cosh (k_y z) \). The mode can further be assumed to be evanescent within the surrounding metal cladding, \( H_y = C_m e^{i \beta x} e^{k_m |z|} \). Substituting these into equation 2.19 and enforcing continuity of tangential \( E \) and \( H \) components, the supported modes are governed by:
\begin{equation}
\kappa \tanh \left( \frac{\kappa g}{2} \right) + \frac{\kappa_m}{\epsilon_m} = 0 \tag{2.22}
\end{equation}

\begin{equation}
\kappa = k_0 \sqrt{n_e^2 - 1} \tag{2.23}
\end{equation}

\begin{equation}
\kappa_m = k_0 \sqrt{n_e^2 - \epsilon_m} \tag{2.24}
\end{equation}

where \( k_0 \) is the propagation constant in free space for a wave with period \( \lambda_0 \) and \( g \) is the gap thickness. \( n_e \) is the effective index for the mode and is related to the mode’s propagation constant as \( \beta = n_e k_0 \).

The transcendental equation \(2.22\) can be solved by iterative methods to calculate an effective index as a function of permittivity and gap. To illustrate the physical significance of the above, the effective index supported by a gold-air gap-gold structure has been calculated and presented in Figure \(2.8\).

Of particular interest is the large effective index of the mode compared to the surrounding ambient. As a result, incident light within the visible spectrum can excite gap plasmons confined by nanoscale metallic particles, as depicted in Figure \(2.8\). Coupled with the high optical density of plasmonic nanoparticles, the phenomena is capable of strongly attenuating incident radiation. For this reason, many groups have leveraged similar structures to realize broadband absorbers and colour features \(29\).

Figure \(2.8\) demonstrates the broad range a tuning that is achievable for the simple 2D structure in Figure \(2.8\); simply by adjusting the gap thickness. Although, to this point, only simple 1D and 2D models have been considered, comparable modes are also excited in 3D structures \(30\).
2.2 Related works in the field of colour tunable structures

A complete review of all works in the field of colour tunable structures would present a significant challenge. Instead, this section will focus primarily on those which relate to the use of nanoparticles and nano-structured materials. Plasmonic colour is both passive (requiring only ambient light) and fairly readily tunable by altering its structure. The combination is highly appealing and, as a result, the field has received enduring attention over the past decade.

2.2.1 Plasmonic structures as pigment

As a source for colour, metallic nanoparticles are attractive due to their high optical density and their potential for superior endurance compared to existing pigments that typically fade over time. To date, much of the work has focused on the use of plasmonic nanostructures for static images. In such applications, full colour graphics can be rendered in a single patterning step. The approaches used by investigators can be broadly categorized into two subgroups. Those which rely on altering the shape or size of a nanostructured layer and those which leverage near-field interactions between metallic nanostructures and an underlying substrate.

Particle shape and size

Many of the reported plasmonic features achieve variable colours by tuning nanoparticle shape or size. Often these structures are realized by top-down patterning such as e-beam or nano-imprint lithography.

Figure 2.9a illustrates one such example. In this work, the researchers relied on
Figure 2.9: a) Colour image rendered using sub-pixels consisting of nanoparticles having variable diameter - particles are supported over a backreflector by e-beam defined resist layer [1]. b) Colour structures with orthogonal asymmetry such that different colueration is observed depending on the polarization of the incident light [2]. c) Colouration of silver coins by laser annealing. Nanoparticle geometry and resulting colour dictated by radiation dose [3].
fabricating an array of sub-cells, each having a well defined particle diameter and spacing \[1\]. As the particle diameter is altered, so too is the resonance peak and perceived colour. E-beam lithography was used to define an array of such pixels to realize a colourful feature.

Figure 2.9b demonstrates yet another approach for realizing a tunable colour response by exploiting the polarization dependence of nanostructures that are not axially symmetric \[2\]. In such structures, a polarization sensitive response can be obtained with an cross structure that is elongated along one axis. As the polarization is rotated, one mode will become more strongly excited and the perceived colour will change.

While most published works have relied on fairly costly nanoscale lithography, recent work has sought to identify more scalable processes. In one recent example, shown in Figure 2.9c, plasmonic colouring of silver coins was achieved by spatially varied laser annealing \[3\]. In this approach, consistent nanoparticle distributions are achieved by controlling the dose. As the field continues to develop, increased focus on scalable fabrication processes is anticipated to be critical for any eventual commercialization.

**Gap controlled colour**

In rendering colourful features, gap plasmons can be tuned by either adjusting the particle size or the gap thickness. In recent years, several groups have demonstrated colour features based on exciting gap modes. Figures 2.10a and b demonstrate two such results. In their work, Miyata et al. achieved tunable colour by adjusting the size of aluminum nanodisks supported over a metal substrate by dielectric of fixed thickness \[4\]. With a single patterning sequence, a relatively broad range of colours could be achieved.
Figure 2.10: a) Variable colour achieved by exciting gap plasmons between aluminum nanoparticles of variable diameter and an underlying aluminum substrate. b) Photographic replication using plasmonic nanoparticles suspended over a backreflector.

Meanwhile, James et al. attempted to reproduce a photograph by varying the size of an aluminum nanorod, supported on a substrate by a dielectric post. Much as was done by Miyata, variable colour was achieved by defining rods of varying size. In addition, James made the point that the gap height could also be varied to access additional colours through interference effects. The latter phenomenon has been deployed by Qualcomm in realizing their interferometric absorber display and it is also the primary mechanism by which colour change is imparted in the structures constructed for this thesis.

2.2.2 Mechanically responsive colour structures

Although many researchers have reported plasmonic materials as optical sensors, relatively few have focused on a mechanically responsive platform. Nevertheless, metallic nanoparticles are well suited to such applications, owing to their high sensitivity to changes within their optical near-field. Of those researchers who have pursued strain
Figure 2.11: a) Colourimetric Sensor, linear chains of Au nanoparticles are suspended within a spun-cast PVP polymer matrix. Variable colour is achieved as pressure is applied and the inter-particle distance is increased \( \text{[9]} \). b) Au nanoparticles are deposited from a colloidal suspension onto an elastomeric surface. Colour response observed as applied strain causes changes in nanoparticle near-field coupling \( \text{[7]} \).

Sensitive devices, most have focused on colour shifts which arise due to particle-particle interactions as discussed in section 2.1.2.

While these are relatively simple to implement, they tend to require high strain. Although this may be appropriate for some use cases, it is not always possible to realize significant strain. This is, perhaps, one of the more compelling reasons for pursuing the deformable structures that will be reported upon through this work.

Illustrated in Figure 2.11a, is work by Han et al. \( \text{[6]} \). From a colloidal suspension of well isolated Au particles, Han chemically initiated the formation of linear chains, inducing a change in the colour from deep red to blue. The chains were then embedded within a polymer-matrix by spin-casting. As pressure is applied, deformation of the polymer induces an increase in the inter-particle spacing and a return to the initial red colour of well isolated particles. Fabrication is quite simple, although the pressures required to induce this change were on the order of \( 10^4 \text{ psi} \).
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Similar efforts have been undertaken by Cataldi et al. \cite{7}. In their work, nanoparticles were deposited on the surface of a PDMS elastomer by self-assembly. Once in place, the surface was subjected to an Au plating process to enlarge the particles and increase particle-particle coupling. Lateral strain applied to the resulting device induces a colour response. As is the case for most similar approaches, strain in the range of 10-20% is required for a visual response.

2.2.3 Electrically responsive colour structures

Finally, actively tunable colour structures remain a source of ongoing interest, particularly in pursuit of reducing power usage for displays. Unlike conventional display technologies that currently dominate the commercial marketplace (eg: OLED, LCD), a plasmonic display has the potential for high resolution and may potentially require fewer supporting materials, such as polarizers or back-lighting.

Many of the initial plasmonic display technologies have been based upon electrochromic style device structures. Figure 2.12\(a\) illustrates one such approach, where the researchers rely upon driving an electro-chemical reaction to achieve tunable colour \cite{8}. An array of gold nano-domes are placed within an electro-chemical cell containing \(AgNO_3\). Silver ions are reversibly plated onto the gold surface, altering the resonance and perceived colour.

Using an alternative approach, Xiong et al. constructed a reflective display technology based on nanolithographically defined nano-hole arrays separated from a back-reflector by a variable dielectric layer \cite{9}. In varying the dielectric thickness, the transmitted colour is also varied and the film acts as a colour filter. The nanostructures are then coated with electrochromic material. The nano-holes themselves act as antennas that allow the electrochromic material to attenuate incident radiation, as illustrated in Figure 2.12\(b\). The resulting display is capable of full-colour, although
it requires independent RGB channels and thus absorbs a significant fraction of the incident power.

Rather than utilize separate RGB pixels, another approach is to realize a single pixel capable of producing a continuum of colour. One such approach, illustrated in Figure 2.12 is based on displacing an ultrathin absorber structure within the standing wave of a mirror subjected to incident radiation \[10\]. For each wavelength, the standing wave has minima and maxima where absorption will be enhanced or reduced. As a result, for each position, there will be a unique colour.

One of the major challenges in realizing the above is in achieving suitable white and blacks. In their work, the researchers achieved this by attempting to select an optimal material for the 10 nm absorber layer. Additional challenges lie in the innate sensitivity of the device to variations in tilt. While this particular example does not rely on plasmon resonant materials, nanostructured films may serve as an improved absorber layer.

Beyond the above, there have been a few other works towards developing a dynamic, electrically tunable structure. Typically, however, these have relied on utilizing the plasmonic layer as an improved colour filter in combination with more conventional liquid crystal technologies. In one recent exception, researchers used liquid crystal materials to excite various modes within a surface plasmon grating \[31\]. In this structure, the effective index of the grating mode varies with the tilting of the liquid crystals and a single pixel could be used to generate multiple colours. Unfortunately, the platform did not have a means to vary the intensity of the reflected colour, limiting its applicability for displays.
Figure 2.12: a) Electro-chemically driven colour display structure. The device derives colour by reversibly plating Ag onto Au nanodomes. As Ag is accumulated, the resonance peak shifts [8]. b) Structure utilizes nanohole films in combination with electrochromic polymer to achieve electrically variable RGB absorbers [9]. c) A thin absorber material is displaced within the standing wave generated by incident and reflected light from a mirror. As the absorber moves, variable colour is observed [10].
Chapter 3

Fabrication Challenges

Fabrication presents perhaps the greatest challenge in the design and realization of dynamically tunable plasmonic devices. To date, most works have relied on one of:

- tuning the lateral distance/coupling between adjacent nanoparticles,
- tailoring the optical response electro-chemically, or
- modulating the background index using liquid crystals to exploit the polarization dependence of nanoparticles having asymmetry.

In general, dynamic control over the nanoparticle ensemble has relied upon realizing well-defined periodic nanoparticle arrays, generally achieved by slow and expensive e-beam lithography. Although highly detailed and colourful static features can be rendered using this approach, dynamic tuning of their colour has been limited to those applications where at least 10% in-plane strain is achieved. Among electro-chemical based approaches, those that rely on morphological changes in the nanoparticle shape or composition will typically have slow response times, changing over the course of tens to hundreds of seconds. Recent work, however, has demonstrated an electro-chemical response which is both fast and capable of full-colour when
using RGB filtering. Nevertheless, this approach also relies on nanoscale lithographic capability.

The simplest route towards dynamic device response leverages the polarization control of liquid crystal materials. In such approaches, incident polarization can be varied to selectively excite different modes of the underlying nanoparticle ensemble. In its most basic implementation, such features allow for continuous control between two colours. In most reported works to date, however, the plasmonic material acts as an improved colour filter rather than the active element. In all such approaches, complexity increases due to the requirement for additional polarizer layers.

Approaches based on MEMs tunable structures have generally focused on longer wavelengths, primarily for compatibility with conventional semiconductor manufacturing processes. For applications targeting the visible spectrum, little has been reported upon. This section will outline the basic characteristics of the tunable structures developed for this thesis along with details pertaining to some of the non-standard processes required for its realization.

3.1 Device Overview and Fabrication Requirements

The operating principle for the devices developed in subsequent sections rely on a deformable air-gap, illustrated in Figure 3.1. For such a structure, colour shifts arise as the nanoparticle coated surface is displaced relative to a reflective film. The change occurs as a result of either the nanoparticle array moving through the varying field of a standing wave or due to near-field coupling with the underlying metal reflector. The physics of these phenomenon have been described in Section 2.1.
**Figure 3.1:** An example of the envisioned tunable structure. Shifts in colour are achieved by displacing the nanoparticle bearing layer relative to a metallic reflector. Although this figure illustrates the nanoparticle layer as the deformable material, the reflector can serve this role as well. Key enabling processes are reliable nanoparticle assembly and realizing a stable deformable device platform.

The key challenges in realizing the proposed structure are:

- developing a simple and reliable nanoparticle assembly process, and
- realizing a stable deformable structure that can be actuated with acceptable forces.

### 3.2 Nanoparticle Assembly

Processes for nanoparticle assembly have received extensive attention in recent years. While many groups have favored structures defined by nanoscale lithography for its flexibility and convenience during initial development work, the following will focus primarily on techniques that may be more immediately amenable to high volume production.
In the course of this work, both silver and gold nanoparticles are deployed interchangeably. In some applications, notably those which required multiple plasma or wet cleaning steps, gold films were preferable due to the superior chemical inertness. In this work, the primary goal was to realize a plasmonic colour response. In subsequent works, the choice between gold or silver to achieve specific transitions will be of greater relevance.

### 3.2.1 Metal island film formation

The formation of metal nanoparticles by thermally activated de-wetting has been widely reported upon and is amongst the simplest means to realize plasmonic surfaces \[32, 34\]. The process and resulting film morphology in the case of gold island formation is briefly illustrated in Figure 3.2. At elevated temperatures, thin metal films agglomerate into nano-sized islands in order to minimize the total surface energy of the system. The primary limitation in producing such metal island films is in ensuring that sufficient temperature is applied to allow for the metal to migrate, and further, that the film is sufficiently thin for island formation to be energetically favorable.

Both silver and gold nano-island surfaces have been fabricated at the Carleton University Microfabrication Facility. Such films were realized by deposition of up to 10 nm of metal using evaporation or DC sputtering, typically on a clean SiO$_2$ surface. Subsequent annealing in nitrogen ambient at 200 C for silver and 400 C for gold is sufficient to form well defined nanoparticle arrays. The two films produce distinct colours. Films based on annealed gold are red when depositing initial films that were very thin (less than 5 nm) and tend towards blue as film thickness and nano-island size increased. Silver particles meanwhile, vary from yellow to orange with increasing
Figure 3.2: a) Ultra-thin gold or silver films are converted to nano-island films by annealing. In the case of gold on SiO₂, 400°C for one hour is sufficient. b) SEM micrograph of gold nano-island films following anneal of 10 nm thick film. c) Atomic Force Microscopy surface profile of a gold nano-island film. d) Size distributions from AFM imaging for a 10 nm annealed gold film.
film thickness.

Despite the enticing simplicity of such approaches, there are some drawbacks. Primarily these relate to the difficulty in controlling island shape and distribution. As depicted in Figure 3.3, the films realized in these works are characterized by a relatively broad distribution of nanoparticle shapes and sizes. Whereas isolated particles have relatively narrow resonant peaks, optical interaction between neighbors along with the presence of a continuum of resonance peaks serve to broaden the response. Several studies have reported upon techniques for controlling and directing the de-wetting process, typically by patterning the substrate or metal prior to annealing \[35, 39\]. As the field develops, repeatable and well defined nanostructured materials may be more reliably formed by such processes.

Although control is limited, such films are useful in developing prototypes of colour tunable structures. For example, Figure 3.4a and b illustrates variable colour response generated by a silver nano-island film separated from an underlying aluminum reflector. The nano-islands in Figure 3.4a are supported by an SiO\(_2\) surface having variable thickness. The variable thickness layer was formed by e-beam evaporation using a purpose designed mask to ensure an approximately linear taper across the length of the wafer. Details for this process can be found in Appendix A. Colour shifts arise due to the nanoparticle displacement within a standing wave as well as near-field interactions between each nanoparticle and underlying aluminum when the dielectric becomes very thin. The underlying physics of this response has been described in more detail in Section 2.1.
Figure 3.3: Optical transmission and SEM micrograph images of gold (left) and silver (right) metal island films. Thermally evaporated gold was annealed at 400 C for one hour while silver was annealed at 200 C for one hour. Nitrogen ambient was used in both cases.
Figure 3.4: a) Annealed silver formed above an aluminum reflector supported by SiO₂ having variable thickness. The tapered oxide is formed by a masked evaporation process described in Appendix A. Thickness ranges from 40 nm to 120 nm. The inset illustrates the same silver island film on a glass substrate. b) Illustrates significant change in perceived colour when a silver nano-particle layer is both well separated and when it is nearly in contact with the reflector.

3.2.2 Self-assembly of nanoparticles from colloidal suspension

Nanoparticle monolayers are often formed by self-assembly [25,40,41]. Nanoparticles suspended in a liquid medium can be deposited onto a surface by a controlled, and typically self-limiting, process. A particular advantage of this approach is the variety of particle shapes and compositions that can be formed chemically with a high degree of control and uniformity. While nano-island films formed by de-wetting are typically constrained in their shape, a wide variety of nanoparticles can be formed and subsequently deposited on a suitably prepared surface. For example, triangular silver nanoplates are commercially available and have been used to coat glass or PDMS coated surfaces, as shown in Figure 3.3.
Figure 3.5: a) Illustration of typical nanoparticle assembly scheme. A colloidal suspension of nanoparticles with a charged surface deposit onto a substrate having opposite charge. b) TEM images of silver nanoplates from nanoComposiX; these particles are among those that have been assembled onto functionalized surfaces at the Carleton Microfabrication Facility. c) Optical reflectance from nanoplates having variable distance to an underlying reflector. d) Optical absorbance of silver nanoplates when in colloidal suspension.
CHAPTER 3. FABRICATION CHALLENGES

Beyond the simplest approaches, generally resulting in randomly dispersed nanoparticle films, there exists significant research into more carefully controlled structures. For example, Langmuir-Blodgett assembly relies on constraining hydrophobic coated particles to the surface of a DI water trough. Particle density at the surface can be tuned and these particles can be subsequently transferred to an acceptor substrate. The approach has been shown to be feasible for realizing relatively dense films \[42\]. Another approach relies on the self-assembly of co-polymer films into nanoscale structures, typically referred to as block co-polymer films \[43\]. The resulting monolayers are intended to provide a nanostructured scaffold onto which plasmonic structures can be deposited. Such approaches are typically referred to as bottom-up approaches compared to top-down approaches which rely on conventional lithographic process blocks. While the former has reached manufacturing maturity, the latter becomes increasingly attractive as pattern feature sizes continue to decrease.

Self-assembly of particles mediated by functional monolayers

Most common chemical reactions for generation of metallic nanoparticles result in a negatively charged surfaces suspended in solution, illustrated in figure \[33\]. A stable surface charge is desirable both to prevent agglomeration of the particles through coulombic repulsion and to provide a simple means of condensing the particles onto a given surface. For negatively charged particles, the surface to be coated is treated to be positively charged and subsequently immersed in the nanoparticle solution. Over time (typically ranging from several minutes to hours), particles adhere to the surface. In general, adhesion relies on Van der Wals interactions between the surface and particle although there are cases where investigators relied on chemical bonding.

It should be noted that the above described process is sensitive to a number of variables. In general, the charges on both the particle surface and the substrate are pH
sensitive while the efficacy of particle-particle repulsion depends on the ionic strength of the solution. A full discussion of zeta potentials, and process optimization is outside of the scope of this chapter but is more carefully considered elsewhere [44][45].

In this work, two primary means for assembling nanoparticles onto surfaces were used. The first, and more common, was the assembly of negatively charged particles onto aminopropyl-triethoxysilane (APTES) or polyethylenimine (PEI) functionalized surfaces. In solution, these layers take on a positive charge, drawing in negatively charged particles. The second, relied upon assembly of positively charged particles onto negatively charged surfaces. Nanoparticles capped with a branched-PEI (BPEI) monolayer are positively charged and are commercially available. Meanwhile, many of the materials common to semiconductor manufacturing can easily be rendered negatively charged with brief exposure to oxygen plasma. In the course of this work both approaches were used to transfer nanoparticles onto SiO₂, PDMS, and Cytop surfaces. A SEM micrograph, in Figure 3.6 shows silver nanospheres assembled onto a Cytop surface as an example. Although the approach was found to be serviceable for initial characterization work, the relatively slow adsorption times and sparse NP concentrations resulted in pale and less visually interesting films. Nevertheless, as bottom-up and self-assembly based fabrication techniques mature, such approaches may become suitable for colour tunable applications.

3.2.3 Nanoparticle transfer processes

Although it is generally possible to form nanoparticles directly on the surface of interest through one of the above described mechanisms, the ability to form them on a donor surface and subsequently transfer them provides additional process flexibility and control. For example, the nucleation process for metal island films differs
between glass or silicon and non-rigid materials such as PDMS. In some cases, it could be beneficial to exploit the properties of a donor surface (eg: temperature or manufacturing compatibility etc.). In the course of this work, a transfer process was evaluated to ascertain whether the nanoparticle array could be optimized separately from the mechanical deformable structure.

Transfer of nanoparticles from a silicon wafer to a free-standing PDMS membrane proceeded as follows. Gold nanoparticle islands were formed on thermally oxidized SiO$_2$ by conventional deposition and annealing processes described in section 3.2.1. The nano-island surface was subsequently treated with HMDS in order to passivate the exposed SiO$_2$ surfaces. Finally, the sample was treated with 5% APTES in water. The APTES treatment provides a bond to the metal nanoparticles through the polarizable amine head group while also bonding covalently to the PDMS network via the exposed silane group. Immediately following APTES treatment, PDMS was spun-cast and cured on the donor surface.

Once cured, the PDMS film with embedded nanoparticles was released by immersing in water with ultrasonic agitation (or alternatively, by etching the SiO$_2$ surface in HF). Initial trials were successful, as illustrated in Figure 3.7. Similar transfer
techniques have been reported elsewhere and may ultimately provide a robust means of creating flexible nanostructured surfaces at high volumes [46].

### 3.3 MEMs Release Techniques

In this thesis, the deformable response was realized by one of two mechanisms. The first was by the lamination of two films and will be discussed in more detail in Chapter 4. The second approach is based on more conventional MEMs fabrication techniques. Specifically, a deformable air-gap device was realized by first building a multi-layer structure with embedded sacrificial materials. Once released, a free-standing bridge
**Figure 3.8:** Overview of MEMs based fabrication process for an electrically tunable plasmon structure. Metal nanoparticles are assembled onto a sputtered SiO$_2$ surface and subsequently coated by UV-patternable photoresist. The photoresist material forms a sacrificial structure upon which a deformable metal membrane can be formed and simultaneously protects the nanoparticles during metal pattern and etch. A final release step removes the sacrificial material while leaving the nanoparticles in tact and preventing collapses of the metal bridge.

can be deformed by a stimulus. The basic process flow is illustrated in Figure 3.8.

The primary challenge presented by a MEMs based approach lies in releasing free-standing structures while preventing collapse or permanent deformation due to large capillary forces. For example, using a wet removal process to dissolve the sacrificial material, the sample must be subsequently rinsed and dried. As the rinse material (eg: water) is removed, capillary forces can pull the newly released structures toward the substrate, typically causing irreversible strain. Examples of both successfully released and clamped structures are shown in Figure 3.9. Over the course of this
Figure 3.9: SEM micrograph images of released Aluminum membranes in a) perspective and b) cross-section views (scale bar is 1μm). Optical microscope images of c) successfully released and d) irreversibly clamped cantilever structures when samples were not properly dried.

work, several techniques were evaluated as potential solutions and were successfully deployed to release structures with air-gaps down to 100 nm thick.

By far, the most prevalent and simplest approaches to avoid capillary effects altogether is by using a dry release process. Such approaches typically rely upon removal of sacrificial material with plasma or vapor (e.g., O₂, HF vapor, or XeF₂ depending on the material). In particular, the use of oxygen plasma in combination with an organic sacrificial material is attractive. However, as the oxygen plasma was found to attack some of the NP materials, wet processes were preferred in this work. Furthermore, the isotropic plasma based tool that was readily available generated significant heat,
leading to damage / blistering of the organic sacrificial layer as it was etched.

Following a wet removal process, drying of the MEMs structure is often achieved by critical point drying. While this method provides reliable release, it was found to be incompatible with some materials (eg: fluoropolymers, PMMA) due to the high pressure involved and cannot be used for all applications. For such cases, a straightforward and effective research-scale technique was developed based on a freeze-dry release process. Here capillary forces are avoided by freezing a solvent with high vapor pressure and allowing it to sublimate.

3.3.1 Critical Point Drying

Critical point drying processes rely on immersing the sample in liquid, typically CO₂, and then converting it from the liquid state to that of a supercritical fluid. From this state, the medium can be controllably converted to gas and pumped away from the sample without damaging fragile structural features such as MEMs bridges or cantilevers.

The critical point drying release sequence used for this work is as follows:

- Sacrificial layer removal: Typically N-Methyl-2-pyrrolidone (NMP), a common solvent for photoresist, at 80°C for 30 minutes

- Immersion in isopropyl alcohol (IPA): IPA is miscible with both NMP and liquid CO₂. A two stage rinse process is used to replace residual solvent trapped near MEMs structures with IPA.

- Critical Point Drying: Without allowing the sample to dry, transfer it into an IPA filled chamber and seal it. Proceed with drying using liquid CO₂ as the working fluid. Critical point drying was performed using a Tousimis supercritical point dryer.
Critical point drying was the principle method utilized for release of free-standing micro-structures in this work. It was however, found to be incompatible when polymer materials comprised a portion of the final structure. For such instances, an alternative approach was developed based on freeze-drying of cyclohexane.

### 3.3.2 Freeze-Dry Release Process

In instances where a portion of the final structure, typically polymeric, was found to be incompatible with the pressures involved in critical point drying, a simple freeze-drying process was utilized as outlined below:

- Sacrificial layer removal with NMP
- Immersion in IPA which is miscible with both NMP and cyclohexane, the selected drying medium
- Immerse in cyclohexane for 30 minutes
- Remove sample from cyclohexane bath and place on a peltier cooler without allowing the sample to dry.
- Reduce temperature below the freezing point while flowing nitrogen ambient, allow 15 minutes for cyclohexane to sublimate until sample is dry.

The above procedure provides a secondary means of drying free-standing MEMs structures without their collapse. Cyclohexane has both a convenient melting point of roughly 6.5 \(^\circ\)C and high vapor pressure. As a result, the residual liquid in contact with free-standing structures can be frozen quickly and conveniently with a Peltier cooler.

From the solid state, drying of fabricated samples sublimation occurred within roughly 10-15 minutes. Maintaining a nitrogen ambient was found to be important,
both to expedite the drying process and to prevent condensation of water from ambient humidity. As the approach relies on the physical properties of cyclohexane, use of high purity grade chemicals is equally important as any impurities are likely remain on the sample. In practice, fresh ACS grade cyclohexane was found to be sufficient for initial test samples.
Chapter 4

Mechanically Tunable Plasmonic Colour

As the field of plasmonics has matured over the past decade, there has been increased focus on its applications. For example, the high optical density and tunability of plasmonic nanoparticles are attractive for developing novel colour responsive materials. In recent years, several groups have reported mechanically responsive materials that utilize resonant metal nanoparticles as the active medium \([6, 23, 26]\). In most such approaches, the colour is tuned by mechanically altering the distance between clustered nanostructures. While clustered, the nanoparticles interact strongly with one another \([13, 17, 49]\). As they are separated, their interaction decreases and the colour changes. The simplicity with which these devices can be fabricated, coupled with the highly sensitive response of nanoparticles to their surroundings, suggests a promising niche in pressure responsive smart film technologies.

Nevertheless, many of the previously reported approaches are limited to applications where significant lateral strain can be imparted upon the film (at least 10\%). In many cases, it would be desirable to integrate responsive colour features alongside other devices, or conventionally printed images, on common plastics such as polyethylene terephthalate (PET). Such features would be highly desirable as a mechanism for verification of secure documents, for example. While flexible, most carrier substrates
will not typically be subjected to forces where significant strain can be achieved. As a result, there exists a need for a mechanically responsive structure that can be integrated onto comparatively rigid carriers.

### 4.1 Device Overview

Like previous works the proposed solution relies, in part, on the mechanical response of a compliant polydimethylsiloxane (PDMS) elastomer (Sylgard 184). However, rather than relying solely on the interactions within a dense particle network, the nanoparticle (NP) surface is instead suspended above an aluminum reflector, as illustrated in Figure 4.1. In this configuration, the perceived colour depends not only on the arrangement of the NP film but also on its position with respect to the reflector.

Reflective interferometric colour features, where a thin absorbing layer is situated within an optical stack with an underlying reflector, have received significant academic [50][51] and commercial interest [10] in recent years. With a properly selected absorbing layer, a large colour gamut has been shown to be achievable. Common absorber materials used in conventional metal-insulator-metal (MIM) structures of this type are molybdenum, chromium, nickel. In the field of plasmonics, significant efforts have also been made in exploiting these effects in order to realize broadband optical absorption across the visible spectrum [52][54]. In general, the functionality of such devices rely on the far-field interaction between the absorber layer and the reflector. For nanoparticle systems, near-field interaction between the particle and reflector has also been demonstrated as a promising technology for colour generation [30][55][56].

Nanoparticle based plasmonic devices are an appealing avenue for novel colour tunable features. They can be formed either by vacuum deposition processes or assembled onto a surface from solution. Their shape and size dependence allows for
CHAPTER 4. MECHANICALLY TUNABLE PLASMONIC COLOUR

Figure 4.1: An overview of the proposed colour tunable device structure. (a) A nanoparticle layer is coated on a thin PDMS film while (b) patterned posts $\approx 0.4\mu m$ thick are applied to the aluminum reflector. (c & d) Once assembled, the PDMS deforms locally around the posts and the nanoparticle to reflector gap is reduced in response to pressure. The perceived colour is a function of the air gap. A pair of commercially available 100$\mu m$ thick PET (Dura-lar) films were used as the top and bottom substrates.

them to be optimized for the application. Finally, their unique optical properties can be leveraged to produce a response that could not be easily duplicated by other technologies. The latter, in particular, would be very useful for verification of authenticity. This chapter will describe the modeling, fabrication and testing of a flexible nanoparticle based mechanically responsive colour feature. In particular, the focus will be on describing the mechanical response of the structure, on modelling the optical system, and providing a proof-of-principle demonstration of the approach.
4.2 Mechanical Response

A significant disadvantage of existing mechanically responsive plasmonic devices is the constraint imposed by the materials. While a single layer tunable feature is attractive, it becomes difficult to tune the response to a particular application. Such changes require introduction of alternative (stiffer or more flexible) materials, rather than simple changes to the mechanical structure. Furthermore, with strains of at least 10% required for significant colour shifts to be observed, it may be quite challenging to realize a responsive feature on common printing substrates using these approaches. The proposed solution, illustrated in Figure 4.2a, is to suspend the deformable PDMS layer above a reflector layer. This arrangement provides sufficient latitude to alter the actuation pressure for a given application by adjusting the PDMS film thickness or the supporting post geometry. In the case of a touch actuated features, it would be desirable to achieve significant colour response with forces that can be easily attained by the human hand.

As pressure is applied to the structure, the PDMS film deforms and is compressed into the underlying gap (Figure 4.2b). As the gap is reduced, a continual change in colour is observed due to optical interaction between the reflector and NP surface. The deformation of PDMS in response to applied pressure was numerically evaluated using FEM (COMSOL) with a few simplifying constraints. The PET plastic was treated as a rigid surface and constrained to vertical movement without rotation, the supporting post was modeled as a fixed boundary, and contact with the aluminum surface was modeled by enforcing an upward force on the PDMS once the gap had been reduced to zero. Without significant changes to the material or fabrication processes, there are two primary variables that can be tuned. With increasing PDMS thickness, the film deforms at much lower pressures; the displacement represents a
Figure 4.2: (a) An overview of the mechanical structure and some relevant variables for controlling the response. (b) Illustrates PDMS deformation across the gap region as a function of pressure when $w_{Sus} = 30\mu m$ and $h_{PDMS} = 8\mu m$; axes have been denoted in a (c) Pressure response with respect to the PDMS film thickness with $w_{Sus} = 30\mu m$ (d) Pressure response with respect to the width of the supporting post with $h_{PDMS} = 8\mu m$. All results are based on finite element method (FEM) simulation using COMSOL with the Young’s Modulus of PDMS set to 1 MPa.
smaller fraction of its total thickness (Figure 4.2c). Similarly, reducing the width of the supporting posts decreases the required pressure by limiting the amount of PDMS that must be displaced for actuation (Figure 4.2d).

4.3 The Nanoparticle Film and Optical models

A variety of techniques for assembling nanoparticles on surfaces have been reported over the past few decades. The use of vacuum deposition followed by subsequent thermal annealing has a long history and remains common [32,57,60]. Such approaches rely on the coalescence of deposited silver or gold films into a disordered array of nanoparticles. While the resulting film can be difficult to optimize, the simplicity makes it attractive for development work and continued investigation is likely to improve the process [35,39]. Self-assembly from colloidal NP suspensions is another very common approach and allows for more control in the size and distribution of the particles [40,41]. While this work utilized 4 nm of thermally evaporated silver for NP formation, illustrated in Figure 4.3b, either of the above techniques would be suitable. The formation of silver nanoparticles on PDMS by physical vapor deposition has been previously demonstrated [61].

4.3.1 Proposed effective index approach for silver film

Direct simulation of randomly distributed films presents a computational challenge. It is significantly more efficient if the film can be accurately treated as a single homogeneous layer with uniform optical properties, as illustrated in Figure 4.3c. Measured transmittance and reflectance results, shown in Figure 4.3a, were used to develop an effective medium model of the film. As the particles are much smaller than the
Figure 4.3: (a) Experimentally measured (dashed) and modeled (solid) transmittance and reflectance from a silver nanoparticle film on a $\approx 4\mu m$ thick PDMS film. (b) SEM micrograph of the nanoparticle layer after thermal evaporation of 4 nm silver onto PDMS. Scale bar is 200 nm. (c) Schematic overview of film stack and how it is being modeled. (d) Extracted effective index values for film as a function of wavelength.
wavelength of light, an electrostatic treatment of the particles and their interactions was deemed reasonable.

When treated in the electrostatic regime, a spheroidal particle in vacuum can be regarded as a polarizable dipole with polarizability,

\[ \alpha = V \frac{\epsilon_{np} - 1}{1 + F (\epsilon_{np} - 1)} \]  

where \( \epsilon_{np} \) is the bulk permittivity of the particle material, \( V \) is its volume, and \( F \) is a parameter that depends on both the shape of the particle and its interactions with neighboring particles \[62\]. When treating the response of coupled dipoles, the interaction terms are absorbed within the factor \( F \). Similarly, when solving for the electro-static dipole response for a non-spherical particle (such as an ellipsoid), factors relating to their shape can also be collected within \( F \). Comparing the polarizability of an isolated sphere and equation \[4.1\] \( F \) has a value of 1/3 in the absence of inter-particle coupling.

In a disordered monolayer each particle would take on one of a continuum of values, due to both variability in size and inter-particle distance. In recent years, several groups have used similar approximations to build models intended to extract geometric data from colloidal solutions \[63\], or to efficiently calculate optical response of a film based on a known particle configuration \[64\]. As our analysis will be restricted to normal incidence, an isotropic response has been considered rather than a fully anisotropic treatment.

For a disordered array of small particles, the effective permittivity of the film can be calculated by weighting equation \[4.1\] with a probability density function \( P(F) \). This function is intended to model statistical variations in both the shape of the particles as well as its interactions. By summing these contributions we arrive at an
average permittivity for the film,

$$\epsilon_{eff} = 1 + q \int P(F) \frac{\epsilon_{np} - 1}{1 + F(\epsilon_{np} - 1)} dF$$  \hspace{1cm} (4.2)

where \( q \) is the volume mass fraction of the nanoparticles.

The optical properties of the NP film were fit to measured transmittance data, illustrated in Figure 4.3b, as follows. Fresnel’s equation for a thin film having finite thickness \( d = 10nm \) and permittivity, \( \epsilon_{eff} \), was used to calculate transmittance while the distribution \( P(F) \) was varied iteratively. At each step, the trial transmittance results were compared against measurement by least squares. In this work, a normalized dual Gaussian for \( P(F) \) was found to adequately describe the collective response.

The fitting algorithm had six free parameters; the first was the volume fraction of the nanoparticles, \( q \). Each Gaussian had associated parameters for their mean value and standard deviation. A final parameter served as a weighting factor between the two Gaussian functions. Guassian functions are both relatively common in nature and serve as a fairly adaptable trial functions for fitting responses that are primarily expected to broaden a primary peak. In the course of fitting, initial conditions were varied to assure convergence to a global minima. To build confidence in this approach, comparison between full-wave calculation and those based on an effective medium approach were performed and will be discussed in the following section.

The surrounding ambient materials were modeled as air \( (n = 1) \) and PDMS \( (n = 1.4) \). The bulk permittivity for silver was taken from Johnson & Christy \[27\]. The resulting effective index of refraction for the film \( \sqrt{\epsilon_{eff}} = n_{eff}(\lambda) - jk_{eff}(\lambda) \) is shown in Figure 4.3d. The influence of the PET substrate was not considered directly in this analysis. However, the measured transmittance has been re-scaled by a factor
of $1/9 = 1.11$ to account for reflectance at the air/PET boundary when measured (see also Appendix B).

The proposed model provides a good approximation for the NP film over most of the relevant wavelengths. The calculated reflectance, however, diverges from measurement at shorter wavelengths. One limitation of this approach is that contributions from higher order modes have been ignored. At very high filling factors, higher order resonance peaks will develop at shorter wavelengths. An improved model would incorporate these effects and could be anticipated to yield a superior match. Nevertheless, the effective optical parameters reported in Figure 4.3d will provide a foundation for exploration of the device response once a reflector has been added to the optical stack.

### 4.3.2 Optical response of proposed device structure using effective index method

Using the effective index approximation for the NP film, reflectance from the structure described in Figure 4.4a is calculated by the transfer-matrix method [65]. The optical stack consists of a PDMS ambient, the NP absorber layer, a variable air gap, and an optically thick aluminum reflector layer. The material data for aluminum was generated by interpolation of data from Rakic [66].

As anticipated, the reflected spectrum shifts as the absorber layer is pushed towards the reflector. Broadly speaking, the response is governed by the interaction between the absorber layer and the standing wave generated by interfering incident & reflected waves. The spatial distribution of these standing wave patterns are frequency dependent. Therefore, as the gap decreases, the absorbance for different parts of the spectrum are enhanced or attenuated.
Figure 4.4: (a) Calculated reflectance spectra as a function of gap between the NP film and the underlying aluminum as shown on right. The effective n & k values from Figure 4.3d were used for the NP film. (b) Reflectance spectra are mapped onto a chromaticity diagram approximating the visual appearance of the device to the human eye. The dashed ellipse circumscribes the region of the colour diagram that is traversed as the air gap is varied between 800 nm (denoted as O) and 10 nm (denoted as X).

The achievable range of colours for this device is depicted in Figure 4.4b. Reflectance spectra for air gaps ranging between 10 nm and 800 nm were calculated and then mapped to a chromaticity diagram. The nanoparticle film is strongly absorbing primarily in the blue portion of the visible spectrum and much more weakly absorbing in the red. As a result, the range of colour in this particular iteration of the device structure is constrained to producing near white to orange & red hues. However, several avenues do exist for improvement of the achievable spectrum coverage.

If the absorbing surface is formed via self-assembly or printing using nanoparticles with a variety shapes and materials, the effective permittivity could be optimized for a larger range of colours. In principle, this could simply involve depositing several different particles at once to provide more uniform absorbance across the visible spectrum. Similarly, it would also be possible to utilize non-plasmonic materials that are used in reflective MIM structures. In general, these metals provide a comparatively neutral response across the visible spectrum, allowing for a larger colour range.
Finally, one interesting possibility to generate a very unique colour shift feature would be to utilize gap plasmons. Gap plasmons are strongly absorbing modes that arise between a nanoparticle and an underlying reflector when the gap is less than 10 nm. The phenomenon has received significant recent attention from a variety of groups as a potential colour feature. As the mode decays very quickly with increased separation, the phenomenon would be highly desirable for realizing a sharp ON/OFF transition.

### 4.3.3 Comparison to full-wave numerical model

The adequacy of the proposed model has been validated against the results of a FEM calculation using a hexagonal array as described Figure 4.5. In this model, the nanoparticles were considered to be hemispherical with a fill factor of 40%. A periodic unit cell was created, using symmetry to reduce the numerical complexity; only normally incident light has been considered for the purposes of this work.

The initial step in this process was to calculate the predicted response of a Ag NP film in the absence of a reflector structure. The results of this calculation were fit using the effective index method described above and are illustrated below in Figure 4.6a. The fit conforms very well to the FEM models and generates effective index values as a function of wavelength, as shown in Figure 4.6b.

The response of the PDMS:Ag:Gap:Al structure predicted from FEM calculations was then compared to those of the effective index model at a selection of air gaps. As illustrated in Figure 4.6c & d, the effective index method provides a good match to the numerical results, particular above 450nm. At shorter wavelengths, the fidelity begins to degrade. This is likely to be due to the presence of higher order responses within the array that can not be modeled as a collection of dipole resonators. Nevertheless, the
proposed model appears to capture the dominant features of the proposed structure.

### 4.4 Fabrication

The fabrication process follows the sequence that was briefly outlined in Figure 4.1. The absorber substrate and reflector substrate are processed separately and subsequently laminated together. 100\(\mu m\) thick Dura-lar clear plastic was used as the carrier for both sides of the device.

#### 4.4.1 PDMS-nanoparticle film formation details

2.2 g of the two-part Sylgard 184 was prepared using the recommended 10:1 mixing ratio. The mixture was subsequently diluted using 12 mL of ACS Reagent grade Hexane and mixed for 3 minutes. PDMS films were formed on clear PET substrates
Figure 4.6: (a) Effective index method was fit to the calculated FEM results for Ag NPs on a PDMS substrate. (b) The extracted complex index as a function of wavelength. (c) Optical response of a PDMS:Ag NP:air gap: aluminum structure as predicted by FEM compared to - (d) the effective index method...
by spin-casting. The solution was dispersed by syringe using a 0.4\(\mu m\) nylon filter at a spin speed of 1000 RPM for a uniform spread. Final spin cycles ranging from 2000 RPM - 6000 RPM for 30s were used to evaporate most of the hexane. The PDMS films were cured on a hotplate for 2 hours at 100\(^{\circ}\)C. Final film thicknesses of approximately 4\(\mu m\) to 5\(\mu m\) were achieved depending on the final spin speed, as measured by contact profilometry (Tencor P1 Profilometer).

The film thickness was selected based on initial experimental work suggesting that PDMS films which were too thick had insufficient restoring force, while films which were too thin required increased actuation forces. The chosen thickness represented a compromise between low actuation and a restoring force sufficient to pull away from the reflector once pressure had been released. Following elastomer formation, silver nanoparticles were formed by thermal evaporation and subsequent annealing.

Silver films were deposited by thermal evaporation in an Angstrom Engineering COVAP tool with a targeted film thickness of 4 nm, as monitored by in-site quartz crystal micro-balance. Deposited films were typically orange with a well-defined absorbance peak rather than something more spectrally broad, indicating dewetting of the film and formation of plasmonic metal islands on the PDMS surface. Subsequent annealing at 120\(^{\circ}\)C was conducted to improve adhesion of the metal islands to the surface.

4.4.2 Reflective film formation

A 100 nm aluminum reflector was deposited on the second PET substrate by evaporation. The gap defining posts were formed using spin-coated SU-8 2010 (a negative epoxy based photoresist) diluted in cyclopentanone to achieve the desired 0.4\(\mu m\) thickness. The posts comprise a series of long 40\(\mu m\) wide stripes and have a pitch of 240\(\mu m\). In addition to providing mechanical spacing, SU-8 was selected to provide
a surface group capable of chemically bonding to the PDMS surface. Lamination is possible due to chemical bonding between the SU-8 epoxy groups and a plasma nitrided PDMS surface [67,68].

### 4.4.3 Plasma Nitrogen bonding

The Ag nanoparticle coated PDMS and patterned SU-8 surfaces were thermally bonded following chemical activation in a nitrogen plasma. Plasma activation was conducted using a March Juniper II RIE etching system and $N_2$ ambient. The coated PDMS films were exposed to nitrogen plasma for 10 s using 100 W of RF power. Following plasma activation, the PDMS and SU-8 surfaces were placed into contact at a temperature of approximately 120°C for one hour. Prior to temperature cycling, the films could be separated and re-positioned. The bond becomes irreversible only after thermal treatment with de-lamination typically occurring at the PDMS-PET interface when forcibly pulled apart.

### 4.5 Results

Characterization of the pressure response was accomplished by means of a strain gauge (Micro-load cell CZL616C) mounted under a microscope objective, as shown in Figures 4.7a & 4.7b. The device under test (DUT) is attached to a rigid polycarbonate (PC) load plate and supported by the gauge. As the plate is loaded with weight, a force is applied to the DUT, which in turn is measured by a piezoresistive bridge. The force is distributed across the DUT by means of a thin elastomeric film roughly 1.5 cm x 0.5 cm; pressure was assumed to have been applied uniformly across its surface. The optical response was acquired with an Ocean Optics 4000 spectrometer
Figure 4.7: (a) Overview of apparatus for testing pressure response. (b) Photograph of test set-up with sample inserted between strain gauge and the load plate. (c) Measured reflectance of the device with increasing pressure. Oscillations due to thin film effects arising from PET-PDMS boundary. (d) Photograph of fabricated device being actuated by bending. An adhesive diffuser layer was applied to the top surface to improve visibility from varied angles.
and is provided in Figure 4.7c. The sample is illuminated through the microscope with a halogen light source. The spectral response of the source was accounted for by measuring the reflectance from a blanket aluminum film and referencing all subsequent measurements to this response.

The oscillations in the recorded spectra of Figure 4.7c are due to index mismatch between the PDMS and PET (these can also be seen in optical transmittance through PET & PDMS available in Appendix B). The period of the fringes observed in Figure 4.7c are consistent with those found from a reference spectra of a PET/PDMS stack of the same thickness, as measured by profilometry.

Significant absorption is also evident at wavelengths lower than 425nm; this feature is due to an adsorption edge in the polycarbonate plate and unrelated to the device (for optical characteristics of polycarbonate plate, see Appendix B). The colour variability observed in Figure 4.7c is due to thickness variations of the spin-cast PDMS film. Once the device is assembled, these variations create a corresponding variation in the gap and colour and can be observed more clearly in Figure 4.8. The underlying reason for such non-uniformity is due to the high evaporation rate of n-hexane during spin-casting. A more uniform elastomer surface should be achievable with additional development work using alternative solvents.

In agreement with expectations, a visually apparent colour shift feature has been achieved that is compatible with touch actuation, as demonstrated in Figures 4.7d and 4.8. The device underwent complete actuation at an estimated pressure of 12 psi, which is lower than anticipated based on initial FEM modelling efforts. This is likely due to the spun-cast PDMS from a dilute suspension being softer and more easily deformed than anticipated or due to the variations in the gap thickness.
Figure 4.8: Mechanically response of proposed device as a function of pressure. Colour non-uniformity due to variability in the air-gap thickness is evident until complete contact has been established. As pressure is removed, the device returns to its original configuration.

4.6 Outlook

To my knowledge, the above represents the first demonstration of a plasmonic pressure sensor that does not require significant strain to be imparted on the carrier substrate. As a result, it may be more suitable for integration on commercial plastics than previously demonstrated approaches. Towards this goal, significant challenges remain. The long term reliability of the PDMS structure requires testing to ascertain whether its deployment would be compatible with the typical strains and temperatures sustained during volume fabrication and over life. The variability in the air gap imparted by the current spin-casting process should also be further developed in order to have more uniform and controlled colour transitions. Finally, the dominant failure mechanism was delamination at the PDMS-PET interface. No attempt was made to enhance adhesion between the two surfaces and this could likely be improved by the addition of an adhesion layer prior to spin-casting.
CHAPTER 4. MECHANICALLY TUNABLE PLASMONIC COLOUR

Optimized nano-particle film

The nanoparticle layer deployed in this structure could be accurately characterized as an array of randomly dispersed silver hemispheres. Both the size and the degree of particle-particle coupling were controlled only by the deposited film thickness. It is believed that significant improvement in colour response and the visual appeal of the feature could be achieved by adopting an engineered nanostructure. For example, using a transfer process similar to the one described in section 3.2.3 would allow for nanostruture definition to be performed and optimized on a donor substrate prior to being embedded within the elastomer. Such an approach could allow for dramatic on-off features by exploiting gap plasmons as shown in section 2.2.1.

Improved modeling

Finally, the model utilized in the above work was useful primarily due to the limited influence of higher-order nanoparticle-substrate coupling. As new devices are produced, presumably leveraging some of these features, improved models would be useful in design and characterization. Accurate full-wave models for complex nanostructures tend to present significant computational challenges. Future development would be significantly improved by continued progress in this space.
Chapter 5

Electro-Mechanically tunable plasmonic colour

Over the past decade, displays based on the controlled reflection of ambient light have received sustained commercial and academic attention. Compared to conventional emissive technologies, those based on reflective structures typically offer greatly reduced power consumption. Demand for portable devices over an expanding range of form factors coupled with the incentive to reduce fabrication costs and extend battery lifetime has fueled ongoing research. Despite this, many existing and proposed solutions suffer from poor colour saturation and brightness due to the use of a RGB sub-pixel. In order to generate red, for example, the blue and green sub-pixels must be rendered fully absorbing (‘off’). As a result, roughly 90% of the incident ambient light must be absorbed in order to generate a single colour. Coupled with spectrally broad reflectivity from the imperfect ‘off’ pixels, the resulting colour can be muted compared to conventional LCD or OLED technologies.

Recent work, based on a variable metal-insulator-metal (MIM) structure, has demonstrated the potential for a reflective display where each pixel is capable of generating a continuum of colours rather than just one \[10\]. Several groups have also
Chapter 5. Electro-Mechanically Tunable Plasmonic Colour

reported similar MIM structures for use as colourful high resolution static images [50][51][69]. In this approach, the gap between a thin optically absorbing layer and an underlying reflector is modulated to achieve the desired colour. Colours arise due to interaction between the absorbing film and the underlying reflector. As the absorber is displaced, absorbance at each wavelength can be either enhanced or reduced. A large colour gamut - including black and white - can be achieved with optimization of the absorber’s complex refractive index [10]. Typically, the absorber is a homogeneous thin metal film (e.g., Ni, Cr, Mo) deposited by physical vapor deposition. Although none of the commonly used materials have ideal n-k values across the visible spectrum, co-deposition of multiple metals has been demonstrated as one method to improve them [10]. Another possibility, which may offer increased tunability and process flexibility, is to use a heterogeneous film consisting of nanostructures or plasmonic metal nanoparticles (NPs).

Several groups have proposed metal nanoparticle based structures to replace conventional pigments (see Section 2.2), to improve absorption efficiency of solar cells [70], or to produce sensors [71]. In these applications, the plasmonic nanoparticles are attractive due to their intense and tunable optical properties. With respect to the above described reflective display, the optical properties of the absorber layer could be tuned by utilizing a combination of particles with various shapes, sizes, or even materials.

Several groups have reported broadband absorber structures by coating a reflector with plasmonic nanoparticles [52][54]; interactions between an underlying spacer, the NP film, and the reflector materials produce a visually black surface. In many of these works, the NP film behaves as a homogeneous layer with an effective index that has been optimized for the task. In other works, the response is due to highly
CHAPTER 5. ELECTRO-MECHANICALLY TUNABLE PLASMONIC COLOUR

absorbing modes that arise within the NP film and reflector gap, appropriately referred to as gap plasmons, discussed in section 2.1.2. For a given structure, these modes are excited at well defined wavelengths which depend on the material, gap thickness and particle size. When particles of varying size are incorporated onto a surface, the combination of several distinct modes provides broad absorbance across the visible spectrum. Alongside their useful optical properties, NP films can be produced by a continually expanding range of fabrication processes. Although e-beam lithography remains common for development work, several techniques are compatible with large area processing. Among these are: vacuum deposition followed by thermal annealing [32,34,57], nano-imprint lithography [72,73], and self-assembly from solution [25,40,11].

Due to their appeal, there have been several recent reports on dynamic tunable displays based on plasmonic nanoparticles. Recently reported on electrochromic display technologies which utilized nanostructured gold and optically active polymers [8,9]. Meanwhile, other works have produced displays which take advantage of the anisotropy of liquid crystal materials in tandem with plasmonic surfaces to realize actively tunable structures [2,31]. A MEMs-based structure whose colour is tuned by controlling the nanostructure pitch have also been reported upon [74].

In this chapter we describe a MEMs based tunable structure, illustrated in Figure 5.1 capable of producing a voltage driven response. Along with an overview of its operation, we will discuss the fabrication and testing of a proof-of-principle device.

5.1 Design Considerations

The essential elements of the proposed MEMs-tunable structure are illustrated in Figure 5.1. A reflective aluminum bridge is suspended above a nanostructured film. As
the voltage between the bridge and an underlying transparent substrate is increased, the gap between them is reduced. Colour changes arise due to the optical interaction between the two surfaces and will be more fully described in section 5.1.2.

Although not depicted, the bridge is mechanically supported by anchors to the substrate on either side. These supports provide the restoring force necessary to prevent immediate collapse of the membrane upon application of potential across the device. A simple 1D model is instructive in understanding the electro-mechanical response. For a given applied voltage, there will exist at least one displacement where the electric and mechanical forces are in equilibrium. As voltage is increased, membrane displacement will also increase, as illustrated in Figure 5.1. The simplest of these structures also have a potential beyond which the electric forces will be sufficient to pull the device into contact. The voltage at which this occurs is commonly referred to as the pull-in voltage.

5.1.1 Electro-Mechanical response

Voltage response

The voltage response of the MEMs based structure depends primarily on the effective electrical thickness of the initial gap and the mechanical properties of the membrane along with the support structure. Some initial finite element modelling was performed to identify structures that were both manufacturable and could be actuated with easily attainable voltages.

To this end, calculations were based on a 2D membrane fixed at either end, illustrated in Figure 5.2d. The membrane’s mechanical properties were based on those of bulk Aluminum, selected primarily for its optical properties. A nominal membrane thickness of 1 \( \mu m \) was selected for its compatibility with manufacturing processes.
\[ F_{\text{net}} = \bar{F}_e + \bar{F}_m \]  \hspace{1cm} (5.1) \\
\[ F_{\text{net}} = -\frac{\varepsilon_0 AV_a^2}{2(d_0 - \delta)^2} - k_{\text{mech}} \delta \]  \hspace{1cm} (5.2) \\
At equilibrium:
\[ V_a = \sqrt{\frac{2k_{\text{mech}}}{\varepsilon_0 A} (d_0 - \delta)^2 \delta} \]  \hspace{1cm} (5.3)

Figure 5.1: Basic model for an electro-optically responsive structure. The reflected colour varies as a function of membrane displacement. The electro-mechanical response of the structure is dependent on both the applied field and the mechanical restoring force.
although membranes as thin as 500 nm were also fabricated in practice.

As observed, both in the 1D model and 2D FEM results, there can be multiple solutions for a given voltage at equilibrium. As a result, direct calculation of displacement as a function of applied voltage can result in convergence issues, particularly at the pull-in voltage. Instead, the average membrane displacement was specified. From there, the voltage to maintain equilibrium was calculated and reliably converged well past the point of pull-in. Direct contact between the membrane and underlying substrate were modeled as an upward force that increased rapidly with displacement following contact (essentially a very rigid spring).

The results of FEM calculations can be observed in Figure 5.2a and b. The response can be categorized into three phases. In the first phase, prior to pull-in, the membrane is pulled inwards with increasing voltage. At each point, there is a well defined and ever increasing potential required to balance the mechanical restoring force. At the onset of the second phase, pull-in is achieved. Beyond pull-in, the voltage required to offset the mechanical forces decreases until contact with the substrate is established. In practice, most of these solutions are never physically realized as the membrane moves into near instantaneous contact with the substrate once the pull-in voltage is reached. Finally, beyond the pull-in voltage increased potential will serve to increase the fraction of the membrane that is in contact with the substrate.

Examining Figure 5.2a, the pull-in voltage can be recognized as the maxima of the initial parabolic response. These peaks have been extracted and presented in Figure 5.2b as a function of the initial air gap. As one might anticipate, increased gap thickness tends to stretch out the voltage response.

Several test structures were fabricated in order to verify that the anticipated voltage response were achievable. Briefly, these devices were fabricated using 2"
Figure 5.2: a) FEM calculated voltage required to achieve equilibrium as a function of membrane displacement for various initial air gap. b) Pull-in voltage as a function of air gap extracted from calculations and from fabricated devices. c) Capacitance-Voltage response for suspended aluminum membranes with varying air gap. d) Illustrative schematic of a 2-D model for the membrane structure along with the C-V test setup. In all cases, the aluminum membrane was 1 \( \mu m \) thick.
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silicon wafers with 100 nm of thermal oxide. Membranes were formed by depositing 1 \( \mu \text{m} \) aluminum over a sacrificial photoresist layer. Variable gap thicknesses were achieved by timed etching of the initial photoresist in an oxygen plasma. The resulting gap thicknesses were estimated based on contact profilometry. The sacrificial removals and release process are described more fully in Section 3.3.

Looking to Figures 5.2b and c, the pull-in response trends behave as anticipated and the required voltages are well within reach of typical lab equipment. For these samples, the pull-in voltage was characterized by measuring the capacitance of the device with increasing bias using a 1 MHz HP4280 CV meter. A sudden increase in capacitance indicates the onset of contact between the membrane and substrate. As anticipated from prior calculations, capacitance increased monotonically beyond this point as the contact surface area increases.

For simplicity, the membranes have been fabricated as a simple bridge anchored on either side. One limitation of this approach in rendering a uniform colour response is that extent of deformation across a given pixel will not be constant. Figure 5.3 illustrates spatial response of the membrane for a sample with an initial gap of 300 nm. Prior to the pull-in voltage significant variation in the residual gap thickness, and thus the anticipated colour, is observed. Only after full contact with the underlying substrate is established can we expect a uniform colour to be observed. As a variable colour pixel, this could be problematic in some applications. Nevertheless, improved structures can be realized.

As illustrated in Figure 5.3b, a substantially uniform membrane displacement can be achieved by altering the design of the mechanical support system. Without change to the material or gap, a significantly more uniform response can be achieved by decoupling the anchors from the membrane through serpentine support structures.
Figure 5.3: a) FEM calculations illustrating the 2D response of an aluminum bridge membrane subjected to voltage. Significant deviation in displacement is observed across the membrane. Colour scale represents vertical deviation of the membrane in nanometres from one that is perfectly flat. b) An improved membrane structure, providing uniform displacement in response to applied electric potential. Deviation is within 5 nm for a deflection of 200 nm.

With variability anticipated to be less than 5 nm, a highly uniform colour response can be anticipated. Similar structures have been deployed empirically by other groups for MIM-type reflective displays \[10\].

**The influence of stress on released membranes**

To this point, the released membrane has been assumed to be free of any stress prior to the application of potential. In many instances, however, the influence of stress can impart significant deformation onto the membrane after its release. An example of this effect is illustrated in Figure 5.4 where a 200 \(\mu\text{m}\) \(\times\) 150 \(\mu\text{m}\) aluminum bridge is deformed by the presence of a dielectric cladding layer; first applied to the bottom of the membrane and then also to the top.

Film stresses arise in deposited films either as a result of defects within the film or
Figure 5.4: Finite Element Method calculations illustrating the deformation of a 1 $\mu$m thick Aluminum bridge as well as the influence of stressed dielectric cladding. The membrane mechanical parameters are assumed to be those of bulk aluminum with an in-plane tensile stress of 20 MPa. The influence of additional dielectric cladding of thickness 400 nm and tensile stress of 20 MPa are illustrated. The mechanical properties of the dielectric cladding are for those of Cytop fluoropolymer, with young’s modulus of 1.5 GPa.
due to differences in the thermal expansion coefficients of various materials within the
structure. In general, thin film depositions are carried out in variable process condi-
tions. In circumstances where deposition occurs at elevated temperatures, film stress
arises as the structure cools to ambient temperature. Upon release from underlying
supporting structure, the residual stresses can severely deform the membrane to the
point that there is too much colour variation within a pixel, the pixel is irreversibly
clamped, or the pixel cannot be actuated. As a result, such stresses are important to
consider and minimize.

In considering the possibility for various device structures, it was found that a
single dielectric cladding under the membrane could severely impact response, to the
point of preventing actuation. The latter was found to occur both in the case of ebeam
deposited SiO$_2$ which retains significant compressive stress as well as in the case of
Cytop fluoropolymer, which has been found to have a residual tensile stress \cite{75}. In
such cases, it was found that using a more symmetric structure significantly im-
proved, though did not eliminate, deformation of the released membrane, illustrated
in Figure \ref{fig:stress_response}.

Fortunately, aluminum thin films deposited by e-beam evaporation have relatively
low stress and can be released and tested without significantly impacting the device
response. Nevertheless, in future iterations it would be preferable to achieve a nomi-
nally flat membrane by optimizing the stress response.

\subsection{5.1.2 Colour response}

The colour response of a reflective layer in proximity to an array of plasmonic nanopar-
ticles has been described, in part, in section \ref{sec:colour_response}. As the distance between them
varies, there are two primary coupling mechanisms through which colour shifts are
achieved. The first arises by interferometric coupling between the nanoparticle layer
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and the standing wave established between incident and reflected fields. The second effect is significant only when the two surfaces are in close proximity. In such instances, near field coupling induce shifts in the plasmon resonance. When resonance occurs within the visible spectrum, the shift is perceived as a colour change.

In this work the structure proposed in Figure 5.1 was realized with an aluminum membrane suspended above an array of gold nanoparticles, formed by thermally induced dewetting, discussed in section 3.2.1. The resulting nanoparticle array, in Figure 5.4a, shows a highly variable ensemble. While a complete optical treatment of the film presents significant computational challenges, the source of its colour can be understood by decomposing it into simpler sub-tasks.

The SEM micrograph from Figure 5.5a can be processed to extract an array of particles having ellipsoidal cross-sections. Once the particle distribution and fill factor are captured, as illustrated in Figure 5.5b, the collective response can be approximated as the aggregate response of each particle in the distribution treated independently.

The contribution from each particle within the assembly was treated as a periodic array having 25% fill factor. Periodicity was enforced by exploiting symmetry at the boundaries of the unit cell, shown in Figure 5.5. At normal incidence, orthogonal perfect electric (PEC) and perfect magnetic (PMC) walls are mathematically equivalent to a periodic structure. These boundary conditions are sufficient to replicate an array of particles where incident light is polarized parallel to the perfect magnetic walls. Although not rigorously accurate, the treatment of each constituent element as a periodic array emulates the effect of a modified near-field due to the presence of other particles.

Full-wave calculations using the above approach were carried out in COMSOL. The physical model for the nanoparticle geometry is illustrated in Figure 5.6. Particles
Figure 5.5: a) SEM micrograph of annealed 10 nm gold island film, similar to those shown in section 3.2.1, was processed to create an array of ellipsoidal particles with distributed radii. b) Distribution of the equivalent radius for the gold nanoparticle with a mean value of 55 nm and a fill factor of roughly 25%. c) Unit cell for computational model, using symmetry to reduce the problem. Each particle is modeled independently as a periodic array. A sum of the contribution from each particle is used to estimate the total optical response of the assembly.
Figure 5.6: a) The aggregate transmittance of the Au nanoparticle assembly on a glass substrate at normal incidence (solid); estimated as the sum of individual particle responses. Example for the response of a small and large particle are also shown (dashed). b) Finite Element Method (FEM) model for one of the constituent Au NPs.

were treated as being primarily cylindrical with an ellipsoidal cross-section, described above. The rounded upper surface was primarily used to prevent computational issues due to an abrupt corner at the top surface. Particle height was defined by the smallest semi-axis, based on the presumption that height would be roughly correlated to size. The particles are supported by a glass substrate and periodic boundary conditions were applied.

After treating each particle separately, the total transmittance across the visible spectrum was estimated with an incoherent sum:

$$T_{\text{total}} = \sum_{i=1}^{N} \frac{T_i}{N}$$  \hspace{1cm} (5.4)

The aggregate transmittance at normal incidence is illustrated in Figure 5.6b.
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When compared to independent contributions from smaller particles, the aggregate response is significantly broadened and red-shifted. Similarly, it is significantly blue shifted from the response of the larger particles within the film.

A broader response can be useful in achieving large colour gamuts based on interferometric effects. Unfortunately, it is relatively difficult to optimize the gold nano-particle film as it has been fabricated here. As mentioned elsewhere, significant opportunities exist for innovations that leverage the simplicity of dewetting processes with the tunability of more complex ones.

Despite these limitations, for the purposes of development and demonstration, the proposed device structure has been realized using the above described NP film. In order to examine some of the features of such a device, the optical response of this NP film in the proximity of a metal reflector was calculated by FEM.

To simplify the problem and focus on the basic features of the response, calculations were performed and have been presented in Figure 5.7 using an average particle having a radius of 55 nm. For a air gap thickness of 210 nm, the reflectance spectrum is nominally comparable to that of a 55 nm particle in the absence of any reflector, though it is slightly modified by the optical cavity in which it resides. As the gap is reduced to 135 nm, interferometric effects substantially increase absorbance at shorter wavelengths. Finally, at 60 nm separation near-field coupling begins to dominate. Significant red-shifting of the resonance is observed, leading to strong attenuation in the red-portion of the spectrum.

The NP film itself can be optimized such that the interferometric response will yield a full colour gamut. Alternatively, one could focus on optimizing the near-field response; exploiting phenomena such as gap plasmons to achieve the desired colours. To the author’s knowledge, the latter approach has so far been limited to static images.
**Figure 5.7:** Spectral response of annealed Au NP film suspended above an aluminum reflector, as calculated by FEM. For these calculations, a mean NP radius of 55 nm and fill factor of 25% were used. As the air-gap between the two films is reduced, significant changes in the optical response are observed. For larger gap thicknesses, the response arises due to far-field interference effects. Near-field interactions dominate as the particles are brought into close proximity, yielding significant red-shifting of the plasmon response.
defined by e-beam lithography. In what follows, the focus will be upon achieving an electro-optical response, with future work being aimed towards optimization.

5.2 Fabrication

The basic fabrication loop for the proposed structure was briefly outlined in Section 3.3. A commercially available transparent ITO coated substrate was first covered by SiO₂ using RF sputtering. The primary purpose of the SiO₂ layer is to prevent electrostatic discharge between the transparent conductor and the aluminum membrane upon contact. As the fabricated device would be subjected to relatively high electric fields, initial depositions were conducted to identify a process that would yield a reliable insulator.

In general, as-deposited films were found to suffer from low breakdown voltages along with visually perceptible absorbance, presumably due to defects in the film. Subsequent furance annealing in oxygen ambient at 400 °C was found to simultaneously improve both. A final SiO₂ film thickness of 200 nm was selected, with breakdown voltages in excess of 20 V.

Following dielectric deposition, a 10 nm thick Au film was deposited by e-beam evaporation and subsequent annealed at 400 °C to form the films depicted in Figure 5.5. The resulting particles were then protected by photo-patternable Shipley S1800 photoresist.

S1800 was deposited as a sacrificial material by spin-casting and baking. Additional post-baking was found to be important to fully out-gas the sacrificial material; approximately 135°C for 5 minutes. An insufficient bake process rendered the device highly sensitive to subsequent thermal processing, resulting in bubbles / deformation. Subsequent to curing, the photoresist was subjected to a timed etch in oxygen plasma
to thin the spacer to the desired thickness. For the demonstrated device, an air gap or roughly 250 nm was selected.

A brief etch in aqua regia (HCl+HNO₃) was sufficient to remove any exposed nanoparticles prior to aluminum deposition. The aluminum reflector membrane was deposited by e-beam evaporation to a thickness of 500 nm. Following aluminum pattern and etching in warm phosphoric acid, device release was carried out by liquid CO₂ critical point drying, as described in section 3.3.1

Subsequent to a successful release, the exposed surfaces should be passivated to prevent uptake of ambient moisture. Ambient humidity is known to contribute to stiction and eventual device failure in successfully released structures. Often the best approach is to rely on hermatically sealing the device following release. Other approaches rely on grafting a hydrophobic polymer group to the surface, typically a fluoropolymer. For prototyping, hexamethydisilazane (HMDS) was found to be suitable. HMDS is commonly used in CMOS lithographic processing to promote photoresist adhesion by preventing absorption of moisture. HMDS passivation is a vapor based process and is ideally suited to coating surfaces, including those within the narrow air gap.

As illustrated in Figure 5.8, released MEMs samples were both successfully released, passivated by HMDS. The resulting devices could be reversibly actuated and were stable for subsequent testing. The C-V measurements captured in Figure 5.8 illustrate both the onset of the pull-in voltage as well as its return when voltage was swept in reverse.
Figure 5.8: a) Surface of released MEMs structure after being coated by Hexamethyldisilazane (HMDS) immediately subsequent to critical point drying. HMDS is commonly used in semiconductor manufacturing to render a surface hydrophobic. The treatment is useful in preventing stiction. b) SEM micrograph of a released aluminum metal bridge with 1.4μm air gap. c) Capacitance-Voltage response of a released bridge structure with air gap of 1.4μm; both the pull-in and return to equilibrium are captured; 150μm x 100μm bridge (left) and 200μm x 100μm bridge (right).
Figure 5.9: Schematic and photograph illustrating test set-up for electro-optical characterization of fabricated devices. Samples were mounted and probed from the lower side of the substrate while the voltage dependent optical response was viewed from the top. An Ocean Optics USB4000 spectrometer was coupled to microscope output to record the spectral response.

5.3 Results

Fabricated devices were electrically probed while being monitored using a microscope objective. The objective served both as a light source and as a monitor for reflected light. The setup, illustrated in Figure 5.9, involved supporting the sample while probing from the underside. In addition to optical images, spectra were recorded using an Ocean Optics USB4000 spectrometer. All reported results were referenced against the spectra recorded for a blanket deposited aluminum film.

The observed colour response is captured in Figure 5.10. At 0 V to 3 V, the response is dominated by interferometric effects described above. At pull-in, a significant red-shift is observed due to near-field coupling. Beyond pull-in, the observed
CHAPTER 5. ELECTRO-MECHANICALLY TUNABLE PLASMONIC COLOUR

Colour is stable. The only significant change is in the gradual increase in contact area with increased voltage. In addition to the primary response, shorter wavelength ripples are also detected. These occur due to thin film interference effects arising due to the glass/ITO/air structure. In future iterations, these could likely be minimized with the addition of anti-reflective structures.

5.4 Outlook

The above-described MEMs tunable plasmon structure demonstrates a platform upon which future reflective plasmon displays could be based. With improving ability to select and design the NP configuration, future versions can be anticipated to be more controlled in their response and cover a broader colour gamut.

Although attractive due to the potential to produce single pixels capable of rendering a full colour spectrum, the standing wave effect does vary with the angle of incidence of the exciting field. The result can be colour shifting when not viewed directly. Alternatively, in the case of black pixels, those regions could transmit light and degrade contrast when viewed at angle. The latter can be improved by optimizing the assembly to achieve wide angle and spectrally broad black by exploiting gap plasmons, described in section 2.2.1 and would be critical to its deployment as a low-power reflective display technology. Gap plasmons are favourable in this regard due to their relative insensitivity to angle.

Furthermore, additional work should be performed in achieving a uniform response by adopting structures similar to those illustrated in Figure 5.3. Finally, the presence of a pull-in voltage deprives the device of some potential tunability by rendering many potential membrane potentially inaccessible in practice. More complex three-electrode structures can be realized that allow full tunability across the gap 10. In
Figure 5.10: a) Illustration of deformable bridge response to applied voltage; gap between nanoparticles and reflector membrane decreases as field is increased. b) Measured spectral response for a deformable bridge as a function of voltage. c) Optical images illustrating the colour response for a deformable bridge. The distance between the aluminum bridge and the annealed gold nanoparticle film varies as a function of voltage. The bridge is 100 $\mu$m $\times$ 200 $\mu$m and has an air gap thickness of 250 nm at 0 V. The circle in the rightmost image illustrates the spot size used in measuring the spectral response.
such structures, the membrane is displaced within a uniform electric field established by two outer electrodes. A given voltage will place the electrode at equilibrium at an arbitrary position between the two outer plates.

Beyond improvements to the existing design, the concept of MEMs tunable structures extends to those leveraging the scattering properties of some plasmonic nanoparticles, described below.

**Electrically controlled scattering towards a transparent display**

In addition to absorbing specific frequencies of light, plasmonic particles of sufficient size will preferentially scatter light at a given frequency. Such particles are essentially invisible at most wavelengths while having high optical density within a narrow range. The intensity of scattered light is directly proportional to the intensity of the electric field in proximity of the scatterer, as described in Section 2.1.2.

An intriguing possibility would be to exploit the above properties using a deformable structure that modulates the distance between an ensemble of scatters and an exciting field. Amongst the simplest methods to achieve such a goal would be to excite a transparent waveguide/substrate such that an evanescent field is present at its surface as illustrated in Figure 5.11b. The intensity level scattered from the device could be controlled with the NP position.

Initial full-wave calculations for such a structure have been performed in COMSOL. A silver nanosphere, scattering strongly within the blue is suspended in air at a variable distance from a glass substrate. In this model, port excitation was used to generate incident light suitable for exciting an evanescent field. Perfectly Matched Layers (PML) were used to prevent artificial reflections from scattered light. The preliminary model is illustrated in Figure 5.11b. As one might anticipate, scattered
Figure 5.11: a) Schematic of potential scattering based transparent display. Resonant particles are suspended within an evanescent field. Intensity levels are controlled by tuning the particle’s position within the field. b) FEM model for the proposed structure. Ag nanosphere is suspended in air above a glass substrate that has been excited in such a manner so as to generate an evanescent field. c) Total integrated scattering intensity as a function of position relative to the glass substrate. d) Illustration of a proposed transparent projector surface previously reported by other researchers [11].
light increases exponentially as the nanoparticle approaches the substrate, shown in Figure 5.11.

Assuming sufficiently narrow resonance peaks, it should be possible to excite the particles with narrow band radiation and deploy them in a form factor that is otherwise nominally transparent to broader illumination. As an example researchers have produced a simple monochrome transparent projector by suspending disperse resonant nanoparticles within a poly-vinyl alcohol (PVA) matrix [11]. Since their work, several other researchers have expanded this effort by proposing and demonstrating materials compatible with full-RGB colour [77, 78]. Nevertheless, to my knowledge, little work has been presented on a structure with electronically addressable pixels. With increased interest in augmented reality and virtual reality, this may be an interesting avenue for future work.
Chapter 6

Summary

The primary goal for this work was to leverage the intriguing properties of plasmonic nanoparticles to realize structures that respond to stimuli, primarily electrical or mechanical. While there has been an abundance of research towards realizing highly detailed and colourful features with such particles, comparatively little has been done to integrate them as dynamic features.

In pursuing this goal, a number of research challenges needed to be addressed.

- Identifying a suitable device structure that would be compatible with targeted uses (eg: responsive authenticity feature);

- Developing the fabrication processes to integrate nanoparticles alongside mechanically (or electrically) tunable structures; and

- Developing models capable of providing an explanation of observed results and a platform upon which to design improved features.

In addressing such challenges, significant efforts were expended in developing a variety of process sequences that were anticipated to be compatible with potential applications. Of these, the structure that was selected to produce a mechanically
CHAPTER 6. SUMMARY

induced response is, to my knowledge, a unique approach and addresses most of the above mentioned constraints.

The proposed electrically tunable structure was primarily inspired by the IMOD display, first developed at MIT and refined by Qualcomm for their Mirasol display. Where the initial work was based on tuning an optical cavity which a movable multi-layer dielectric stack, the work in this thesis relies on an ultra-thin plasmonic layer to act as a tunable absorber. Furthermore, where initial efforts relied on RGB sub-pixels which dramatically reduces the brightness of the reflected image, the path proposed within this thesis offers potential benefits in achieving full-colour response from a single pixel, particularly when coupled with gap plasmon structures for achieving broad colour gamuts.

In my view, the structures and processes realized in this work provide a platform upon which improved colour response, uniformity, and utility can be pursued.

6.1 Academic Contributions

Work from this thesis has resulted in a pair of publications:

• Rankin A, McGarry S "A flexible pressure responsive device based on the interaction between silver nanoparticles and an aluminum reflector", Nanotechnology, Volume 29, Number 1, 2017.


The first publication focused primarily on the response of metal nanoparticles in proximity of a reflector and provided a proof-of-concept. The second is based on the
work described in Chapter[4]. Several patent applications deriving from this work and related works are also in progress.


The above works are a result of collaboration with the Bank of Canada and are intended to protect intellectual property developed during the course of our investigation, targeted towards use as a security feature in currency.
List of References


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Appendix A

Tapered film thickness by masked e-beam deposition

Over the course of this work, a need occasionally arose to deposit varying amounts of a material onto a given substrate, as illustrated in Figure A.1a. In particular, this would often be useful during e-beam deposition to vary dielectric thickness in order to observe its influence on perceived colour of NP-Dielectric-Reflector stacks.

As outlined in Figure A.1b, the e-beam evaporation setup at Carleton consists of a pocket for holding source material along with a rotating stage onto which the samples to be coated can be placed. The evaporating source material is physically separated from the sample by a relatively long throw distance and, for this purpose, was considered to provide nominally uniform deposition rate to any exposed surface within the sample.

A tapered deposition was achieved by inserting a mask in the deposition path. The mask consists of open regions that permit deposition and opaque regions that block it. The shape of the open region was defined such that there would be a roughly linear grade with increasing radius. As a result, linearly graded depositions of any material that can be deposited by evaporation were achieved.
Figure A.1: a) Example of a tapered oxide deposited on a 4” silicon wafer by inserting an optimized mask between the sample and the evaporation source. b) A basic illustrating of the essential elements of the evaporation setup at Carleton University. c) Schematic of a representative mask that allows for linearly decreasing deposition thickness as a function of radial position.
The mask design ensures a linearly decreasing evaporation “dose” with increasing radius. The fill factor for the mask as a function of radius is defined as:

\[
ff(r) = \frac{r_{\text{max}} - r}{r_{\text{max}} - r_{\text{min}}} \quad \text{(A.1)}
\]

where \( r_{\text{max}} \) and \( r_{\text{min}} \) denote the maximum and minimum radial positions of the sample within the coordinate system of the rotation stage.

In polar coordinates we can find an angle \( \phi(r) \) for each radial position that will satisfy the constraint. This relationship defines the boundary of the mask.

\[
\int_\phi^\pi r d\theta = \frac{\pi}{2} \frac{r_{\text{max}} - r}{r_{\text{max}} - r_{\text{min}}} \quad \text{(A.2)}
\]

\[
\phi(r) = \frac{\pi}{2} \left( 1 - \frac{r_{\text{max}} - r}{r_{\text{max}} - r_{\text{min}}} \right) \quad \text{(A.3)}
\]
Appendix B

Optical Transmittance of selected materials

A PET-PDMS stack was utilized in fabricating a mechanically responsive structure. During optical characterization, fringes were observed in the spectral response. These fringes arise due to thin film interference effects of the $\approx 4\mu m$ thick PDMS and PET substrate. Optical transmittance for these materials was measured in isolation of the plasmonic absorber structure and is shown in Figure B.1.

During optical characterization of the mechanically responsive plasmonic structure, significant absorbance was observed at short wavelengths, particularly those less than approximately 425 nm. In characterizing the strain response of the device, a polycarbonate plate was used to support and distribute the applied load to the device under test. As illustrated in Figure B.2, the material imparts significant loss to short wavelength light.
Figure B.1: Optical transmittance of PET substrate compared to PET-PDMS stack across the visible spectrum.
Figure B.2: Optical transmittance through a polycarbonate plate. The material absorbs significant energy above 425 nm.