Indefinite metamaterials for optical applications

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NANYANG
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**INDEFINITE METAMATERIALS FOR OPTICAL
APPLICATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2015

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Abstract

The resolution of conventional optical systems is limited because of Abbe's diffraction limit, which dictates that objects placed closer than approximately half the wavelength of light used cannot be completely resolved. Hence, it becomes imperative to find means of performing near-field (Superlensing) and label-free real time far-field super-resolution imaging (hyperlensing) at the nanoscale.

Although by utilizing anisotropic permittivities, metal-dielectric multilayers have been successful in reconstructing the high-frequency components from sub- λ objects, yet they remain cumbersome and expensive to make. Most of the multilayer structures require multiple vacuum deposition cycles and are plagued by stringent requirements on surface roughness of metallic layers. In contrast to the multilayer structure here we propose a 3D hyperbolic metamaterial model composed of metallic nanorods arranged in sea-urchin geometry as a hyperlensing device, which is capable of projecting and magnifying diffraction limited information into the far-field at Near-infrared (NIR) frequencies. The hyperlens generates a band of flat hyperbolic dispersions in spherical coordinates, which in turn supports the propagation of high wave-vector spatial harmonics leading to far-field super-resolution imaging. Using full-wave Finite-difference time-domain (FDTD) simulations with diffraction limited trimer, quadrumer and ringed objects etched on thin perfect electric conductor (PEC) films, we show that the hyperlens model can achieve magnification factors of up to 10X in the far-field ($\sim 4.5\lambda$ from object's surface) under a light source with a wavelength of $1\text{ }\mu\text{m}$, with successful resolution down to 220 nm ($\sim \lambda/5$). The magnified image field distribution projected into the far-field is shown to follow the object under reduction in symmetry.

A possible method for the fabrication of envisaged AuNWA-PDMS composite metamaterials is presented. The method shown is capable of yielding thin flexible polymer films embedded with free-standing metallic nanowires. Further,

fabrication of diffraction-limited objects for both Superlensing (slits on film) and hyperlensing (slits on curved Cr-caps) are presented.

These results are important for making progress in the realization of real-time bio-molecular imaging systems, eliminating the need for near-field scanning, destructive electron microscopy and various image post-processing techniques.

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Abbreviations

AFM	Atomic Force Microscopy
ALD	Atomic Layer Deposition
AZO	Aluminum Zinc Oxide
EDX	Energy Dispersive X-ray Spectroscopy
EFC	Equi-frequency Contour
FDTD	Finite-Difference Time-Domain
FESEM	Field Emission Scanning Electron Microscopy
FIB	Focused Ion Beam
HMM	Hyperbolic Metamaterial
ITO	Indium Tin Oxide
MIM	Metal Insulator Metal
NIR	Near Infrared
NMM	Nanowire Metamaterial
SHL	Sea Urchin Hyperlens
SRR	Split Ring Resonator
XRD	X-ray Diffraction

Chapter 1

Introduction

This chapter provides a brief introduction to the thesis exploring sub-wavelength imaging beyond the diffraction limit using metamaterials lenses. The current state problem, significance, our hypothesis and research scope will be presented in this chapter, followed by brief introduction of the structure and contents of later chapters. Previewed results of this research, the novelty and contribution will also be addressed at the end of this chapter.

1.1 Problem Statement

Since their invention a few centuries ago, optical microscopes have revolutionized not only the field of biology but also microelectronics, by allowing us to peek beyond what's visible to the naked eye. Nevertheless, nature puts a fundamental limitation on the smallest objects that can be resolved by a conventional microscope to nearly half the wavelength of light used ('Abbe's Diffraction Limit').¹ It arises because the high-resolution details from sub-wavelength objects are contained within the high-frequency components, which decay evanescently from the object's surface.

Researchers have explore various techniques to surpass this limitation including fluorescence based microscopy²⁻³ and super-oscillatory functions⁴⁻⁵ but they require either fluorescence tagging of samples or suffer from speed limitation because of serial scanning principle. Another alternative proposed was using metamaterials consisting of metal-dielectric multilayer structures⁶⁻⁷ which were shown to be capable of performing hyperlensing. Nevertheless, the metal-dielectric multilayer metamaterial suffer from various drawbacks: firstly they are extremely cumbersome to fabricate, as typical structures require ~50-100 deposition cycles depending upon the exact structure required, they are extremely sensitive to the quality of film deposited, where rough films lead to debilitating losses in the object fields.

Here we propose a lens structure inspired by sea-urchins to be capable of projecting diffraction-limited object in the far-field. The idea is whether uniaxial anisotropic metamaterial consisting of nanowires embedded in dielectric matrices are capable of reproducing the object fields both in the near-field and far-field. In the near-field case, the wires are free-standing and vertical while in the far-field projection they are arranged in a sea-urchin geometry, projecting radially from the inner curvature of the hyperlens to the outer curvature. Such a design would imply a transition from a type-II metamaterial to type-I, or a negative permittivity instead of being negative in a plane to just being negative along a particular axis.

1.2 Objectives and Scope

The objective of the present work is to design nanostructured devices capable of breaking the fundamental diffraction-limit of light, thereby assisting in increasing the resolution of conventional microscopy systems. Such systems would allow propagation of high-wave vector components, which invariably carry the high resolution information about the sub-wavelength objects.

Here we propose a design based on anisotropic indefinite metamaterials consisting of metallic nanowires embedded in a dielectric host matrix. Superlensing, or image reproduction in the near-field of the meta-lens is first investigated. Next, the structure is bent in a hemispherical shape, leading to nanowires projecting from the inner curvature to the outer and its magnification properties with regards to hyperlensing is studied. A fabrication technique is explored for realization of metal nanowire embedded thin polymer films.

1.3 Dissertation Overview

Chapter 2 presents a brief introduction to the field of metamaterials in general with emphasis on a sub-class known as indefinite metamaterials. Recent progress in application of such metamaterials for super-resolution imaging both in the near- and far-field is discussed in detail. The chapter also identifies the challenges present in imaging using such metamaterial devices.

Chapter 3 presents full-wave finite-difference time-domain (FDTD) simulations for a nanowire-polymer superlenses.

Chapter 4 presents full-wave finite-difference time-domain (FDTD) simulations of a sea-urchin hyperlens (SHL) using plethora of diffraction limited objects. Typically sub-wavelength nanoring, trimer and quadramer holed objects were imaged using the SHL. Even with reduced symmetry in the object, the SHL was able to magnify and project sub-wavelength information to the far-field.

Chapter 5 shows the detailed process for fabrication of composite metamaterials composed of free-standing and well-separated metallic nanowire arrays inside dielectric matrices. Various characterization techniques including FESEM, EDX, XRD and UV-vis confirm the transfer of nanowires inside the dielectric matrix.

Chapter 6 presents fabrication of sub-wavelength structures for use as objects in superlensing and hyperlensing applications. Objects for superlensing are milled on flat Cr films using FIB and e-beam lithography while objects for hyperlensing are obtained by FIB milling of Cr-caps.

Chapter 7 gives a brief summary to the thesis together with possible future directions of research. Two possible direction presented relate to optical cloaking using nanowire metamaterials and formation of a flat lens by using junction between tilted type-I nanowire metamaterials.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. Establishing a method for fabrication of metal-dielectric nanocomposite metamaterials consisting of Au nanowires embedded inside flexible polymer matrices.
2. Modeling a sea-urchin inspired hyperlens design consisting of metallic nanowires projecting radially from the inner curvature of the hyperlens to the outer. This design was shown to be successful in projecting diffraction limited sub wavelength information in the far-field where it can be manipulated by conventional optical microscopes. Resolution down to $\lambda/5$ was obtained at a wavelength of 1000 nm.

3. Fabrication of sub-wavelength objects for potential applications in Superlensing and Hyperlensing. A method was developed to fabricate sub-wavelength object on curved Cr-caps using focus ion beam milling.

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Chapter 2

Literature Review

A brief introduction to the concept of metamaterials is provided. In particular, detailed literature study for imaging in the near-field (Superlensing) and far-field (Hyperlensing) is presented in order to put the work in context.

2.1 Metamaterials : A brief review

Over the last decade, research in the field of metamaterials has experienced an extensive boost, mainly due to the renewed interest in NIMs (Negative Index Materials) as proposed originally by Victor Veselago¹ in 1968 and reconsidered by John Pendry² in 2000. Metamaterials are artificially engineered materials, which exhibit electromagnetic properties that are not available in nature. These materials gain their electromagnetic properties from the geometric shapes of their constituent building blocks rather than from their atomic composition. This implies that the metamaterial – ‘atoms’ or – ‘building blocks’ consist of many real atoms, usually arranged in a periodic fashion to exhibit a tunable electrical or magnetic response, which gives rise to their specific properties. One important feature is that the size of the metamaterial – ‘atoms’ is sub-wavelength, typically about one order smaller than the free space wavelength at which the resonance occurs. This is the exact reason why metamaterials are different from photonic crystals (for which the unit cell size is of the order of the free space wavelength).

The most famous class of metamaterials consists of the so called LHMs (Left Handed Materials) or NIMs. Invisibility cloaks are another fancy application in the field of metamaterials, which belong to the field of transition optics (when refractive index is between 0 and 1). By tuning the refractive index values to near zero, it is also possible to slow down light and in the limit “freeze” photons. Properties of metamaterials arise from the interaction of the waves with the metamaterials – ‘atoms’. The interaction is usually described by the effective material parameters, the electric permittivity ϵ and magnetic permeability μ . These parameters provide information on how the material interacts with externally applied electromagnetic fields. Both the permittivity and permeability values have certain frequency dispersion. Based on the effective ϵ and μ values at a certain frequency, all possible materials can be classified according to their electromagnetic response as is shown in Figure 2.1.

Figure 2.1 Material classification based on effective parameters.

From Figure 2.1 it is clear that the behavior of the propagating waves is really counter-intuitive. It arises because of the fundamental difference between phase velocity and group velocity of a wave. If one would consider the propagation of a wave-packet in a RHM (Right Handed Material) and LHM, the group velocity will be the same (in the direction of wave-packet propagation) while the phase velocity for the LHM propagates in the opposite direction unlike RHM. It would imply that for RHM the direction of energy flow (pointing vector $\vec{S}$) is the same as the direction of wave vector $\vec{k}$, while it's the opposite for a LHM.

Materials for which the real part of permittivity and permeability are negative at the same frequency were labeled by Veselago as left handed materials, due to the fact the electric field $\vec{E}$, the magnetic field $\vec{B}$ and the wave vector $\vec{k}$ form a left handed triplet. These materials do – to the best of our knowledge – not exist in nature. Therefore when Veselago published his controversial paper in 1968, it was still unclear if it would be possible to fabricate such materials, and how it would be done. In 2000, Pendry picked up the old ideas from Veselago and proposed a first practical realization of a “*superlens*”, which was fabricated a few years later (Figure 2.3). Together with Pendry's paper, some practical realizations of LHM were also reported in microwave frequencies. These first publications gave rise to a major boost in the field of metamaterials, resulting in many new ideas and designs to make LHMs in all possible wavelength regimes. When LHMs are considered theoretically, based on Maxwell's equations, the conclusions are valid in

any wavelength regime, because they do not take into account the physical shape of the materials, but only its effective parameters, which are used when solving those equations. The most famous application of LHMs is undoubtedly a flat lens, as illustrated in Figure 2.2. On the interface between a RHM and LHM, light rays are refracted at the same side with respect to normal, which results in one focal point inside the slab of LHM and one in the image plane. One of the remarkable properties here is that the object is imaged at the other side of the lens at a distance $2d$, where d is the thickness of the slab.

Figure 2.2 Imaging by a slab of LHM.

In 2000, Pendry expanded the concepts developed by Veselago, and pointed out that LHMs are not only useful in designing flat lenses, but on top of that, also have enhanced resolving power as compared to traditional optical imaging systems. When considering classical optical systems, it is well known that the resolution of any imaging device is limited. This limitation is commonly known as the ‘diffraction limit’ of light. When an object is imaged using a lens, the smallest distance between two points in the object that can still be resolved in the image, is given by equation:

$$\Delta x \propto \frac{\lambda}{2 \cdot NA}$$

This distance is proportional to the wavelength of light (λ) used and inversely to the numerical aperture (NA) or the refractive index n , since $NA = n \cdot \sin\theta$. Therefore in most systems the maximum obtainable resolution is about half the wavelength. The limitation is related to the fact that the smallest details of a structure are composed of high frequency components. These high frequency components are contained within the

evanescent fields of the electromagnetic waves which are non-propagating modes that decay exponentially with the distance from the source. Therefore in a classical imaging system, they do not reach the other side of the lens, and hence do not contribute to the resolution of the image (Figure 2.3). Pendry concluded that in order to transfer the evanescent field components to the other side of the lens, one should correct for the amplitude, but not for the phase of the waves. Moreover, he proved theoretically that this is possible with a NIM slab, since the evanescent waves can be amplified in amplitude, providing a compensation for the exponential decay inside the NIM slab. One should also note that this is only possible, due to the fact that on both sides of the interface, ε and μ have equal magnitude but opposite signs, resulting in perfect impedance matching. The flat lens as originally proposed by Veselago, allows near-field imaging with resolution beyond the diffraction limit, which can be exploited in different applications. Many of the possible applications of NIMs still have a long way to go before they can be realized in practice. At this point, the research in this field is still mainly focused on realizing NIMs for different wavelength regimes, especially for near infrared (NIR) and visible wavelengths. For practical applications, the developed materials should be optimized and fine-tuned in order to match the specific requirements, such as impedance matching to the surroundings, and minimizing the intrinsic losses of the NIM layer.

Superlens : The NIM superlens which was introduced earlier has potential applications in imaging (microscopy), lithography and optical data-storage. The most limiting factor for realizing these applications is in the fact that the super-resolution (beyond the diffraction limit) is only limited to the near-field, which means that both the object and the image have to be located very close to the surface of the lens (Figure 2.3). Moreover, the intrinsic material losses in the NIM slab can also decrease the amplitude of both the propagating and the evanescent waves, which reduces the final attainable resolution of the image. Despite the different limitations, for certain applications, the design of the NIM and the desired application might be matched in order to still be able to obtain an optical system which can do better than any classical equivalent.

Figure 2.3 Differences between a conventional lens and a superlens.

Far-field superlens : A far-field superlens³ is an extension of the classical superlens, which combines a NIM with a diffraction grating. The surface plasmons on the interface of the NIM can couple to the diffraction grating, which can convert them into propagating waves that can be collected in the far-field, as shown in Figure 2.4. For imaging applications, this lens is already an improvement with respect to its classical equivalent, since it allows imaging from near field to far field. However, the image retrieval is not trivial, since the high-frequency near field (non-propagating) components have been converted to lower frequency far-field (propagating) components. Therefore, in order to reconstruct the object from an image plane, one has to mathematically correct for the presence of the diffraction grating.

Figure 2.4 Comparison between a conventional lens and far field Superlens.³
Conventional lens (left), far-field Superlens (right).

2.1.1 NIM Realizations:

Poor Man's Superlens

One of the first practical realizations of a superlens was already suggested by Pendry, consisting only of a thin slab of silver. When the thickness of such a slab is made sufficiently small, the system can be described in the electrostatic limit, which implied that electric and magnetic fields can be decoupled. This means that a superlens can be constructed by only having a negative value for ϵ or μ . Therefore, in the case of the silver slab, the negative ϵ enabled imaging with super-resolution for p-polarized or TM waves, regardless of the value of μ . This example was already dealt with theoretically by Pendry, as illustrated in Figure 2.5. Due to the fact that only electric contributions are taken into account, this version of the superlens is also referred to as a 'Poor Man's superlens'.

Figure 2.5 Simulated results for imaging by means of a 40nm thick silver slab; (left) imaging setup, (middle) the electrostatic potential in the object field and (right) the electrostatic field in the image plane, with and without the silver slab.

This ‘Poor Man’s superlens’ was realized shortly afterwards, yielding the first proof for the validity of Pendry’s work. The structure that was used is illustrated in Figure 2.6. It consists of a quartz substrate, on which the object was patterned into a chromium film. On top, a dielectric spacer of PMMA (Poly Methyl Methacrylate) a 35nm silver film and a layer of photoresist was deposited. Upon illumination from the backside, the object was imaged into the photoresist, which could be verified using an AFM (Atomic Force Microscope) after development. As such, features with line widths up to $1/6^{\text{th}}$ of the incident wavelength could be resolved, which is illustrated in the word ‘NANO’ in Figure 2.6

Figure 2.6 Illustration of the poor man’s Superlens.

Basic NIM designs :

In NIMs, both a negative electric and a negative magnetic response have to be created at the same wavelength. This is realized by using resonant structures in a clever way, such that the frequency bands with negative permittivity and permeability overlap. In some designs these responses are generated using one single structure, while in other ones, the electric and magnetic resonators are separate structures. All of these structures have one thing in common: they combine inductive and capacitive elements, and therefore, most of them can be modeled using equivalent RC-circuits as illustrated in Figure 2.7. By tuning the value of the capacitance and inductance of the structures, the resonant frequency can be tuned to the desired value.

Figure 2.7 LC-circuit and it's resonant frequency

In the end, for obtaining both negative electric and magnetic responses, the structure needs to exhibit an out-of-phase response to both the electric and magnetic field component of the exciting electromagnetic wave. The capacitive elements deliver the electric resonance, whereas the inductive elements deliver the magnetic resonance. Some practical illustrations are given in the following paragraphs for different wavelength regimes.

First realization in microwaves

The first true negative index materials were realized at microwave frequencies (~GHz). For these frequencies, the size of the structures is in the millimeter range, which provided a lot of flexibility in designing and fabricating these structures. A typical design at these

frequencies generates a negative magnetic response in a so called (double) Split-Ring Resonator (SRR), and a negative electric response in long metallic wires (Figure 2.8).

Figure 2.8 First metamaterials at microwave frequencies, (a) SRR provides a magnetic resonance, (b) long metallic wires provide a negative electric response and (c) the combination of both structures in practice.

First NIMs at visible and NIR wavelengths

In the quest for NIMs at visible and NIR wavelengths, many different concepts have been studied over the past years. In a first approach, many designs were relying on the microwave SRR structures, which could be scaled down and simplified in shape, in order to create them by e-beam lithography. However this is not the full end of the story, because all concepts cannot generally be scaled down, without incurring any change in the physics that is involved. The major challenge is to create magnetic resonance at optical wavelengths, since many metals already have a negative permittivity in NIR and visible wavelength region. In conventional (magnetic) materials, the highest resonance frequencies are located in the microwave region of the EM-spectrum. Therefore, at shorter wavelengths, magnetic resonances have to be induced using the electric field components, in order to create displacement currents which can generate a negative magnetic response. This implies that in the first designs in which SRR were scaled down, their orientation with respect to the fields was changed as illustrated in Figure 2.9, and the complexity of the structure has been reduced by switching to a single split ring. The smallest U-shaped resonator Figure 2.9b was reduced in size up to $\sim 200\text{nm}$, which exhibited a magnetic resonance at $\sim 1.5\mu\text{m}$. Moreover, a 3D structure consisting of

stacked layers of U-shaped SRRs Figure 2.9c has been realized recently, with a resonance wavelength of $\sim 2.5\mu\text{m}$.⁴

Next to SRR, another interesting structure for creating magnetic resonances is a Metal-Insulator-Metal (MIM) structure, which has been used in much different geometry already. The most famous example being the double fishnet,⁵ which is until now the NIM with the shortest resonant wavelength of 780nm.

Figure 2.9 SRRs designed for NIR applications (a) geometry and field orientation (b) smallest design with resonance at $1.5\mu\text{m}$. (c) 3D stacking of U-Shaped SRRs⁴.

The magnetic resonance in MIM is a consequence of opposite displacement currents in the top and bottom metal layers, which induces a strong magnetic resonance in the insulator layer, which opposes the magnetic field of the exciting wave. This particular design is quite similar to the microwave example discussed previously, in which the SRR has been replaced with a MIM-resonator, which also can be modeled using an LC-circuit, comprising of 2 capacitors and 2 inductors (Figure 2.10a). For the electrical resonance, the wires consist of MIM-wires along the direction of the electric field (Figure 2.10b). Combining the two elements, one gets a structure that looks like a fishnet (Figure 2.10c) and exhibits a negative refractive index in the near infrared.

Figure 2.10 Double fishnet NIM (a) polarization at the magnetic resonance and LC equivalent scheme; (b) the different constituents resulting in a negative n ; (c) SEM image of the final structure⁵.

For these types of fishnet structures, interferometric measurements have shown a negative phase velocity⁵ providing a through left-handedness of the layer. Moreover, recent experiments on multilayer stacks have shown negative refraction in prism structures of these MIM layers⁶. Figure 2.11 gives an overview of these results.

Figure 2.11 Sample structure and experimental results of an MIM multilayer stack of 21 layers. The prism structure was created by ion beam writing. By scanning the

wavelength, the transmitted beam shows different refraction angles, ranging from positive to negative values for the refractive index⁶.

The examples presented above give clear evidence for the predicted left handed behavior in materials which have simultaneous negative values for the real part of permittivity and permeability. In different wavelength regimes ranging from microwaves up to visible wavelengths, negative phase velocity, negative refraction and imaging with resolution beyond the diffraction limit have been proven with different structures. We now know the problems associated with these ‘traditional’ metamaterials designs. Firstly since these designs rely on ‘resonances’ in various nano/micro structures, they come with added losses in the system. Secondly, these ‘traditional’ metamaterials designs also have a certain region of operation, meaning that they only work at particular wavelengths as they are based on resonance mechanisms and depend upon the overlapping of the regions where both ϵ and μ are negative. Thirdly, these materials are not easy to fabricate as most of these rely on precise nano-fabrication techniques such as e-beam lithography or Focused Ion Beam (FIB). These problems are solved when one looks into ‘*indefinite*’ materials, which are not completely detached from their traditional meta-metamaterial brothers but somehow circumvent the problems associated with them. We will discuss them in the next section.

2.2 Indefinite Metamaterials

Metamaterials whose dispersion relations are hyperbolic are also known as ‘indefinite’ or ‘hyperbolic’ metamaterials (HMMs). The term ‘indefinite’ here denotes the unbounded k-vector components that are supported inside the medium. For these materials the value of their dielectric permittivity is negative along a particular direction as compared to the other two orthonormal directions. For eg. for an uniaxial anisotropic material $\epsilon_z < 0$ (permittivity along the z-axis) and $\epsilon_{x-y} > 0$ (permittivity in the x-y plane). This is only a particular subtype from the gamut of different types of indefinite materials.⁷ It is also possible to have permittivity designed in a certain way so that it’s negative along two orthonormal directions ($\epsilon_{x-y} < 0$) and positive along the third one ($\epsilon_z > 0$). These are referred to as Type II Indefinite Metamaterials⁷ in contrast to the Type I as described

above. Their dispersion characteristics are somewhat different from each other (Figure 2.13). Figure 2.14 shows the different ways in which these materials can be implemented in practice. High- aspect ratio nanowires embedded in dielectric materials gives Type I indefinite metamaterial. On the other hand thin metal-dielectric multi-layers give Type II indefinite metamaterial. It has been earlier shown that indefinite metamaterials offer unique ways of interaction with point dipoles/emitters⁸. This interaction is interesting because of the unique dispersion relation characteristic of these indefinite metamaterials (Figure 2.12).

Figure 2.12 shows the dispersion relation for an isotropic medium (left) and anisotropic medium (right). The allowed wave vectors are denoted by blue while the direction of the group velocity is given by the red arrow.

In the case of isotropic materials the dispersion relation given by

$$\frac{k^2}{\varepsilon} = \frac{\omega^2}{c^2}$$

which, in the k -space or the momentum space describes a spherical iso-frequency surface (or surface for a fixed frequency; Figure 2.12a). Since there can be no k -value higher than the radius of the sphere, it applies a cut-off to the wave numbers. This implies that there will be decay in the k components higher than the radius of the iso-frequency sphere, hence it wouldn't be picked up by the conventional lens. In stark contrast to these materials a material which is very strongly anisotropic allows propagating waves inside the bulk of

the metamaterial without any cut-offs being present. For uniaxial materials where $\epsilon_z \equiv \epsilon_{\parallel}$, $\epsilon_x = \epsilon_y \equiv \epsilon_{\perp}$ the dispersion relation for the waves with TM-polarization is given by:

$$\frac{k_{\perp}^2}{\epsilon_{\parallel}} + \frac{k_{\parallel}^2}{\epsilon_{\perp}} = \frac{\omega^2}{c^2}$$

Figure 2.13 shows the different classes of indefinite media that are available. Iso-frequency contour for (a) isotropic dielectric is a sphere, (b) type I HMM (Hyperbolic Metamaterial). (c) type II HMM (this type of HMM has a certain minimum value of k , $k_{\min}$, below which it reflects all the waves. For both (b) and (c) there is no upper bound available for the wave-vectors.

Figure 2.14 (left) Type II realization consisting of metal-dielectric multilayers. (right) Type I HMM made from metal nanowires embedded in a dielectric host. Permittivity is negative along the wire axis, and positive in the other two orthonormal directions.

Figure 2.15 The equi-frequency contour (EFC) for a TM polarized light in HMM. Grey circle is the EFC in air, while the green hyperbola is the EFC in the indefinite metamaterial. The dashed line is due to the conservation of the tangential component of the wave vector along the interface.

In order to understand the negative refraction property of the indefinite metamaterial we have to look into the dispersion plots as shown in Figure 2.15. The grey circle represents equi-frequency contour (EFC) in air, while the EFC for a TM polarized light is hyperbolic in the k_x - k_z plane (green curve). Here, we assume that the light propagation is along the positive z -axis. Since the x -component of wave-vector is conserved across the air-metamaterial interface, the wave refracted inside the metamaterial is in opposite direction as compared to the incident light. S_i represents the incident pointing vector, and the change to S_r shows the process of negative refraction. Hence the figure, represents a TM wave which is incident from air/free space and undergoes negative refraction in the metamaterials as shown by the Poynting vector S_r as compared to the incident light.

2.3 Superlensing

As discussed before NIM were proposed to achieve sub-wavelength imaging² or imaging below the diffraction limit of light. The sub-wavelength resolution for these superlenses depend on both the propagating and the evanescent waves and hence those materials were also referred to as NFSL (Near field Superlenses). The minimum

resolution of 40nm was achieved using the i-line (UV) (365nm) sources⁹ and similar superlenses which were based on Al instead of Ag were proposed to be operative in the deep UV region¹⁰ and 20nm features were shown to be theoretically achievable. These NFSL (both Ag and Al) are advantageous because of their ease of fabrication (being just thin metallic layers), instead of complicated periodic structures. Other groups have used these thin metallic films to show imaging beyond the diffraction limit both theoretically and experimentally¹¹⁻¹³. However these methods suffer from intrinsic loss of absorption ($\epsilon'' > 0$) since they are mostly made of thin metallic layers, having non-zero value for the imaginary part of the dielectric permittivity. This intrinsic loss results in the image being blurred and limits the formation of a perfect image on the other side of the lens. Also, the layers have to be very thin ($\ll \lambda$, wavelength), in order to be in the electrostatic limit, as required by², implying that the evanescent components are not able to travel long distances inside the superlens leading to very short object and image distances.

An approach which mitigates the problems mentioned before, makes use of high-aspect ratio nanowires arranged in arrays inside dielectric materials has been theoretically put forward.¹⁴⁻¹⁵ The restoration of evanescent waves in these materials is not based on the resonant mechanisms as described previously but is due to the particular form of equi-frequency surface as was evident from Figure 2.13. This leads to the transport of the evanescent waves due to the relatively flat equi-frequency dispersion characteristics. Resulting in the image reconstruction of the object not only with low loss but also over a range of frequencies which is broad. These aligned metallic nanowires possess anisotropic optical properties with $\epsilon_z < 0$ and $\epsilon_{x-y} > 0$ and in¹⁶ were shown to be able to achieve broadband all angle negative refraction and superlens imaging¹⁶⁻¹⁷ and as mentioned before these materials are also known as '*indefinite*' materials.¹⁸ Due to the challenge in manufacturing extreme high aspect ratio nanowires, most of the experimental demonstrations have been limited to the microwave region of the spectrum¹⁹⁻²⁰. In²¹ the authors have demonstrated a low-loss three-dimensional metamaterials nanolens, with a resolution of at least $\lambda/4$ at NIR wavelengths and over distances of 6λ .

2.4 Hyperlensing

Although the invention of optical microscopy gave an unprecedented fillip to the fields of micro-technology, medicine, and biology, the resolution of those ubiquitous conventional optical lenses has been fundamentally constrained by the ‘diffraction limit’ of light for several centuries. It dictates that objects placed closer than approximately half the wavelength of light source ($\sim\lambda/2$) can’t be successfully resolved.²²⁻²³ The unresolvable high-resolution details from sub-wavelength objects are encoded within high spatial frequency components, which decay evanescently from the object’s surface (see Figure 1a).²⁴⁻²⁶ On the other hand, conventional optical lenses allow for propagating waves to pass through but are unable to carry the evanescent components (Figure 1b). Techniques such as fluorescence based microscopy,²⁷⁻²⁸ scanning near-field optical microscopes (SNOMs),²⁹⁻³⁰ and super-oscillatory functions³¹⁻³² allow circumventing the limitation, yet they suffer from the compromise in speed and the requirement of fluorescence tagging. The growing field of plasmonics and metamaterials (MMs) has shown tremendous promise in applications related to sub-wavelength imaging,³³⁻³⁴ optical cloaking,³⁵ and solar energy conversion³⁶ amongst others. Superlensing based on a thin film of Ag was proposed theoretically in the seminal work by Pendry³³ and later demonstrated experimentally³⁴ to image sub-wavelength objects in the film’s near field. This concept which was later explored by other groups,³⁷⁻³⁹ is based on resonant excitation of surface plasmon polaritons (SPPs) across thin plasmonic metal films leading to enhancement of object’s evanescent components.³³ However, these superlenses suffer from high optical losses, and small object-to-image transfer distances. For example, Fang et al⁴⁰ was only able to transport images with an object-to-image transfer distance of $\sim 0.2\lambda$. Hyperlenses were proposed to overcome this limitation by projecting high-resolution information as propagating waves into the far-field.

A sub-section of MMs known as Hyperbolic MMs (HMMs), has one particular Cartesian permittivity tensor component opposite in sign to the other two, giving rise to their hyperbolic dispersion, and to their nomenclature.⁴¹⁻⁴³ HMMs have recently been attracting a lot of interest from researchers,⁴⁴⁻⁴⁶ mostly in the studies related to thermal transport,⁴⁷ enhancement of spontaneous emission,⁴⁸⁻⁴⁹ transport of acoustic waves,⁵⁰ and

both near-field and far-field super-resolution imaging.⁵¹ Typically the most popular HMM is obtained by engineering electric only (where $\mu > 0$) composite materials consisting of thin alternate metal-dielectric multilayers, which have found uses in sub-wavelength imaging⁵²⁻⁵³, sub-wavelength lithography,⁵⁴ sub-diffraction focusing of energy,⁵⁵⁻⁵⁶ and in engineering the lifetime of dipole emitters.⁵⁷⁻⁵⁹ The first state of the art imaging demonstration of a one-dimensional hyperlens at ultraviolet frequencies was obtained through conformal deposition of Ag/Al₂O₃ multilayers on a hemi-cylindrical cavity on a quartz surface.⁵² Resolution close to $\sim\lambda/2.9$ was obtained at a wavelength of 365 nm. A two-dimensional hyperlens operating in the visible region was later demonstrated by depositing alternating layers of Ag and Ti₃O₅ onto a hemi-spherical cavity in quartz and a resolution of $\sim\lambda/2.6$ was obtained at a wavelength of 410 nm.⁵³ Although metal-dielectric multilayer structures are capable of magnifying images and projecting them into the far-field, there are several drawbacks: firstly, the fabrication process is extremely tedious and time-consuming. Since it involves several vacuum depositions cycles (16 alternate layers were deposited by Liu⁵², while 18 were used by Rho⁵³). Since the film quality (for eg. low surface roughness and small grain size etc.) is very crucial in order to minimize scattering losses, the fabrication conditions are very stringent. Secondly, hyperlensing mechanism in curved metal-dielectric multilayers is based on coupling of plasmon resonances across the thin metal-dielectric layers, which makes it highly susceptible to losses. Finally, it can only function at a designated frequency region, which is mainly defined by the structural dimensions and material composition of the metal-dielectric multilayer hyperlens.

For next generation MMs, indefinite mediums composed of metallic nanowires embedded in dielectric matrices are considered as one of the promising candidates since they are easily tunable and have lesser energy losses. More importantly, they are not constrained by the ubiquitous metamaterial requirement of magnetic resonance.⁶⁰⁻⁶¹ They have been previously shown to produce all angle negative refraction⁶⁰⁻⁶¹ and sub-wavelength imaging.⁶²⁻⁶⁴ Endoscopes made from tapering nanowire arrays have been shown in the past but they can only reproduce the fields near the surfaces.⁶⁵⁻⁶⁶ Kawata et al²⁵ numerically showed color imaging using stacked nanorod arrays and the idea of magnification using tapered nanorod arrays. Nevertheless, the imaging capabilities of

these nanorod array based hyperlenses still remain largely unexplored. Tapered arrays of metallic wires were shown theoretically⁶⁵ to magnify electromagnetic information on one of its edge to the other, but the resultant magnified image was shown to be limited to the near-field of the nanowires. Here we propose a sea-urchin hyperlens (SHL) composed of hexagonally arranged metallic nanorods embedded in a dielectric medium and arranged in sea-urchin geometry as a hyperlens design working in the NIR (See Figure 1c to 1e). We show numerically that when conformed to a hemispherical surface the hyperlens is capable of projecting images from sub- λ objects into the far-field, which in turn can be easily brought to focus by conventional microscope objectives.

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Chapter 3

FDTD Simulations for Nanowire Metamaterials

In the following chapter finite-difference time-domain simulations were performed for superlens imaging of sub-wavelength slits using hexagonally arranged nanowire metamaterials embedded inside a dielectric medium. In the later part, electromagnetic beam propagation through nanowire metamaterials with gradient was also studied.

3.1 Simulating slit objects

In order to understand the applicability of the proposed meta-lenses, we perform full-wave simulations taking into consideration the structure and respective material properties. We use FDTD LumericalTM, a commercial solver for performing electromagnetic simulations. The model consists of an object in the form of a very small slit, with width $w \ll \lambda$, etched into a thin mask which sits on top of our meta-lens as shown in Figure 3.1. A TM plane wave is incident from the top of the mask so as to couple to the sub-wavelength slit. Material properties for Ag were obtained from Johnson and Christy,¹ while the respective parameters in the simulation were taken as: $w=50\text{nm}$, $H=500\text{nm}$, $d=20\text{nm}$, $t=50\text{nm}$, $a=40\text{nm}$. Periodic boundary conditions are used along the x-axis. As long as the characteristic lengths in the lens are small as compared to our wavelength of interest, we remain in the domain where effective media description of these nanorods is applicable.²⁻³ Since the wavelength in our case is much larger than the slit width, nanorod diameter or nanorod separation ($\lambda > w, d$ or a), variations within the meta-lens at those sub-wavelength scales are not ‘visible’ to the incoming radiation which only experiences the effective optical properties of the composite structure. We use this arrangement to simulate the effect of single and double slits on top of these metamaterials.

Figure 3.1 Schematic of the nanowire metalens structure with an object on top. Various dimensions indicated in the structure are assumed to be $< \lambda$. w : width of the slits, a : centre to centre distance between nanorods, d : diameter of the rods, H : height of the rods and t : thickness of the object/mask.

The distribution of electric field intensities in the meta-lens is shown in Figure 3.2 at three different wavelengths ($\lambda=391.3\text{nm}$, 435.5nm and 491nm). After exiting the slit

object the beam splits into two and then is refocused by the lens on the other side. The image/focal spot moves closer to the lens with an increase in the source wavelength, as the electromagnetic energy from the source spreads out lesser.

Figure 3.2 E field intensity distributions in nanowire meta-lenses. From left $\lambda = 391.3$ nm, 435.5 nm and 491 nm. H in all three cases is 700 nm. The focus of the object is clearly seen forming on the other side of the meta-lens. These are 2D simulations.

Since 2D simulations fail to take into account the actual curvature of the individual nanowires and the influence of nearby nanorods, 3D simulations were performed for hexagonal arrangement of these nanorods using periodic boundary conditions, now both in x-axis as well as y-axis. Figure 3.3 shows the E field intensity plots for 3D simulations and it is clearly visible that the meta-lens indeed performs focusing of the sub-wavelength object ($w=50$ nm and $\lambda=466$ nm). Again incoming plane wave splits into two beams, also showing that these lenses can perform beam splitting.

Figure 3.3 E field intensity distributions in the meta-lens at 466nm. The arrows indicate the focusing action in the lens. Structure boundaries are indicated by white lines.

Now we look at the detailed simulations for an Al based superlens, Figure 3.4, and perform sub-wavelength imaging using these lenses. A TM polarized plane wave (360nm-1200nm) over visible to NIR wavelengths is incident upon two ‘conventionally’ diffraction limited slits.

Figure 3.4 shows the FDTD simulation setup for the Al based superlens. A finer mesh (2.5nm) is applied to have more accurate results. Fields are recorded at different distances below the superlens as well as at different wavelengths. The two slits have a width (w) of 100nm and are placed (d) 100nm apart in a 1:1 configuration.

Figure 3.5 below shows the cross section E-field of the simulation setup, showing the transfer of energy from sub-wavelength objects to the imaging planes on the other side of the lens. The corresponding field slices at various distances below the lens (15 nm to 123 nm) and at various wavelengths (360 nm to 1200 nm) are shown in Figure 3.6. From (left) it is clear that the image contrast becomes worse as we move further away from the lens-air interface. Image contrast is defined as $(I_{max} - I_{min}) / (I_{max} + I_{min})$. It is also clear that closer we are to the lens-air interface, effects of the individual nanorods

Figure 3.5 Cross-section E-field plots showing the imaging process through Al superlens. (left) 1200nm ($\lambda/12$) wavelength (mid) 960nm ($\sim\lambda/10$) (right) 300nm ($\lambda/3$). It is clear that with decreasing wavelength, the fields diverge more while travelling towards the other end of the lens.

become more apparent. The signatures of the nanorods are visible in the plot (15nm) in the top figure as wiggles. It is also clear that the maximas of the image curves are not exactly at the centre of the rectangular slits. We attribute this to the individual nanorods and coupling between neighboring nanorods leading to energy shifts in the transverse directions. In the bottom figure it is also clear that at a certain fixed distance below the lens (here 40nm), decrease in wavelength leads to worsening of the image contrast, which one could intuitively guess as lower wavelengths lead to higher beam splitting. It has been mentioned⁴ that an image contrast of at least 0.11 is required to produce any effect on most commonly used negative photoresists. After doing some image contrast calculations one can approximately say that the sub-wavelength resolution is not possible in our lens (for the specified parameters) below ~ 500 nm light wavelength.

Figure 3.6 (top) plot of electric field E (a.u.) on a horizontal line, as a function of the distance below the lens from 15nm to 123nm. (bottom) plot of electric field E (a.u.) as a function of the wavelength, from 360nm to 1200nm, at a distance of 40nm below the lens, with lens thickness (H) 700nm. In both the plots, the black dot-dash line represents the slits/objects. The slits have a width (w) of 100nm with center to center separation (a) of 100nm

Figure 3.7 plot of electric field E (a.u.) on a horizontal line, as a function of the distance below the lens from 15 nm to 75 nm, at a distance of 40 nm below the lens, with lens thickness (H) 700 nm. In both the plots, the black dot-dash line represents the slits/objects. The slits have a width (w) of 50 nm with center to center separation (a) of 50 nm.

In the second case we consider the two slits with width 50 nm and center to center separation as 50 nm. Figure 3.7 above shows the E field as a function of distance below the lens-air interface. If we again go through the image contrast analysis, it turns out that for distances above ~ 40 nm the image contrast goes below the critical limit. Making the objects thinner and bringing them closer makes the image contrast go bad at shallower depths. Implying that harder the diffraction condition, closer we have to be to the lens to observe the image (using a SNOM for eg.). These plots show that the Al nanowire metamaterial lens, is able to resolve two 50 nm objects placed with a gap of 50 nm. The wavelength used above is ~ 1200 nm (NIR region) giving $\sim \lambda/24$ resolution in imaging.

3.2 Imaging a complete 2D object using superlens

Next we perform a full-wave 3D simulation to test the imaging, with the object ('NTU') on top of the Al nanowire lens. A 100 nm layer of Cr serves as the mask with ('NTU') etched into it having 50 nm thin lines. We then perform two simulations with orthogonal polarizations. This is done as the slit only couples to TM polarizations and not TE. In other words the slit will only couple to polarizations which have E field vectors perpendicular to the axis of the slit. Figure 3.8 shows the result of the two perpendicular polarizations. It's clear that the object is reproduced on the other side of the lens, if one combines the two E-field distributions in one. This is possible as Maxwell's equations are linear and allows for the linear sum of the two polarizations.

Figure 3.8 (top) NTU object made from 50 nm thin stripes etched on Cr-mask on top of Al meta-lens ($H=700$ nm, $t=100$ nm). (left) E field distribution at the image plane located 50 nm below the lens, for polarization of the incoming field along the x-axis, (right) E

field distribution at the image plane located 50 nm below the lens, for polarization of the incoming field along the y-axis.

3.3 Beam Steering using nanowire metamaterials

Anisotropic MMs based near-field and far-field sub- λ imaging typically employs constant filling fractions of metallic inclusions inside dielectric media, along different axes of the metamaterial device. In metal-dielectric multilayers the respective layer thicknesses are mostly kept constant, while in naturally occurring 2D-crystals they are inherently fixed because of inter-planar distances between metallic 2D planes, as a consequence, a single equi-frequency dispersion relation is sufficient to describe the propagation of electromagnetic energy inside the MM, provided that the conditions for effective media description of MMs is valid (implying that the conditionality of the metallic inclusions being ‘sparsely’ distributed in the dielectric medium and the typical length scales in the medium being much smaller than the wavelength of light being used ($d \ll \lambda$) are valid). Similarly, for vertical cylindrical metallic nanowires embedded in dielectric matrices, the angle of negative refraction for an obliquely incident Gaussian beam can also be accurately predicted by banking on a single equi-frequency contour (EFC).

Here, we study the effect of gradient in the filling factor (ff) within the NMM, on the propagation of electromagnetic energy using effective medium description. Whether continuously changing EFC is sufficient to predict the propagation of electromagnetic energy inside the gradient index metamaterials. Employing full-wave FDTD (LumericalTM) simulations a simple NMM setup was designed, consisting of cylindrical Au nanowires ($r_a = r_b = 25$ nm) arranged hexagonally and embedded in alumina (Al_2O_3). The centre-to-centre separation between the wires is set as $a \sim 150$ nm while their height is kept as $H = 2$ μm . Since cylindrical nanowires have no variation in the filling factor along the nanowire length (or z-axis), implying that the filling factor at the air-MM interface (f_a) and at the MM-air interface (f_b) is the same ($f_a = f_b$). In such cylindrical nanowire arrays with $f_a = f_b$ only one hyperbolic EFC is sufficient to describe wave propagation inside the NMM.

Figure 3.9 y -component of magnetic field (H_y) showing the transmission of a Gaussian beam ($\lambda = 864$ nm) impinging on various NMMs at an angle of 45° : (a) $r_1 = 25$ nm, $r_2 = 25$ nm (b) $r_1 = 25$ nm, $r_2 = 50$ nm and (c) only dielectric (Al_2O_3). Negative refraction in (a) and (b) while positive refraction in (c). The NMM is $2 \mu\text{m}$ thick and is composed of AuNWs embedded in a dielectric medium.

A Gaussian beam with a beam waist of $1 \mu\text{m}$ and a wavelength of $\lambda = 864$ nm is incident on the cylindrical NMM at an angle of 45° and refracts negatively as shown in Figure 3.9a which, as mentioned earlier, can be easily understood from its single equi-frequency contours(EFC). This is the ubiquitous NMM that has been demonstrated experimentally to perform negative refraction and super-lensing. Typically the fabrication of such a

NMM involves electrodeposition of metallic nanowires inside Anodic Aluminium Oxide (AAO) templates.

In order to study the effect of variation in the filling factor along the length of the NMM, cylindrical nanowires are modified to conical nanowires with $r_a=25$ nm, $r_b=50$ nm as shown in Figure 3.9b (right), where r_a and r_b denote the radii of the top and bottom surfaces of the conical NWs. This setup provides a gradual increase in the ff of the metal in the dielectric as we travel from the top surface to the bottom surface of the nanowire metamaterial. Even though the beam refracts negatively again, the angle of refraction has been reduced as compared to NMM composed of perfect cylinders as shown in Figure 3.10 and Figure 3.11b.

Figure 3.10 $\text{Re}(P)$ measured 100 nm below the metamaterial showing the effect of a Gaussian beam traversing through various NMMs incident at an angle of 45° : (black line) $r_1 = 25$ nm, $r_2 = 25$ nm (blue line) $r_1 = 25$ nm, $r_2 = 37.5$ nm, (red line) $r_1 = 25$ nm, $r_2 = 50$ nm and (green line) only dielectric. With increase the angle of cone tapering angle for the nanowire there is a decrease the angle of negative refraction is evident. When no NMMs are present, the Gaussian beam, as expected, is refracted in the positive x-axis direction. The NMMs have a thickness of 2 μm , from the top edge of the metamaterial to the bottom edge.

Due to the presence of a gradient in the filling factor along the length of the metamaterial, we cannot rely on a single EFC to describe beam propagation inside the metamaterial; instead, we have to consider a band of EFCs where the energy flow inside the metamaterial is constantly changing direction depending on the z -position/vertical-position inside the NMM. As can be seen in Figure 3.11b, when the filling factor increases with the z -position inside the metamaterial, the poynting vector initially has a large angle of refraction but with the increase in the depth inside the metamaterial, due to steeper hyperbolic dispersion relation the angle of refraction starts to reduce, which can also be seen from the Figure 3.11b. For an inverse structure with $r_a=50$ nm, $r_b=25$ nm, the Gaussian beam initially propagates almost perpendicular to the air-MM interface, and then curves away along the direction of negative refraction with increase in depth along the NMM vertical axis as shown in Figure 3.11c. The operation of beam propagation inside the NMM with gradient in filling factor can be explained accurately by using the EFCs as shown in Figure 3.12. Flat dispersion curves are conducive in supporting transport of large wave vector components which enable better reproduction of sub-wavelength information.

Figure 3.11 Poynting vector plots for beam propagation through gradient nanowire metamaterials (a) cylindrical nanowires with $r_a=r_b=25\text{nm}$, (b) conical nanowire with $r_a=25\text{nm}$ and $r_b=50\text{nm}$, (c) conical nanowires with $r_a=50\text{nm}$ and $r_b=25\text{nm}$, (d) only dielectric, showing positive refraction of the incoming beam along only one direction.

In Figure 3.12 we can see that for the NMM with ff increasing from top to bottom, the sharper hyperbola near the object causes the beam to refract sharply, but as the beam propagates along the vertical direction in the metamaterial, the angle of negative refraction reduces. While in the reverse structure, the EFC near the top surface of the metamaterial is quite flat while as the beam propagates in along the $-z$ direction the beam starts curving along the higher negative refraction direction, which is also quite evident it's EFC. This is quite similar to what was obtained using the full-wave electromagnetic simulations (FDTD), implying that the results obtained using the effective medium approximation are quite suitable in predicting the behaviour of beam propagation inside the metamaterials with gradient in the filling factor along the its length.

Figure 3.12 Equi-frequency contours (EFC) plots for nanowire metamaterials having gradient in the filling factor along its length, showing the direction of energy propagation, (a) the filling factor decreases from the top surface to the bottom (b) the filling factor increases from the top surface to the bottom surface of the MM. Poynting vector plots (S , power flow) for a Gaussian beam incident on nanowire metamaterials at an angle of 45 degrees, beam diameter being 8microns.

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Chapter 4

Finite-Difference Time-Domain (FDTD) Simulations for Imaging using a Sea-urchin Hyperlens

Superlenses though being able to resolve diffraction limited objects, reproduce the sub-wavelength information in the near-field. In this chapter we perform full-wave FDTD simulations for a sea-urchin based hyperlens consisting of nanowires projecting radially outwards from the objects. It is shown that the proposed hyperlens is able to resolve diffraction-limited objects down to $\lambda/5$ in the far-field.

4.1 Introduction

In the previous chapter we have seen how superlenses resolve the sub-wavelength objects. Nevertheless, the diffraction-limited information is only reproduced in the near-field of the lens. In order to extract the fine features, near-field scanning techniques have to be employed. Typically such near-field techniques involve Scanning Near-field Optical Microscopes (SNOM) and their variations such as Scattering SNOM (or sSNOM). As mentioned previously these techniques are serial in nature due to their pixel-by-pixel scan and hence fail to provide real-time resolved images of diffraction limited objects. In this chapter we will look at a design for projecting sub-wavelength information in the far-field. Such a technique would allow easier integration with conventional optical microscope objectives and assist in increasing their resolution.

Light scattered from diffraction limited objects consists mainly of two components: high frequency (high resolution information) and low frequency (low resolution information) about the object (Figure 4.1a). The low resolution information from object is propagating in nature and can be manipulated by conventional optical lenses. While the high resolution information from the object decays evanescently away from the objects surface. It is the loss of this high resolution information, which leads to diffraction limit for sub-wavelength objects. Here we look at a unique geometry consisting of Au nanowires arranged in sea-urchin geometry, projecting radially from the inner surface of the hyperlens to the outer as shown in Figure 4.1e. We envisage this sea-urchin hyperlens to be able to project the diffraction-limited information in the far-field, where it can be manipulated by conventional optical microscopes (Figure 4.1d).

Figure 4.1 Schematic for the hyperlens structure and imaging principle. (a) radiation scattered from a sub-wavelength object is composed of: low $\vec{k}$ (low resolution; propagating) waves and high $\vec{k}$ (high resolution; evanescent) waves. (b) transmission of scattered waves through convention lens, superlens, and hyperlens. (c) conversion of evanescent waves into propagating waves and their projection into far-field through a hyperlens. (d) schematic for typical hyperlens imaging setup, with a beam incident on the object from top while the far-field image is coupled to the objective lens of a microscope from bottom. (e) geometry of the Sea-urchin Hyperlens (SHL) where it is composed of individual nanowires arranged in sea-urchin geometry spanning from the inner curvature of the hyperlens to the outer curvature. R_{in} denotes the inner radius of the hyperlens while R_{out} the outer radius.

4.2 Effective Medium Theory and Optical Transfer Function (OTF)

We first consider a bulk wire metamaterial consisting of parallel metallic nanowire arrays embedded hexagonally in a dielectric host matrix. In such a uniaxial anisotropic metamaterial, the permittivity components under effective medium description are given by:¹

$$\varepsilon_{xy} = \varepsilon_d + \frac{p\varepsilon_d(\varepsilon_m - \varepsilon_d)}{\varepsilon_d + (1 - p)(\varepsilon_m - \varepsilon_d)q_{eff}}$$

$$\varepsilon_z = p\varepsilon_m + (1 - p)\varepsilon_d$$

where ε_m and ε_d are the permittivities of metal and dielectric, respectively. ε_{xy} and ε_z are the permittivities perpendicular to the wires and along the nanowire axis, p being the filling fraction of the metal component in the dielectric. Figure 4.2a shows the real effective permittivity values of different tensor components for Au (orange), Ag (green) and Al (black) wire metamaterials with $p = 0.2975$ ($f_a = 29.75\%$). Curves with downward triangles show permittivity components for Au with $p = 0.074$ ($f_b = 7.4\%$). Respective metal permittivities have been obtained from Johnson and Christy² (Au, Ag) and Raćik³ (Al), while ε_d was taken as ~ 2.3 without loss.

As the filling fraction of Au inside the dielectric matrix decreases, the cross-over point ($\varepsilon'_z = 0$) undergoes a red shift (shown by blue arrow). Nevertheless, the indefinite regions ($\varepsilon'_z < 0$ and $\varepsilon'_{xy} > 0$) are broadband in nature, where the cross-over point for Au is $\lambda_{Au}^o \sim 560nm$, above which the nanowire metamaterial becomes indefinite (while for Ag, $\lambda_{Ag}^o \sim 460nm$), whereas Al remains indefinite throughout the region under consideration. Even though Al and Ag offer deeper anisotropy in permittivity and broader indefinite regions ($|\varepsilon'_z|_{Al/Ag} > |\varepsilon'_z|_{Au}$ for a given λ), yet they are plagued with either oxidation issues or higher optical losses in this spectral range.

Figure 4.2 Permittivity components for anisotropic nanowire media. (a) Real parts of anisotropic permittivity components along z axis (hollow symbols) and x/y axis (filled symbols) for Au nanowire metamaterial with a filling factor f_a ($\sim 29.75\%$). Downward triangles represent permittivity with filling factor f_b ($\sim 7.4\%$), whereas the plot color represents the material composition for different nanowires: Au (orange), Ag (green) and Al (black). $\lambda_{Au/Ag}^\circ$ denote the respective cross-over wavelengths when $\epsilon'_z < 0$. (b) Dispersion diagram of the Nanowire Metamaterial (NMM) for three filling factors, f_a is the inner surface, f_b the outer surface and f_c is the surface at the metamaterial's center. The circle at the center represents the dispersion in air, while the arrows mark the direction of power flow when a beam impinges on the metamaterial from air. S_i is the incident Poynting vector, $S_{r,a}$ represents the Poynting vector inside the metamaterial

corresponding to a filling factor of 7.4%, similarly $S_{r,b}$ corresponds to a filling factor of about 29.75%.

The special properties of hyperbolic media are derived from the equi-frequency contour (EFC) for TM (extraordinary) polarized waves in the medium, given by:

$$\frac{(k_x/k_o)^2}{\epsilon'_z} + \frac{(k_z/k_o)^2}{\epsilon'_x} = 1$$

where k_x and k_z are corresponding wave vector components in the xz plane. Since in air, $\epsilon'_z = \epsilon'_x = 1$, the equi-frequency contour becomes a circle with unit radius (shown in Figure 4.2b, grey circle), while in the indefinite regime since $\epsilon'_z, \epsilon'_x < 0$, the EFC becomes a hyperbola (curves f_a , f_b and f_c in Figure 4.2b). This implies that there is no cut-off in the wave-vector components supported by the media, allowing for transmission of high wave-vector components which carry super-resolution information about the objects, inside the medium.

The transition from a bulk nanowire metamaterial to a SHL involves arranging the nanowires in a hemispherical geometry, so that the nanowire metamaterial extends from the inner surface of the hemisphere to the outer surface (see Figure 4.1e). This implies a permittivity transformation from rectangular to spherical coordinates $\epsilon_z \rightarrow \epsilon_\rho$ and $\epsilon_{xy} \rightarrow \epsilon_\theta$. It holds particularly true in the case of metal-dielectric multilayers, as the permittivity values in rectangular and spherical coordinates are interchangeable, because of the filling fraction remaining constant along the radial direction. On the contrary, SHL provides a gradient in filling factor along the length of the nanowires, from its inner curvature to the outer.

The Optical Transfer Function (OTF) for an ‘effective slab media’, which gives the ratio between the image field and the corresponding source field for each plane wave component, is given by ⁴⁻⁵

$$T(k_x) = \frac{1}{\cos(k_z d) - \frac{i}{2} \left(\frac{k_z \epsilon}{\epsilon_x k_z^*} + \frac{k_z^* \epsilon_x}{\epsilon k_z} \right) \sin(k_z d)}$$

wherein k_z is obtained from the iso-frequency curves for the nanowire hyperbolic metamaterial from Figure 4.2b, here $k_z^* = \sqrt{\varepsilon k_o^2 - k_x^2}$. ε is the permittivity of the medium surrounding the hyperlens and is taken to be 1. Plots in Figure 4.3a have taken into account the actual material losses present in Au for calculating the transmission through the nanowire slab lens. The transmission of different k_x components through the slab lens have been normalized to $k_o (= 2\pi/\lambda)$. The OTF obtained for $d = 5\lambda$ matches closely with results elsewhere,⁶ for $\lambda = 1550\text{nm}$, where sub-wavelength imaging resolution close to $\sim\lambda/5$ is obtained.

Figure 4.3 Optical Transfer function for nanowire media. (a) Optical Transfer Function (OTF) calculated for an un-bent Au nanowire dielectric metamaterial configuration with $d = 2\lambda$, $r = 25\text{ nm}$, $a = 87.3\text{ nm}$. (b) cross-section corresponding to white dashed line in (a) for $\lambda = 1000\text{nm}$ (black line), OTF for $d = 0.2\lambda$ in air (green line), OTF for $d = 2\lambda$ in air (red line).

In Figure 4.3b OTF slice for $\lambda = 1000\text{ nm}$ is plotted, where $k_x/k_o < 1$ represents the low $\vec{k}$ components of the object, remaining in the propagating mode regime, where the electromagnetic waves can be manipulated by conventional optics. Here the OTF remains above 0.8, showing that the low-frequency information about the object is transmitted quite efficiently. With $k_x/k_o > 1$, we step into the evanescent regime, where it's the loss of these components that contribute to the diffraction limit in conventional optical systems. Several resonance modes are seen in the meta-lens, which lead to the transmission of these high $\vec{k}$ modes. As a check, when we replace the nanowires and

dielectric in the metalens with air, we get a unit OTF for $k_x/k_o < 1$ and an exponential decay when $k_x/k_o > 1$, which is to be expected as the high-k components decay exponentially away from the lens and are hence unable to contribute to the image formation. With a ten-fold increase in the length of the metalens from 0.5λ to 5λ , the transmission of higher wave-vector (k_x, k_y) components through the lens is diminished. This decrement would lead to lower resolution factors at the same wavelength, compared to thinner metalenses.

The lowest limit over which the transmission through the NMM gives acceptable (distortion free) imaging, is approximated by the half intensity criterion. It's defined as $I_o/\sqrt{2}$, where I_o is the transmission in the propagating region ($0 \leq k_x/k_o \leq 1$). Since the intensity in the propagating regime is not constant, we take $I_o = I(k_x/k_o = 0.5) \sim e^{-0.21}$ giving $I_o/\sqrt{2} = 10^{-0.56}$ (shown by horizontal dashed line in Figure 4.3b). According to aforementioned criterion, the highest achievable resolution using the NMM is $\sim \lambda/(2 * 2.77) \sim \lambda/5.54$.

4.3 Imaging diffraction limited objects using SHL

In order to demonstrate the far-field sub- λ imaging capability of SHL, simulations were performed for the following situation: transporting an image corresponding to a set of different 2D, diffraction limited objects, from the inner curvature of the hyperlens to the outer, and then as propagating harmonics into the far-field.

Full-wave 3D simulations were based on a commercial-grade simulator using FDTD method (Lumerical).⁷ Sub-wavelength objects were etched onto a 100 nm thick PEC film. The simulation region spanned $6\lambda \times 6\lambda \times 8\lambda$, along the x, y and z axes, where the inner curvature of hyperlens has a radius (R_{in}) of $0.5 \mu\text{m}$, the hyperlens thickness ($R_{out} - R_{in}$) being $2 \mu\text{m}$. Perfectly matched layer (PML) boundary conditions were employed in all the directions so as to completely reduce reflections from the simulation boundaries.

A radially polarized source, having a slowly varying Gaussian envelope is incident on the diffraction limited objects, described by the following equations: $E_x = \sin(\varphi)e^{-(x^2+y^2)/2\sigma^2}$, $E_y = \cos(\varphi)e^{-(x^2+y^2)/2\sigma^2}$, $E_z = 0$, $\varphi = \arctan(y/x)$

and $\sigma = (FWHM)/(2\sqrt{2\ln 2})$. The exponential terms represent the Gaussian envelope of the source and the sine/cosine terms create the radial polarization (Figure 4.4). The injected source has a full width half maximum (FWHM) of $8\ \mu\text{m}$, which is relatively large, as compared to the dimensions of the hyperlens' inner hemisphere but is chosen so as to have uniform illumination on different sub-wavelength objects, as the incoming beam would then be relatively flat. The source is injected into the simulation from a square area with side $350\ \text{nm}$, so as to confine the source energy inside the inner hemisphere and on the respective sub- λ objects contained therein. The wavelength of the incoming radiation is taken to be $\lambda = 1000\ \text{nm}$ ($= 300\ \text{THz}$).

Figure 4.4 Field plots of the Gaussian light source injected into the simulation. (a) E-field plot of the radially polarized Gaussian source at a wavelength of $1000\ \text{nm}$. (b) x-z plane E-field cross-section at $y = 0$. The FWHM of the Gaussian source is set as $8\ \mu\text{m}$. (c) E-field vector profile of the source which is injected into the simulation, with the inset showing the field vectors for radial polarization.

Hexagonal arrays of nanowires were then arranged in sea-urchin geometry, with individual nanowires projecting radially outwards from the inner curvature. The nanowires have a diameter of $50\ \text{nm}$ ($r_a = 25\ \text{nm}$) at the inner hemisphere and $100\ \text{nm}$ ($r_b = 50\ \text{nm}$) at the outer, with the center-to-center distance between the neighboring nanowires being $a_a \sim 87.3\ \text{nm}$ and $a_b \sim 349\ \text{nm}$ respectively at each of the hyperlens' respective edges. This implies a filling factor $f_a = 27.95\%$ at the inner boundary of the hyperlens and $f_b =$

7.4% at the outer boundary, where the calculation is performed by taking the arc length between neighboring nanowires as the center-to-center distance (a_x ; $x = a, b$) in the unit cell. In order to record the fields propagating into the far-field by the hyperlens, field monitors are placed at various distances: 0.5 μm , 1.5 μm and 2.5 μm , from the hyperlens' outer surface.

E-field vectors oscillating perpendicular to sub-wavelength slits couple effectively to them, while slits parallel to the polarization of the incoming fields don't.⁸⁻⁹ Hence, in order to excite the complete sub-wavelength object in a single illumination, and to couple the source to the hyperlens, a radially polarized source, having a slowly varying Gaussian envelope is incident on the diffraction limited objects (Figure 4.4). Thereby, at each point on the object, a waveguide mode is excited, hence avoiding polarization insensitivity of the objects with respect to the incoming radiation

Various diffraction limited objects were imaged using the SHL in order to check its imaging performance. A nanoring object, as shown in Figure 4.5b, was etched into a 100 nm ($\sim \lambda/10$) thick PEC film, the lateral etch thickness of the ring being 50 nm with the center-to-center separation of 450 nm along the ring diameter, which falls just short of the diffraction barrier ($\sim \lambda/2$). Furthermore, the incoming radially polarized Gaussian source is incident on the object from the $+z$ direction and propagates through the hemisphere with the hyperlens being wrapped around it. Figure 4.5a shows the time averaged Poynting vector plots measured at various distances from the hyperlens' outer surface, where the nanoring is magnified and thereby completely resolved in the far-field. Since the magnification factor of a hyperlens is approximately given by the ratio of its outer and inner radii, R_{out}/R_{in} (see Figure 4.1e),¹⁰⁻¹¹ the magnification factor (at a distance of 2.5 μm) for the SHL is approximated to be ~ 10 since $R_{out} \sim 5 \mu\text{m}$, while R_{in} is fixed at 0.5 μm . The normalized electric field intensity ($|E/E_o|^2$) cross-sections for x-z plane ($y = 0$ plane), shown by the dashed lines in Figure 4.5a, are plotted in Figure 4.5c. With the increase in distance from the hyperlens, the electromagnetic energy in the image plane spreads out, with a corresponding decrease in its peak intensity. E-field intensity at the image plane attenuates by a factor of ~ 0.5 after propagating a distance of 1 μm from the hyperlens. The peak-to-peak distance in the image, 2.5 μm from the hyperlens (blue curve, Figure 4.5c) is $\sim 4.9 \mu\text{m}$, which corroborates closely with the

expected hyperlens magnification factor ~ 10 . Dotted vertical lines represent the cross-section of the nanoring object in Figure 4.5c. Hence, SHL magnifies the sub-wavelength nanoring object and projects it into the far-field, above the diffraction limit, which can then be imaged by a conventional microscope objective.

Figure 4.5 Nanoring object imaged through SHL. (a) 3D Poynting vector plots at different image planes, magnified using SHL at various distances from the hyperlens. (b) 3D schematic of the nanoring sub-wavelength object used to obtain images in (a), the center-to-center separation is 450 nm ($< \lambda/2$) while the thickness of the ring is 50 nm ($\sim \lambda/20$). (c) E-field intensity at different distances from the hyperlens, corresponding to power flow vector plots in (a), shown with dashed lines. The vertical dashed lines in (c) represent the nanoring object with center-to-center separation of ~ 450 nm.

In order to confirm the contribution of SHL in far-field super-resolution imaging, control simulations were performed in the absence of nanowires from the dielectric

matrix. Figure 4.6a to 4.6c show the normalized E-field ($|E/E_o|$) cross-section for beam propagation through the SHL. Nanoring object used previously (in Figure 4.5b) is placed at the inner curvature of the hyperlens with: only SHL (Figure 4.6a), only air (Figure 4.6b), and only dielectric ($\epsilon = 2.3$) (Figure 4.6c). In the presence of SHL, object field distribution is magnified and projected into the far-field, while replacing the hyperlens with a dielectric (air, $\epsilon = 1$), fields decay away from the inner surface of the hyperlens.

Figure 4.6 Normalized E-field profiles showing propagation of radially polarized Gaussian source through SHL. Beam propagation through: (a) SHL, (b) only air ($\epsilon = 1$), and (c) only dielectric ($\epsilon = 2.3$). (d) y-z plane normalized E-field ($|E/E_o|$) cross-section at $x = 0 \mu\text{m}$, $2.5 \mu\text{m}$ below the SHL's outer surface, demarcated by dashed lines in (a), (b) and (c). (e) E_y plot corresponding to $|E/E_o|$ plot in (a), showing fields propagating into the far-field, direction being represented by white arrows.

In air, $\epsilon_i = 1$ (where $i = x, y, z$), resulting in a circular EFC with a unit radius, imposing a cut-off for wave-vector components ($k_x/k_o > 1$) (Figure 4.2b) supported in the medium. Although, in the presence of dielectric ($\epsilon = 2.3$) the EFC becomes a circle of radius ~ 1.5 , the cut-off in the wave-vector components (k_x/k_o) still remains. Figure 4.6d shows the normalized E-field values recorded at a distance of $2.5 \mu\text{m}$ below the hyperlens' outer surface, demarcated by horizontal dashed lines in Figure 4.6a – 4.6c. An order of magnitude enhancement is observed in $|E/E_o|$ due to the presence of SHL compared to when the SHL is absent: $|E/E_o|$ is $\sim 3.2 \times 10^{-2}$ with SHL and between 1×10^{-3} to 5×10^{-3} without the hyperlens.

Corresponding to the normalized E-field profile in Figure 4.6a, its y-component (E_y) is plotted in Figure 4.6e. Alternate change of sign in E_y indicates the propagating nature of the waves, which are projected into the far-field (shown by arrows). Due to the absence of SHL, the lack of nearly flat and unbounded EFC, leads to the loss of sub-wavelength information from the object as its propagation is not supported inside the SHL medium.

Going further below the diffraction limit, a smaller nanoring object was imaged, with a center-to-center separation of 250 nm ($\sim \lambda/4$) (Figure 4.7). The SHL is able to successfully resolve the smaller nanoring system with an image magnification of $\sim 9X$ at a distance of $2.5 \mu\text{m}$ from the hyperlens.

Figure 4.7 Smaller nanoring object imaged through SHL. (a) Shows poynting vector plots for the images magnified using SHL structure at different distances below the hyperlens. (b) 3D schematic of the PEC sub-wavelength object, the center-to-center radius is $\sim 250 \text{ nm}$ ($\lambda/4$) while the thickness of the ring is $\sim 50 \text{ nm}$ ($\sim \lambda/20$). (c) E-field intensity plot corresponding to the dashed lines in (a) at different distances below the hyperlens. The dashed vertical lines indicate the size of the nanoring object with outer radius being 300 nm and inner radius being 200 nm.

Since a nanoring object has infinite symmetry planes through the origin, an object system with reduced symmetry was employed for imaging through SHL. An equilateral nano-hole trimer system¹¹, as shown in Figure 4.8b, with a hole diameter of 100 nm and triangular edge length of $\sim 220 \text{ nm}$ ($\sim \lambda/5$) has only three symmetry planes along the perpendicular bisectors of its edges. Poynting vector plots in Figure 4.8a show successful projection of trimer object information into the far-field using the SHL. Image magnification is further corroborated by the E-field intensity ($|E/E_0|^2$) plots shown in Figure 4.8c, where dashed vertical lines represent the object cross-section, corresponding to two neighboring holes in the trimer system. The field intensity slices at each of the

image planes in Figure 4.8c correspond to the dotted lines in Figure 6a. The peak E-field intensity decreases as the image is magnified with the increase in distance of the image plane from the hyperlens.

Figure 4.8 Imaging a trimer-holed object using SHL. (a) Poynting vector plots for images corresponding to a trimer object system, magnified using SHL, at $1.5 \mu\text{m}$ and $2.5 \mu\text{m}$ from the hyperlens. (b) 3D schematic of the sub-wavelength object, consisting of holes at the vertices of an equilateral triangle, with an edge of 220 nm ($\lambda/5$) and hole diameter of 100 nm ($\lambda/10$). (c) x - z plane E-field intensity ($|E/E_0|^2$) cross-section at $y = 0.4 \mu\text{m}$, at different distances away from the hyperlens, shown by dashed lines in (a). Vertical dashed lines in (c) represent the object cross-section.

The SHL is further also able to resolve a quadramer-holed object (Figure 4.9a), with center to center separation between neighboring nanoholes at 200 nm along the edge of the square and the hole diameter as 100 nm . The Poynting vector plot at a distance of $2.5 \mu\text{m}$ away from the hyperlens shows that the sub-wavelength object is clearly resolved in

the far-field, even though there is some overlap between the corresponding peaks, the image still remains resolvable where the magnification factor of ~ 9.5 is achieved.

Figure 4.9 Quadramer holed object imaged through the SHL. (a) 3D schematic of the quadramer holed object, with center-to-center distance between individual holes (along the square edge) being ~ 200 nm ($\lambda/5$), where the diameter of the individual holes is ~ 100 nm ($\lambda/10$), (b) corresponding poynting vector plots for the quadramer object in the far-field, at a distance of 2.5 μm from the hyperlens.

4.4 Imaging low-symmetry broken-nanoring objects using SHL

We have already shown in the previous section how different diffraction limited objects (i.e. trimers, quadrumers and nanorings etc.) are imaged using the SHL. In each of those situations, a magnified and resolvable image of a sub- λ object is projected into the far-field. In order to further test the imaging capabilities of the hyperlens with reduced symmetry in the diffraction-limited object, the nanoring object (from Figure 4.5b) is split into a broken-nanoring (BNR) system as shown in Figure 4.10a1, wherein the azimuthal span of the ring extends from 0° to 90° and 180° to 270° , 0° being the direction along the positive x-axis. The BNR setup is different from the ubiquitous double slit object^{9, 12} used conventionally for super-resolution imaging demonstrations, since it allows for continuous variation in inter-slit gap, within a single object. Consecutively, the azimuthal span of the BNR is reduced in 30° steps from Figure 4.10a1 to 4.10c1. It is to be noted

that while quadrumer/trimer object has four/three symmetry planes, BNR shown in Figure 4.10a1 to 4.10c1 has two such planes.

Figure 4.10 Poynting vector plots for diffraction limited Broken Nanoring objects, having dual planes of symmetry around the origin. Objects have a decreasing azimuthal span: (a1) 0° - 90° , 180° - 270° , (b1) 30° - 90° , 210° - 270° , and (c1) 60° - 90° ; 240° - 270° , around the origin respectively. The images projected into the far-field, corresponding to their respective objects, are plotted as a function of distance from the hyperlens, (a4, b4, c4): $0.5 \mu\text{m}$, (a3, b3, c3): $1.5 \mu\text{m}$, (a2, b2, c2): $2.5 \mu\text{m}$.

The Poynting vector plots are obtained for each of the broken nanoring object at different distances from the hyperlens, as shown in Figures 4.10a2 to 4.10a4. Intensity at the image plane decreases as the distance from the hyperlens is increased, additionally, as the surface area of the sub-wavelength object is reduced, there is additional drop in the intensity at the image plane. Intuitively, this is because of the decrease in light transmission through the reduced surface area of the sub-wavelength object. In the

Poynting vector plots, the central circle (orange) denotes the inner hemisphere of the hyperlens containing various aforementioned sub- λ objects. The azimuthal spread of image fields from BNR objects are contained within dashed lines (yellow) on the image planes, which act as guidelines corresponding to the BNR object. Since the plot in Figure 4.10c2 is cutoff, image with larger area ($8\ \mu\text{m} \times 8\ \mu\text{m}$) is shown in Figure 4.11.

Figure 4.11 $8\ \mu\text{m}$ by $8\ \mu\text{m}$ poynting vector plot corresponding to Figure 4.10c2.

In order to further reduce the object symmetry to unity, the two components of BNR are reduced azimuthally along opposite directions i.e. top component is rotated clockwise, while the bottom component, anti-clockwise (Figure 4.12a1 to 4.12c1). It can be seen in the corresponding Poynting vector plots that there is a 1:1 correspondence between the objects and the image, where the image components follow the transformations produced in the objects. Hence, even under symmetry reduction in the object, SHL is able to project the diffraction limited information to the far-field.

Figure 4.12 Poynting vector plots for diffraction limited BNR objects, having single plane of symmetry around the origin. Objects have a decreasing azimuthal span: (a1) 0° - 90° , 180° - 270° , (b1) 0° - 60° , 210° - 270° , and (c1) 0° - 30° , 240° - 270° . The images projected into the far-field, corresponding to their respective objects, are plotted as a function of distance from the bottom surface of the hyperlens, (a4, b4, c4): $0.5 \mu\text{m}$, (a3, b3, c3): $1.5 \mu\text{m}$, (a2, b2, c2): $2.5 \mu\text{m}$.

4.5 Conclusions

In conclusion, in the present chapter we have systematically explored the far-field sub-wavelength imaging of various diffraction-limited objects using SHL. Using finite-difference time-domain simulations we show that diffraction-limited objects in the range: $\lambda/2$ to $\lambda/5$ can be successfully magnified by SHL and projected into the far-field. It is the anisotropic permittivity induced by Au nanowire arrays, in spherical geometry, which supports the propagation of high-resolution information through the hyperlens. We further showed that SHL is able to resolve sub-wavelength information in the far-field

even under reduced symmetry in the object. At a wavelength of $1\mu\text{m}$ the imaging resolution of the sea-urchin hyperlens is shown to be $\lambda/5$. The progress made so far will pave the way for designing and realization of real-time bio-molecular imaging systems using conventional optical microscopes.

Although experimental methodology for realization of SHL geometries is still lacking, yet one of the potential methods available to achieve the same is by using the nanoscale pores in either AAO (anodic aluminum oxide)¹³ templates or block co-polymer films¹⁴ as channels for nanomaterial growth. The necessary curvature for hyperlensing could be obtained by anodization of the curved Al-foils¹⁵. In another work,¹⁶ high resistivity impurities in Al was utilized to prepare pre-formed (i.e. curved) AAO templates which were later electrodeposited with Ag.

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Chapter 5

Fabrication of Metal-dielectric Nano-composite Metamaterials

In the previous section simulations for super-/hyperlens devices were shown. Taking design cues, in the present section we look at the fabrication methodology of the envisaged structures and at possible ways in realization of desired metal-polymer nano-composite metamaterials. Section-wise Fabrication techniques and methods for preparation of thin polymer films embedded with ordered Au nanowires will be presented.

5.1 Fabrication of Au nanowire array (AuNWA)-polymer composite

5.1.1 Synthesis of AuNWAs using electrodeposition

First step in the preparation of metal-polymer nanowire composite films is the synthesis of regular and free-standing nanowire arrays supported on a solid substrate. One of the most common techniques used therein is the synthesis of one-dimensional nanomaterials by deposition of materials inside nanoscale pores of different templates (for eg. Anodic aluminium oxide (AAO) templates,¹⁻² polymer track etch membranes³ etc.). Vertical and through-hole AAO templates with 60 μm thickness and pore diameter ranging from 40 to 70 nm were obtained from PuYuan Nano Inc.

Firstly, a thin Cr-film (~ 10 nm) is thermally evaporated on top of the AAO templates, which acts as an adhesion layer for further layers to be deposited. Ag layer with a thickness of ~ 300 nm was then evaporated on top of the Cr film. During thermal evaporation process, the deposition rate for Ag was kept at ~ 1.5 $\text{\AA}/\text{s}$ and for Cr at 2 $\text{\AA}/\text{s}$. It was observed that $\sim 80\%$ of the films delaminated from the AAO template in further fabrication processing steps, in the absence of Cr adhesion layer.

A thick layer ($\sim$ few microns) of Ni was electroplated on top of the Ag film using a two electrode nickel bath setup with Ag rod acting as the cathode. The thick Ni layer not only acts as a support for the silver layer but also as a sacrificial layer later on in the processing. After the deposition of conducting support/sacrificial layers on the AAO membranes, the nanoscale pores in the membranes were electrochemically filled with Au. The electrochemical deposition of Au was performed using a commercial electroplating solution (Tecnic Gold 25ES). The electroplating solution was cooled $\sim 5^\circ$ to 10°C and deposition was then performed under potentiostatic ($V \sim -950$ mV) conditions. In general, solution cooling allowed for better electrodeposition of metal inside the AAO pores because of lower thermal fluctuations, thereby reducing variation in nanowire length distribution across the template. Pt mesh was used as the anode while the Ag film deposited earlier formed the cathode with NaCl electrode being used as the counter electrode. The length of the nano-pillars was controlled using the amount of charge deposited during electrodeposition. Au nanorods of length ~ 450 - 500 nm are obtained

after depositing ~ 500 mC of charge during the deposition. Schematic for the steps presented thus far is shown in Figure 5.1a-c.

Figure 5.1 schematic representations of fabrication steps involved in embedding hexagonally arranged free-standing AuNWAs into flexible bulk PDMS/PMMA films. (a) through-hole empty anodic alumina (AAO) template, (b) thermal evaporation of 10nm Cr film on the back surface, (c) thermal evaporation of 250 nm Ag followed by electroplating of a thick Ni film, (d) electrodeposition of AuNWAs into the pores of AAO, (e) conformal bonding of sample on glass surface using a sodium silicate (liquid glass) solution, (f) complete dissolution of AAO template in 0.5M NaOH soln. followed by supercritical drying in liq.CO₂, (g) infiltration of PDMS (in 65% hexane) solution onto the AuNWAs, (h) selective etching of Ni and Ag sacrificial layers respectively and the AuNWA-PDMS film lift-off from the substrate.

5.2.2 Bonding on glass substrates

Next step in the fabrication process is the bonding of the thick Ni backing on to a glass slide, which will act as a superstrate for the sample. Individual glass slides were cut into square pieces ~ 2.5 cm x 2.5 cm and then cleaned by ultra-sonication in acetone and ethanol. Oxygen plasma was then performed for ~ 5 minutes (@100W, Pressure 70 mTorr) on the cleaned glass slides along with the Ni-backed AAO templates, leading to the formation of a thin layer of NiO (this is clearly visible due to a colour change from silver grey to deep blue/black). The oxygen plasma processing step renders both Ni and glass surfaces hydrophilic which later assists in their bonding. It is important to note that the material used for bonding glass to NiO surface should maintain sample flatness and be strongly resistant to chemicals used in processing steps thereafter. Sodium silicate solution (Na_2SiO_3 or ‘liquid glass’) was employed as the bonding agent since it forms a strong adhesion and maintains the flatness of the sample. Liquid glass solution has been shown previously⁴ to be effective in preparation of ultra-flat and solvent-resistant gold surfaces. 50 μL of sodium silicate solution is carefully drop-casted on the hydrophilic NiO surface and the pre-cleaned glass slide is immediately inverted and slowly left on top of the Cr surface. Care should be taken to make sure that sodium silicate solution spreads uniformly, forming a thin conformal layer between the two surfaces (Figure 5.1e). Samples are then kept in an oven for 12 hrs at 70°C , followed by 120°C again for 12 hrs. Application of heat allows for slow release of water from the sodium silicate network leading to the formation of glass, strongly bonding the two surfaces together.

The samples were later immersed in a 0.5 M NaOH (sodium hydroxide) solution for >5 hrs so as to completely etch away the AAO template (see Figure 5.1f). It is to be noted that with higher concentrations ($>1\text{M}$) of NaOH the film was observed to delaminate within a few hours. With higher concentrations or longer etching durations of NaOH sol. the sodium silicate network would be attacked considerably, causing weakening of the bonding between Ni film and glass superstrate. Under favorable conditions, sodium silicate forms a strong adhesion layer between the NiO surface and the glass substrate, keeping the Ag film with nanowires, conformal, even in presence of strong bases. Figure

5.2a-c shows FESEM images of the Au nanowires after complete dissolution of the AAO templates, followed by supercritical drying which is explained in the next section.

Figure 5.2 (a-c) FESEM images of Au nanowires after dissolution of AAO templates in 0.5M NaOH soln. followed by supercritical drying at different magnification factors (d) without supercritical drying.

5.2.3 Supercritical Drying

After the removal of AAO template supporting the nanowires, the samples are slowly immersed in a series of beakers containing DI (ultrapure) water in order to remove the NaOH solution and the dissolved aluminum oxide template. The presence of either NaOH or DI-water in the gap between nanowires prevents their aggregation or collapse,

in contrast to when the sample is allowed to dry in air, slow evaporation of water results in capillary forces causing the collapse of nanowires into bundles (see Figure 5.2d).

In order to prevent the collapse of the Au nanowires upon dissolution of AAO template, super-critical drying was performed on the samples. After AAO was etched away in NaOH soln., the sample was carefully immersed in ultrapure absolute ethanol (99.99%) for ~5hrs, followed by immersion in fresh absolute ethanol two more times. This is done to remove any residual alumina/NaOH impurities from the nanowire sample. The supercritical drying chamber was filled with ultrapure ethanol and the nanowire sample is inserted inside it. The critical drying process in principle involves replacing the ethanol present between nanowires with liquid carbon dioxide, followed by an increase in the temperature and pressure to beyond the critical conditions.⁵ Above the critical T and P, liq. CO₂ exists in gaseous state, which is then exhausted from the system, thus avoiding meniscus pinning effects which lead to nanostructure collapse. Critical drying step significantly improves the sample quality, resulting in higher turnover of free-standing nanowire arrays. (see Figure 5.2a-c)

5.2.4 Polymer penetration

Fabrication of Au-NWA/PDMS or Au-NWA/PMMA composite films is performed by penetrating the respective polymers (PMMA or PDMS) in the gaps between neighboring nanowires. Typical length scales for distances between the nanowires are around ~30-40nm, which inevitably makes it difficult for penetration of polymers in the inter-nanowire spaces. The main reason being the generally high viscosity of the polymers under consideration.

The polymers were diluted in organic solvents so as to reduce their viscosity and thereby help in their penetration inside inter-nanowire spaces. PDMS prepared in 10:1 (base : cure) ratio was diluted in 65% n-hexane and then drop casted on the AuNWA sample prepared previously. PMMA (120k) was dissolved in xxxx to make xx M polymer solution. Degassing is performed by keeping the samples under vacuum (better than 30 in of Hg) for 10hrs. Extended vacuum duration allows polymers to effectively penetrate the small gaps (30 - 40 nm) between the nanowires. Samples were then

annealed at 50°C for 5hrs under vacuum. The sample with nanowire arrays and PDMS are then peeled off from plastic cups. Small parts of the PDMS were removed so as to expose the sides of the thick Ni film. The electroplated Ni film is then etched in a 1M FeCl_3 (Ferric Chloride) solution. Etching was performed for 2 days after which the transparent PDMS film containing a blood red hue (from Au nanowire arrays) floated to the top of the etching solution. As seen in the transmission mode (Figure 5.3a), a reddish-brown colour indicated the presence of AuNWA, indicating that Au nanowires have indeed been transferred to the polymer. This process results in the formation of thick (~mm scale) PDMS films.

Figure 5.3 (a) AuNWAs-PDMS composite metamaterial sample immersed in water. (b) perspective photograph of the sample.

Figure 5.4 shows the AuNWA-PDMS sample wherein the nanowires with diameters of ~40-70 nm are embedded in the PDMS matrix. It is to be noted that Au nanowires remain well separated and maintain their anisotropic orientation which is perpendicular to the substrate. The FESEM image in Figure 5.4 confirms the successful penetration of the polymer matrix in the sub-100 nm gaps between the nanowires.

Figure 5.4 AuNWAs with 40-70nm diameter embedded in PDMS film. The nanowires are flushed onto the surface. The large scale bars in both images are 1000nm.

Various research groups have looked into the penetration of polymer materials within the arrays of metallic and semiconducting nanowires with pitches ranging from upwards of 200 nm⁶, this is the first time sub-100nm penetration of Au nanowire arrays has been reported to the best of our knowledge this is the first time that sub-100nm inter-nanowire gaps have been infiltrated with a polymer, previous reports showed successful infiltration of nanowire gaps in the micron scales.⁶⁻⁸

In Figure 5.5d the EDX spectra corresponding to the FESEM image in Figure 5.5a (pink square) is shown, while the respective atomic%/weight% from the sample is shown in Table 1., Implying that the sample is comprised of Au, Si and O atoms. While the Au EDX signal comes from the nanowires, Si and O EDX signals come from the siloxane chains in PDMS. Further corroborating evidence is obtained by XRD spectrum of the sample, shown in Figure 5.5b where ubiquitous peaks corresponding to different crystal planes of Au is ostensible.

Figure 5.5 (a) EDX spectrum of the pink inset of the AuNWAs-PDMS film. EDX confirms the presence of elements: Au, Si and O, indicating the presence of AuNWs embedded inside PDMS (siloxane molecule chains). (b) XRD spectrum of the free standing gold nanowires. (c) UV-vis absorption spectrum of the AuNWA-PDMS samples showing the absorption peak corresponding to the dipole resonance of Au nanowires @ $\lambda \sim 520$ nm.

Table 5.1 Atomic% and weight% contributions corresponding to EDX plot in Figure 5.5

Element	Weight%	Atomic%
O K	15.93	45.64
Si K	24.86	40.58
Au M	59.21	13.78
Total	100	

UV-visible absorption spectrum from the sample was obtained in the transmission mode. The characteristic surface plasmon resonance (SPR) peak for Au is observed at a wavelength of ~ 520 nm. This corresponds to the dipolar resonance of the individual Au nanowire in the arrays. Hence, combining FESEM, XRD, EDX and UV-vis characterization techniques, it can be confirmed that the fabrication technique presented thus far was able to successfully transfer free-standing Au nanowire arrays into a flexible polymer (here PDMS).

5.2.5 Ultra-microtomy

The sample prepared earlier consists of Au nanowires embedded in a thick polymer (PDMS/PMMA) matrix. This resulted in a PDMS film with thickness ~ 1 mm containing the AuNWAs (length $\sim 1 \mu\text{m}$) with preserved orientation and nanowire spacing with the nanowire arrays being flushed onto one edge of the PDMS host matrix. As shown earlier in Chapter 2, for superlensing applications it becomes imperative for the nanowires to extend from one end of the polymer matrix to the other, since the high resolution information decays evanescently away from superlens edges. Ability to fabricate thin sample slices will enable nanowires to span from one edge of the sample to the other, enabling the ability of the sample to act as a superlens. Ultra-microtome sectioning was performed on the samples in order to obtain thin ($\sim 0.1 \mu\text{m}$ - $1 \mu\text{m}$; depending on the length of nanowires) slices of the composite metamaterial lens.

In order to perform ultra-microtomy the composite metamaterial sample has to be embedded inside an epoxy host, with the sample surface being kept parallel to the epoxy block. Figure 5.6 shows photographs of various steps involved in embedding the sample inside an epoxy block. Flat pieces of PDMS (2 cm x 2 cm x 0.2 cm) are obtained by using the PDMS kit by mixing silicone elastomer and curing agent in the ratio 10:1. Araldite 502 kit with BDMA is used as the embedding epoxy medium. Firstly, the surface of PDMS is cleaned thoroughly in DI water and later dried. A small (few μL) drop of araldite is placed on the PDMS base and the sample is slowly lowered on it, face down, with nanowires facing the PDMS base. This will ensure that the sample surface is

parallel to the PDMS base. The sample is then cured for 24 hrs at 60°C in an oven. A separate PDMS block is fabricated and a 0.5 cm x 0.5 cm through-hole cavity is carved out from its center (Figure 5.6c). Surface of PDMS base (Figure 5.6b) and PDMS block (Figure 5.6c) were activated by performing O₂ plasma for ~24 sec at 70% power.

Figure 5.6 Fabrication sequence for embedding AuNWA-PDMS sample inside epoxy. (a) 2mm thick flat PDMS base (b) ~1mm x 1mm sample adhering on the PDMS base using araldite epoxy glue (c) 5mm x 5mm hole carved out of PDMS block. (d) block in (c) is sealed on top of PDMS base in (b). (e) the cavity in the block filled with epoxy (f) back surface of the PDMS block after peeling off from the PDMS base. (g) epoxy block with sample after removing the surrounding PDMS block.

The block was then combined with the base forming a mold as shown in Figure 5.6d. The mold was later filled with araldite (Figure 5.6e) and left to cure for ~24 hrs to form a backing support for the sample. Figure 5.6f shows the sample after the PDMS layer was peeled off, with the sample being parallel to the epoxy block. Figure 5.6g shows the final sample with the AuNWA-PDMS embedded in araldite and the sample being flushed on the surface.

The glass transition temperature (T_g) for PDMS is ~-125°C, implying that above this temperature PDMS will remain flexible and below it, PDMS will behave like a solid.

While performing microtomy under cryo- conditions the sample and the glass blade are cooled down to below T_g by liq. N_2 (-196°C). Sample hardening allows for easier sectioning of the AuNWA-PDMS sample. Samples containing metal nanowires embedded in PMMA offer the advantage of easier sectioning, since the glass transition temperature for PMMA is $\sim 105^\circ\text{C}$. High T_g eliminates the need for sample cooling and makes sectioning easier.

In order to check the sectioning properties of PMMA under ultramicrotome, bare PMMA was sectioned using a glass knife at room temperature. The sections obtained as shown in Figure 5.7 have different colors corresponding to the thicknesses of the sections obtained. Typically the dimensions of the sections obtainable from glass knives depend on the length of the sharp regions on the knife's edge which is typically $\sim$ few mm. The sections obtained are large ($\sim$ few 100 μm to few mm) and have imperfections (from the glass knife) only to a certain extent. Most of the areas obtained are flat, as is evident by the nearly uniform coloration.

Figure 5.7 Optical microscopy transmission images of bare PMMA thin films, sectioned using room temperature ultramicrotome. White scale bar in all image is $100\mu\text{m}$.

In addition to preparation of AuNWA-PDMS samples shown in Figure 5.6g, another sample was prepared where a $\sim 1\text{mm}^2$ of the sample was completely embedded inside epoxy. It was then sectioned using a glass knife at room temperature in order to get the cross-section of AuNWA-PDMS samples. The thin slices obtained were then deposited on TEM grids using metallic loop tool for performing FESEM (Figure 5.8). An array of Au nanowires with a height of $\sim 250\text{nm}$ can be seen sandwiched between the epoxy layers. There is some amount of physical damage (distortion) in the nanowire layer, possibly due to the mechanical forces from the glass knife during the sectioning process. The cross-section slices obtained from microtome, in addition to previous characterizations, confirm the presence of nanowires within the polymer matrix.

Figure 5.8 FESEM images of the AuNWA-PMMA composite cross-section at different magnifications placed on top of a TEM Cu-grid. The scale bar in all FESEM images is $1\mu\text{m}$.

5.3 Conclusions

In the present chapter we have outlined in detail, the steps developed for fabrication of metamaterials composed of metallic nanowire arrays in polymer matrices. The free standing nanowire arrays maintain their orientation and the sample shows their successful transfer into the polymer, as evidenced from various characterization techniques including cross-section slices using microtomy.

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Chapter 6

Fabrication of Diffraction-limited Objects for Imaging

In Chapter 5 process for fabrication of metal-dielectric composite metamaterial films was described, in the present chapter, we focus on the fabrication of sub-wavelength objects for superlensing and hyperlensing applications. Scanning near-field optical microscope (SNOM) imaging was done to observe light transmission through the object. While FDTD simulation was performed for the diffraction limited object in hyperlensing.

6.1 Introduction

In general the sub-wavelength objects for demonstration of Superlensing and Hyperlensing are fabricated directly on the lenses, such as the flat/curved metal-dielectric multilayer structures. Once the object is fabricated, it permanently remains on the lens and hence hampers its usability. Here we look at object fabrication for Superlens and hyperlens wherein the flexible free floating lens can be deposited directly on top of the respective objects.

6.2 Diffraction-limited Objects for Superlensing

We have designed the sub-wavelength objects to take the following values: $\lambda/2$, $\lambda/3$ and $\lambda/4$, in order to check the imaging from sub-wavelength structures using the nanowire MM hyperlens in a flexible matrix. Here $\lambda=632$ nm (He-Ne laser wavelength). Figure 6.1

Figure 6.1 Fabrication of sub-wavelength objects for Superlensing using FIB. (a) cross-section schematic of the sub-wavelength object for superlensing (b-d) FESEM images

(top view) corresponding to the Focus Ion Beam etched samples where Cr + AZO layers have been removed, with center-to-center separation between the etched slits (x) ranges from 316nm ($\sim\lambda/2$), 210nm ($\sim\lambda/3$) down to 160nm ($\lambda/4$).

Shows the three sets of sub-wavelength objects fabricated using FIB milling of Cr films. There is a layer of AZO below the Cr film in order to improve the conduction properties of the film. It can be seen that the etching tradeoff between complete etching of Cr versus the removal of central island between the slits. It was observed that if the slits are etched completely the central island between the slits would disappear in its entirety. So in order to have the slits we only remove the Cr film at the two locations partially.

In general after completely etching through the conducting thin films the, the etched regions should appear brighter

Figure 6.2 (a-b) Atomic Force Microscope profile (left : perspective view) and (right: top view) of the sub-wavelength objects fabricated using FIB ($x \sim \lambda/2=316\text{nm}$), (c) height profile of the sub-wavelength slits, showing the asymmetry produced due to the milling process of the FIB system. Right slit is deeper than the left by approximately 20nm, which was confirmed again using high aspect ratio AFM tips.

Initially the sub-wavelength objects were fabricated using FIB milling, but a few issues were encountered. The slit side walls were not vertical and the centre-to-centre gap

beyond $\lambda/3$ was not easy to obtain. These problems were solved by using e-beam lithography instead. Fig 3. Shows the AFM and FESEM images of the sub-wavelength slits, where nearly vertical side walls are evident. In the SEM images one can observe that etched Cr regions appear darker indicating that the film has been completely etched through. This would allow for higher light transmission through the slits under laser illumination.

Figure 6.3 AFM (perspective view) and FESEM (top view) images of sub-wavelength objects in the form of two parallel lines, fabricated using e-beam lithography. Taking the operating wavelength as 632nm, the center-to-center distance between the objects is varied: $\lambda/2$, $\lambda/3$ and $\lambda/3.5$.

6.2.1 Scanning Near-field Optical Microscope (SNOM) Imaging

After the fabrication of sub-wavelength object using FIB/e-beam lithography, the object was checked for light transmission using a Scanning near-field optical microscope operating at 632nm wavelength (He-Ne laser).

Figure 6.4 Scanning Near-field Optical Microscope (SNOM) scan of the sub-wavelength slits using a He-Ne laser @632nm.

Insert optical microscopy images of the sub-wavelength object fabricated using e-beam lithography

6.3 Diffraction-limited Objects for Hyperlensing

In Chapter 4, detailed FDTD simulations were performed to study far-field imaging and magnification through sea-urchin hyperlenses. It was shown that in order to project the sub-wavelength information into the far-field, where it can be picked up by a conventional microscope, the lens requires a curvature. While in Chapter 5 we outlined steps to fabricate nano-composites consisting of metallic nanowires embedded in flexible dielectrics. In this section a possible method for the fabrication of objects on a curved surface is presented.

Dilute aqueous suspension of silica (SiO_2) microspheres (radius $\sim 3.5 \mu\text{m}$) were spin coated on quartz substrates at ~ 4000 rpm and then dried at ambient conditions. Though most of the microspheres ended up in clusters of 2-4 spheres (shown in Figure 6.5a), yet isolated and well separated ($>20 \mu\text{m}$) microspheres were available as well. A ~ 75 nm thick Cr film is thermally evaporated on top of the sample, which results in the formation of Cr caps on top of the silica microspheres and a Cr film on the quartz substrate.

Figure 6.5 (a) Silica (SiO_2) microspheres with a diameter of $3.5 \mu\text{m}$ on quartz substrate after thermally evaporating a 75 nm Cr layer. Strong charging effects are evident because

of discontinuity of Cr film between the Cr caps and Cr film on quartz. (b) trimer system of Cr coated silica microspheres.

Since the evaporation was performed in the perpendicular direction to the substrate, a disconnect is formed between the Cr-caps and Cr-film. Charging effects are hence expected and observed under FESEM imaging, as is evident in Figure 6.5a and 6.5b, in the form of bright spheres and dark lines. The FESEM image was also not stationary because of the considerable charging effects, eventually making it extremely difficult to mill sub-wavelength features (or objects) on top of the Cr-capped microspheres.

In order to mill diffraction limited objects using Focused Ion Beam (FIB) the charging effects have to be made minimal, otherwise the object's integrity and structure is compromised. The charging problem was overcome by performing ALD (Atomic Layer Deposition) of ~50 nm AZO (Aluminum Zinc Oxide), before the deposition of Cr layer. AZO, much like ITO (Indium Tin Oxide), is a conducting and transparent oxide¹ and hence would allow for minimization of charging effects without decreasing the light transmission through the system. After ALD, AZO forms a conformal layer both on the SiO₂-Quartz substrate and would allow us to eliminate charging effects while performing FIB. After ALD of AZO layer 75 nm of Cr was thermally evaporated on top of the samples. Figure 6.6 shows the FESEM images of Cr/AZO/SiO₂ samples where it can be seen vividly that most of the charging effects have been eliminated and the surface of Cr films can be seen clearly compared to the images in Figure 6.5. Eliminating the drifts caused by charging effects enables precise and controlled milling of sub-wavelength objects on top of the Cr-caps.

Figure 6.6 silica microspheres coated with 75 nm Cr using thermal deposition system. Silica microspheres are first coated with a thin layer ($\sim 50\text{nm}$) of AZO before performing the thermal deposition using ALD. Charging effects are eliminated because of sandwiched AZO layer.

FIB milled objects on the Cr-caps are shown in Figure 6.7a (top view) and 6.7b (52° perspective view), where two types of objects fabricated were the ubiquitous double slits and the trimer holed objects at the corners of an equilateral triangle. Earlier, in Chapter 4, the trimer-holed object system was simulated for imaging using the sea urchin hyperlens.

Figure 6.7 images (side view and top view) after FIB milling of objects (three holes and double slits) on Cr caps. The side view is taken after tilting the sample to an angle of 52° . The holes have a diameter of 100nm with a center to center separation of 200nm. The slits have a width of 100nm with a center to center separation of 200nm and a length of 500nm.

The slit width in Figure 6.7a is ~ 100 nm, with distance between the two slits being ~ 200 nm. Whereas the holes have a diameter of ~ 100 nm with center-to-center separation of ~ 200 nm. Since the milling process doesn't take into account the curvature of the Cr film, some parts of the silica microspheres are expected to be etched away. This should only add to minor reflection losses from the slits. These objects fabricated would fall just below the diffraction limit when the light source operated at visible frequencies (400 nm - 700 nm).

6.4 FDTD Simulations for Hyperlens Objects

In the previous section, FIB milling was performed on 3D Cr caps atop silica microspheres to provide curvature for hyperlensing applications. It becomes imperative to perform FDTD simulations in order to analyze the field distribution and beam propagation through the hyperlens objects. Figure 6.8 shows a schematic for the proposed setup where light is incident on the substrate from the bottom. Thermally evaporated Cr film acts as a mask and light is only allowed to pass through the areas with circular opening in the Cr film or the areas covered with silica microspheres. It has been previously shown that the microspheres have a property of focusing the light into a cone, which has been utilized by various groups to perform sub-wavelength lithography, projections etc.²⁻⁴ The light concentration effect would allow for higher incident E-field

Figure 6.8 schematic showing two FIB milled sub-wavelength ($<\lambda/2$) slits on the silica microspheres. Light polarizations parallel to the slit is TE (Transverse Electric) and the perpendicular to the slits is TM (Transverse Magnetic). In the experiments light is incident from the bottom towards the quartz substrate. Thin AZO layer under the Cr surface is not shown in the figure.

Figure 6.9 shows the E-field intensity distribution inside the silica microspheres using an incident plane wave ($\lambda=534$ nm), where the focusing action of the microsphere is apparent. In these simulations the actual fabricated structure is taken into consideration,

including the ~50 nm AZO spacer layer. It can also be seen that the TM polarized (E vector perpendicular to the slits; Figure 6.9a) source couples to the slits while the TE polarized (E vector parallel to the slits; Figure 6.9b) doesn't. Propagation of the polarized light through the microsphere also doesn't alter the polarization state of the incoming light source. In addition to recording the E fields on the cross section of the device, Figure 6.9c and 6.9d show the E fields on top of the slits (corresponding to dotted lines in Figure 6.9b and 6.9a).

Figure 6.9 (a) (b) (c) (d) E-field distributions : (top left) TM polarized incident plane wave, (top right) TE polarized incident plane wave, (bottom left) at the top of slits along the dotted lines in top left figure, TM polarized (bottom right) at the top of slits along the dotted lines in top right figure, TE polarized. All the plots have the same scale in order to make the comparison easier.

Interference patterns are produced inside the microsphere because of the interaction of the incoming refracted waves and the light waves that are reflected from the silica-Cr

interface. Fields produced therein are ~3 times stronger for TM polarization compared to TE, implying that the E-field intensity is ~10 times stronger. It is to be noted that although the ~75 nm Cr layer only allows light to transmit through the sub-wavelength objects, the gap between the Cr-caps and Cr-film allow light to couple out from the sides.

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Chapter 7

Discussion and Future Work

This chapter brings together different sections of the thesis in a conclusive manner. Ideas about probable high impact future directions are also discussed, including optical cloaking of objects and design of tunable flat lensing devices based on nanowire-polymer composites.

7.1 Summary

Smallest objects that can be resolved using conventional optical microscopes are limited by the ‘diffraction-limit’ of light. In the thesis work presented herewith we have successfully proposed and demonstrated the design of metal-dielectric nanowire composite metamaterial lenses for applications in sub-wavelength imaging. Initially, hexagonally arranged arrays of metallic nanowires were shown reproduce diffraction-limited information in the near-field of the meta-lens. One needs to be present in the n

to perform superlensing: reproducing the sub-wavelength information from objects, in the near-field of the lens. Nanowires arranged in sea-urchin geometry were later shown to be indeed capable of projecting diffraction-limited sub-wavelength information to the far-field. We further proposed a realistic method for fabrication of metal-dielectric composite metamaterial consisting of metallic nanowires embedded in dielectric matrix. In order to test the imaging capabilities of the metalenses, methods for fabrication of sub-wavelength objects were also presented. Particularly, a unique method for the fabrication of objects on curved Cr-caps was employed for hyperlensing application.

Although the Au nanowire-polymer composites were shown to be successful in resolving sub-wavelength details in the near-field (when flat) and far-field (when curved into a SHL), losses can become a matter of important consideration. Recently there has been a shift towards all dielectric metamaterials in order to minimize the losses from traditional plasmonic metals. In principle as long as the conditions for anisotropy in permittivity tensor are maintained, the imaging principle should hold.

7.2 Future Work

7.2.1 Deposition of AuNWA-PDMS thin films on Superlens and Hyperlens objects

Thin films of AuNWA-PDMS composite metamaterial obtained by ultramicrotomy is to be deposited on top of the sub-wavelength objects fabricated earlier using e-beam lithography and focused ion beam techniques. In the case of superlens, a scanning near field optical microscope scan will then be performed to record the fields in the near-field of the superlens. In the case of hyperlens, the thin metamaterial slice has to be deposited on top of the FIB milled Cr-caps. It becomes essential that the film conforms to the surface of the Cr-cap. Another crucial consideration is the fact that under the process of depositing lenses on top of the Cr-object, the microsphere should remain stationary

7.2.2 Cloaking using nanowire embedded inside flexible polymer matrix

Cloaking especially in the optical regime is one of the more fancier applications of metamaterials which has generated a lot of interest.¹⁻³ It typically involves engineering the permittivity values of the cloak between 1 and 0 (1 at the outer surface and 0 at the inner). As we have seen earlier in Chapter 4 (Figure 4.2), filling factor of the metal component in the dielectric is one of the main factors governing anisotropic permittivity tensor components. Hence by choosing the best parameters of the nanowire-polymer composites objects should in principle be cloaked effectively from incoming electromagnetic radiation.

Figure 7.1 Schematic showing the nanowire-polymer cloak surrounding a PEC object.

Inset shows the transition between a cylindrical and conical nanowire as a means of controlling the permittivity parameters of the cloak at different interfaces.

Figure 7.1 shows the schematic for the envisaged cloak consisting of metal nanowire-polymer composite, wrapped around a PEC object. Inset shows that by varying the radii at the two edges a cloak matching the required permittivity parameters can be obtained. In Figure 7.2 shows E_y for a plane wave ($\lambda = 550$ nm) impinging on the PEC object only (Figure 7.2a) and cloak on PEC object (Figure 7.2b). From preliminary simulation results it can be seen that in the presence of only dielectric, large reflections are produced, while in the presence of the cloak (Figure 7.2b) those reflection are suppressed. Although the field distribution on the behind the object is not ideal, we believe it can be mitigated by managing loss inside the cloak.

Figure 7.2 E_y field distribution of a plane wave impinging on (a) dielectric wrapped around a PEC object. (b) cloak wrapped around a PEC object.

7.2.3 Tunable flat lensing based on ENZ nanowire metamaterials with gradient

Another application for the composite nanostructures under study is their use as a flat lensing device. It was shown previously⁴ that an interface of two epsilon-near-zero (ENZ) metamaterials can function as a light concentration device.

Here we used a type-I HMM consisting of metallic nanowires embedded in a dielectric matrix as the building block for the flat lensing device. As a preliminary study we performed 3-D FDTD simulations for the flat lens composed of nanowire type-I HMMs which are rotated by $\sim 10^\circ$ with respect to their anisotropy axis. As we have seen in Chapter 3 that by tailoring the filling factor of the metallic component inside the dielectric host, electromagnetic beam can be bent inside the metamaterial. Since the two rotated type-I HMMs bend light towards the interface region between them, by tuning the nanowire radii along the anisotropic axis of HMMs the focus produced by the flat lens can be modified.

Figure 7.3 (a) $|E/E_0|$ plot of the proposed nanowire based tunable flat lens. (b) $|E/E_0|$ control plot without the nanowire metamaterial. Plane wave with wavelength of 871 nm is incident from the top of the lens while cross-section of the near-field focus is measured along the dashed lines.

Figure 7.3a shows the normalized E-field distribution for a plane wave ($\lambda = 781$ nm) incident on type-I nanowire HMM junction. The focusing action of the flat lens is evident while in the absence of the HMM, most of the incoming radiation is transmitted through the dielectric (Figure 7.3b). Figure 7.4 shows the Poynting vector plots corresponding to dashed lines in Figure 7.3a and 7.3b measured at a distance of 100 nm below the lens.

Figure 7.4 Poynting vector plot corresponding to dashed lines in Figure 7.X at a distance of 100 nm below the flat lens. Red lines correspond to plot without the HMM while black lines show P in the presence of HMM.

In the presence of HMM a sharp focus is produced near the flat lens while in its absence the focus disappears. Future work will involve the effect of beam steering on the focus.

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