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Light Propagation and Imaging in Indefinite Metamaterials

By

Jie Yao

A dissertation submitted in partial satisfaction of the requirements for the degree of

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in

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in the

Graduate Division

of the

University of California, Berkeley

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Fall 2010
Abstract

Light Propagation and Imaging in Indefinite Metamaterials

by

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Doctor of Philosophy in Applied Science & Technology

University of California, Berkeley

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Unlike any traditional materials, indefinite materials possess very unique optical properties. The principal components of its permittivity and/or permeability tensors are not all with the same signs, resulting in a hyperbolic dispersion relation. Such extraordinary dispersion leads to a number of interesting phenomena, such as negative refraction of light at its interface with normal materials, the propagation of electromagnetic waves with very large wave vectors which are evanescent in natural dielectric materials.

Due to the development of metamaterial research and nanofabrication techniques, we have successfully created a type of metamaterial made of parallel silver nanowires embedded in porous alumina matrix. Both effective media theory and finite element simulations showed that such metamaterial possesses indefinite permittivities. We performed optical measurements of visible and infrared light transmitted through such metamaterials. By using an NSOM system capable of mapping the light field distribution with sub-wavelength resolution at both the surface of the nanowire metamaterial and the 3D space near the surface, we have demonstrated all-angle negative refraction and slab lens imaging of visible light in nanowire metamaterials.

The nanowire metamaterials hold the indefinite permittivity over a broad frequency range from visible to infrared, therefore negative refraction phenomena are not restricted in a narrow band any more. By avoiding magnetic resonance, the nanowire metamaterials show substantially reduced energy loss and make negative refraction possible in bulk materials.

Since the indefinite materials support the propagation of very large k waves, deep
sub-wavelength 3D nanocavities can be made from them. Theoretically there is no lower limit to the size of the cavity with ideal indefinite materials. Unlike traditional dielectric cavities which resonate at higher frequencies when the cavity size reduces, indefinite cavities with sizes several orders different may resonate at the same frequency and same mode order. Furthermore, the size dependence of quality factor due to the radiation loss also shows an inversed behavior compared to traditional dielectric cavities.

Another interesting phenomenon we have discovered is the abnormal diffraction inside the nanowire metamaterials. The hyperbolic iso-frequency contours of such materials are “flatter” for light with longer wavelengths, because of the strong dispersive behavior of the metal in the metamaterials. Since the Poynting vector is normal to the iso-frequency contour, the diverging angle of diffracted light inside the nanowire metamaterial decreases as the wavelength gets longer, which is the opposite to the diffraction in dielectrics. The flat iso-frequency contour together with the large k wave transmission may lead to the possibility of deep sub-wavelength imaging or lithography with the nanowire metamaterials.

Besides the research on indefinite metamaterials, I also studied the “2D optics” of surface plasmons. Based on the interference of surface plasmons, sub-wavelength patterns can be lithographically created on a metal surface. We also predicted the existence of surface plasmon beats formed by the interference of two different modes excited on the same thin metal film.
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PUBLICATIONS AND PRESENTATIONS


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Chapter 1

Introduction

1.1 Manipulation of light with metamaterials

The development of human society is always associated with, and to some extent propelled by the discovery of new materials. A good example is the progress of human civilization from Stone Age to Bronze Age, and then to Iron Age[1]. In the last several centuries science and technology have been developed to an unprecedented height, accompanied with which are the discovery and invention of millions of new types of materials, natural and artificial. A large category among them is optical/photonic materials, which are used to generate, detect or manipulate optical electromagnetic waves. For instance, different kinds of semiconductors, including Silicon, Gallium Arsenide, Indium Phosphite, etc. have been used for sources or absorbers of photons. Dielectric materials that are transparent in certain frequency ranges, like glass, sapphire, Calcium Fluoride, are widely used in optical devices to control the propagation of light and its phase.

However, the ability to manipulate light is limited by the optical property of naturally available materials. For example, the interaction between the magnetic component of light and natural materials is very weak, therefore, the magnetic response of natural materials at optical frequencies, which is quantitatively denoted as permeability ($\mu$), is always 1.

Before the attempt to expand the optical property of natural materials, we need to understand how light is propagating inside a dielectric medium. Natural dielectric materials are made of different types of atoms or molecules. From classical point of view[2], each atom/molecule can be treated as a dipole when an electric field is applied. When the dipole is in an optical field, it will oscillate at the same frequency as the applied field. And an oscillating dipole will radiate an electromagnetic wave also with the
same frequency as the applied field, but the phase of the radiation will be altered due to the light-matter interaction process. So the total field will be an integration of the original field with the re-radiated field. Because all of them are with the same frequency, the wave will be oscillating at the original frequency, but its phase and velocity may have been changed. Such changes are determined by electromagnetic responses of the building blocks (atoms/molecules) of the material and are usually treated as the manifestation of the optical property of a specific material. Very importantly, because the size of the atoms and molecules are much smaller than the wavelength of light, the detail of the atomic lattice cannot be seen by the light wave and the whole material is treated as a homogeneous medium.

Figure 1.1 shows several different materials where the ratio between the lattice constant and the wavelength of electron wave or electromagnetic wave propagation in them plays very important role in determining the material properties. In the semiconductor structure in Fig. 1.1(a), the electron wavelength is comparable with the period of the atomic lattice. Therefore energy gap is formed due to Bragg diffraction of electrons and leads to all the semiconductor properties. The same effect also happens for electromagnetic waves as shown in Fig. 1.1(b), where the period of the hole array in the photonic crystal is close to the wavelength of propagating light inside the dielectric. On the other hand, when the wavelength is much larger than the period of the material, the periodic structure cannot be seen and the wave will behave as if it is propagating in a homogeneous media. For example, for visible light propagating in a natural crystal, such as diamond shown in Fig. 1.1(c), the light wave cannot differentiate every single atom in the crystal, therefore the material exhibits a homogeneous optical response. Metamaterial is designed in the same principle.

In an article published in 1999, Pendry[3] proposed the idea of creating artificial materials composed of meticulously designed “atoms” in order to achieve properties that can not be reached by naturally available materials. It was pointed out that by introducing inductance and capacitance with appropriate orientation and magnitude into the artificial atoms, they can interact with the magnetic component of the electromagnetic waves passing through the composite material, therefore create a material with magnetic response at high frequencies. For such materials, magnetic permeability ($\mu$) is not unity any more. For some structures designed by Pendry, $\mu$ values can even be negative. Although Pendry only discussed about magnetic response at Gigahertz frequencies, this concept is not limited in this region. Following works have demonstrated magnetic response at frequencies in Terahertz region which has never been observed in natural materials[4],[5].

In fact, the tuning of materials optical property can be traced back to a paper published in 1996[6], in which Pendry discussed about the possibility of decreasing the plasmon
frequency of a material by using “diluted metal” and therefore controlling a material’s electrical response to light. Although the concept of metamaterial has not been brought forward in that paper, the basic principle is the same.

Fig. 1.1 Relationship between the periodic material structures and the waves propagating in them: (a) High resolution Transmission Electron Microscope (HRTEM) image of an AlAs layer (brighter) on top of a GaAs layer (dimmer)[7]. (b) Scanning Electron Microscope (SEM) image of a defect cavity in a photonic crystal structure[8]. Light with frequency lying in the band gap of the photonic crystal is not allowed to propagate in the periodic structure, therefore is confined in the defect cavity. (c) A natural diamond crystal which shows uniform optical property throughout the whole crystal[9]. (d) Metamaterial made of artificial atoms of double split ring structure and linear metal wire[10].

With both electrical and magnetic response under control, metamaterials enable free tuning of materials’ optical property. The optical properties can be extended into regions that have never been achieved before, where negative refraction of light has been
observed. Furthermore, they can also be tuned independently at different locations inside the same material. This powerful ability greatly enhanced our control of the propagation direction and the phase of light propagating in such materials, and built the foundation for the new research field of transformational optics[11],[12]. Many new applications are in view, for example, the invisible cloak which eliminates the scattering of light from an object and makes the object invisible[13-19].

1.2 Metamaterial designs toward negative refraction of light

We are focused on the important metamaterial application of achieving negative refraction of light. In 1960s, Veselago suggested that negative refraction of light can be found in a material with simultaneously negative permittivity and negative permeability[20]. As described by Maxwell’s equations, the electric field $E$, the magnetic induction $B$ and the wave vector $k$ of a propagating electromagnetic wave follow a “right-hand” rule. However, the Poynting vector, which represents the direction of the energy flow, is determined by $E \times H$, which is in the same direction as $k$ only when magnetic permeability $\mu$ is positive. When $\mu$ takes negative sign, the energy flow will be in the opposite direction to the wave vector. Such material was referred to as “left-handed” by Veselago. He further showed that at the interface between a left-handed material and normal right-handed material, light will be bent to the same side of the surface normal as the incident beam, i.e., the light will be negatively refracted. However, negative magnetic response was not found in any materials at that time. It takes more than three decades before researchers were able to meet such requirements by using metamaterials[21-23]. The metamaterials’ ability of freely tuning magnetic response makes the negative refraction of light achievable.

Soon after Pendry’s theoretical prediction, various metamaterial designs have been explored and negative refraction has been experimentally demonstrated. In 2001, negative refraction was demonstrated in microwave region by using double split ring structure as shown in Figure 1.1(d). Later on, such phenomenon was also shown in different structures at optical and even visible frequencies[24-26].

Earlier designs for achieving negative refraction have fundamental limitations. For instance, enormous energy loss and narrow band are associated with magnetic resonances required to achieve negative magnetic response; fabrication of nanostructures much smaller than the wavelength of visible light is a great challenge using tradition top-down serial fabrication methods. Such problems are even more severe when researchers tried to achieve negative refraction at optical frequencies. In order to overcome the above difficulties, a new metamaterial with indefinite permittivity was designed. Indefinite optical properties refer to permittivity or permeability tensors whose principal elements
are not all with the same sign, unlike natural materials such as dielectrics (all elements are positive) or metals (all elements are negative at certain frequency). By taking advantage of indefinite permittivity, we first demonstrate negative refraction of light in bulk metamaterials at visible frequencies. Such indefinite optical properties was achieved in metamaterials made of silver nanowire array embedded in aluminum oxide matrix, which can be efficiently fabricated using bottom up fabrication approach. “Bottom up” techniques refer to the formation of micro- or nano-structures based on the self-assembly of atoms, molecules or other building blocks of materials.

This dissertation is concerned with my research work on nanowire metamaterials with indefinite permittivity. In chapter 2, the unique dispersion relation of indefinite material and the theoretical foundation of negative refraction in indefinite material are explored. Chapter 3 provides details about the fabrication of nanowire metamaterials. The demonstrations of negative refraction in nanowire indefinite material and slab lens imaging are given in chapter 4. Based on the unique hyperbolic dispersion of indefinite metamaterials, very large wave vector can be achieved and light can be confined in 3D deep subwavelength nanocavities. Related work is presented in chapter 5. Chapter 6 discussed about the anomalous diffraction phenomena observed in nanowire metamaterials. Besides the nanowire indefinite metamaterials, the research on surface plasmons and applications, such as surface plasmon beats and lithography are discussed in chapter 7.
Chapter 2

Indefinite Metamaterial

2.1 Hyperbolic dispersion and negative refraction in an indefinite material

Indefinite material refers to anisotropic media in which not all of the principal components of electrical permittivity and magnetic permeability tensors have the same sign. The behavior of wave propagation and various unique effects in indefinite materials were first explored by Smith and Schurig[27].

To understand how the indefinite permittivity of a material leads to negative refraction[27],[28], let us first consider the transverse-magnetically (TM) polarized electromagnetic waves propagating in a uniaxial anisotropic material. The dispersion relation of such TM waves is given by

\[
\frac{k_v^2}{\varepsilon_p} + \frac{k_p^2}{\varepsilon_v} = \frac{\omega^2}{c^2}
\]

(2.1)

where \(c\) is the velocity of light in vacuum, \(k_v\) and \(\varepsilon_v\) are wave vector and permittivity components perpendicular to the optical axis, \(k_p\) and \(\varepsilon_p\) are parallel to the optical axis and \(\omega\) is the angular frequency of light.

At a constant frequency, the allowed \(k_v\) and \(k_p\) values form iso-frequency contours in momentum space. For natural anisotropic materials, such contours are usually a series of ellipses (for isotropic materials, they are reduced to a series of circles). However, when the permittivity components \(\varepsilon_p\) and \(\varepsilon_v\) have opposite signs, the above dispersion relation results in hyperbolic iso-frequency contours as shown in Fig. 2.1. The negative refraction ability of such materials is also illustrated in Fig. 2.1. For obliquely incident light from free space with a wave vector \(\vec{k}\), the direction of refracted light can be
determined from the fact that its group velocity is always normal to the iso-frequency contour. Given that the tangential wave vector at the interface should be conserved and the causality theorem (that is, the energy flows away from the interface) should be satisfied, the Poynting vector $\vec{S}$, which represents the energy flow direction, deviates from the wave vector and undergoes negative refraction, although the refraction for the wave vector is still positive.

Fig. 2.1 Hyperbolic iso-frequency contour for an anisotropic material (green) when $\varepsilon_r > 0$ and $\varepsilon_p < 0$, and circular iso-frequency contour for an isotropic medium such like air (gray). For an oblique incident light from air, the Poynting vector is negatively refracted inside of the anisotropic material, although the wave vector undergoes positive refraction.

### 2.2 Indefinite permittivity of nanowire metamaterials

A typical realization of the indefinite metamaterial is composed by arrays of parallel metallic nanowires such as silver, gold, etc. embedded in a dielectric matrix. As long as the period of the nanowire array is much smaller than the working wavelength, the structure can be characterized as a homogeneous uniaxial anisotropic material with a permittivity component parallel to wires ($\varepsilon_r$) and another component vertical to wires ($\varepsilon_p$) [28],[29]
\[ \varepsilon_p = p\varepsilon_m + (1-p)\varepsilon_d \]
\[ \varepsilon_v = \frac{[(1+p)\varepsilon_m + (1-p)\varepsilon_d]\varepsilon_d}{(1-p)\varepsilon_m + (1+p)\varepsilon_d} \]  

(2.2)

where \( p \) is the filling ratio of metal, \( \varepsilon_m \) and \( \varepsilon_d \) are the permittivity of metal and dielectric, respectively.

Based on the effective media approximation above, \( \varepsilon_p \) is negative while \( \varepsilon_v \) keeps positive over a broad wavelength range from visible to near-infrared, as shown in Fig. 2.2a and 2.2b. The isofrequency contour of light inside such material is therefore hyperbolic and fulfills the requirement for achieving negative refraction.

![Figure 2.2](image)

Figure 2.2. \( \varepsilon_p \) and \( \varepsilon_v \) values (real part) as functions of wavelength of EM waves in vacuum calculated from Eq. 2.2. Alumina permittivity \( \varepsilon = 2.4 \) was used [30],[31] and the data for permittivity of silver were obtained from literature [32]. The blue curves represent the results for volume filling ratio \( p = 0.1 \) and the green ones for \( p = 0.2 \). In both cases, there are broad bands from visible to infrared over which \( \varepsilon_p \) and \( \varepsilon_v \) have different signs and therefore hyperbolic isofrequency contours can be realized.

The validity of the effective media approximation applied above has been verified by simulations. Using COMSOL Multiphysics™, a commercialized software based on the finite element method (FEM), we performed full-wave simulations considering the typical nanowire dimensions and real material permittivities for \( \text{Al}_2\text{O}_3 \) (\( \varepsilon_{\text{Al}_2\text{O}_3} = 2.4[30],[31] \)) and \( \text{Ag} \) (\( \varepsilon_{\text{Ag}} = -21.6+0.8i[32] \)) at the wavelength of 660nm. In order to have
a better comparison with the real structure we fabricated in experiments, which will be
discussed in the next chapter, the silver nanowires were arranged in hexagonal lattices in
simulations. Shown in Figure 2.3 are the refraction of light beams transmitted through
nanowire metamaterial slabs and an ideal indefinite material slab whose parameters are
obtained using Eq. 2.2, the same as the results shown in Figure 2.2. The identical
behaviors of wave propagation in the idea indefinite slab and the nanowire slabs are
evidence of the indefinite property of the nanowire metamaterials.

From the effective media approximation it is also expected that at the long wavelength
limit, the light refraction through the nanowire metamaterials is independent of the lattice
orientation. Figure 2.3(a) and 2.3(b) demonstrate that the lattice orientation has negligible
effects on the light refraction. In fact, under the effective media approximation, negative
refraction also works for random nanowires, although the simulated structure here has
hexagonal lattices.

![Fig. 2.3 Finite element simulation results of negative refraction at the interfaces between indefinite
materials and air. (a), (b) A beam of light at 660nm free space wavelength gets negatively refracted when it
is transmitted through a nanowire metamaterial slab. The silver nanowires embedded in alumina matrix
formed hexagonal array and the orientation of the lattice is different in (a) and (b). The radius of the silver
wire, the lattice constant, and the length of the wires are 30nm, 110nm and 1.5μm, respectively. The
incident angle is 30 degree. (c) The nanowire metamaterials is replaced by a homogeneous indefinite
medium (εr = 5.28 + 0.038i and εp = -4.8 + 0.24i, which are calculated from equation 2.2). The
identical behaviors of wave propagation in all 3 cases are evidence of the indefinite property of the
nanowire metamaterials.]

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Consequently, a great advantage of such metamaterial is that with the same composing material the general materials property can be tuned by a single parameter of filling ratio $p$ as shown in Fig. 2.2. Smaller filling ratio means less metal inclusion in our metamaterial and therefore the Ohmic loss is relatively small. On the other hand, large filling ratio is required in order to push the working band to higher frequency, as we can see in Figure 2.2. Considering the above restrictions and our fabrication capability, we chose a filling ratio in the range of 0.18 ~ 0.2 in our experiment.

2.3 Conclusions

In this chapter, we presented the theoretical background of the negative refraction ability of nanowire metamaterials. Based on the effective media approximation, the electric permittivity tensor of the metamaterials composed of metal nanowire array can be indefinite over a broad frequency range. Due to the hyperbolic dispersion relation for the indefinite materials, negative refraction can be achieved at the interface between indefinite and normal materials.
Chapter 3

Bottom-up Fabrication of Nanowire Metamaterials

The design of the nanowire metamaterial takes advantage of the bottom-up fabrication technique based on the silver nanowires growth inside self-assembled porous alumina template and hence large scale sample manufacture is possible. The nanoporous template based metal nanowire array can be efficiently fabricated with an aspect ratio greater than 1000, which are not achievable with traditional top-down approaches. Nanowire array with a few tens of nanometer in diameter are obtained routinely. Techniques such as two-step anodization, pre-pattern induced self-assembly have been used to further improve the optical property of such nanowire materials and make them suitable for photonic applications such as negative refraction and imaging.

3.1 Self-organized anodic aluminum oxide template

Self-ordered nanoporous materials such as molecular sieves, track-etched polymer, nanochannel array glass, radiation tracketched mica, block copolymers and anodic aluminum oxide (AAO) have been applied as the mask or the template for the nanostructure fabrication[33],[34], because they provide feature sizes that are hard to achieve with current top-down fabrication technologies. Among them AAO based template has great advantages over the others due to the well-ordered pore distribution, high pore density and the high aspect ratio of pores. Moreover, the thickness, diameter and pitch of the pores inside the AAO can be precisely tuned during fabrication, which is of great importance for metamaterial application sicne it makes the optical property of the final material controllable. As a transparent dielectric, Alumina is directly used to compose the metamaterial since there is no strict restriction on the materials for dielectric matrix. Meanwhile, silver is chosen as the metallic nanowire material for its least loss at optical frequency.

The AAO templates are prepared by electrochemical anodization in an acidic solution.
Most widely used electrolytes for anodization include oxalic acid, sulfuric acid and phosphoric acid. The formation of alumina starts from the surface of aluminum metal facing the electrolyte. During the anodization process[35-37], oxidation of aluminum metal occurs at the metal/oxide interface by the migration of oxygen containing ions (O$^{2-}$ or OH$^-$) from the electrolyte by the following reaction

$$2\text{Al} + 3\text{O}^{2-} \rightarrow \text{Al}_2\text{O}_3 + 6e^-. $$

The porous structure indicates a dissolution process in part of the aluminum oxide layer. It is caused mainly by electric-field-enhanced reaction of the formed oxide layer

$$\text{Al}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} (\text{aq}) + 3\text{H}_2\text{O}. $$

The positions of the pores are induced by the concaves at the top surface of aluminum before anodization. The oxidation of aluminum and the dissolution of the oxide at the bottom of each pore are in equilibrium, hence a straight pore can be formed all the way into the metal layer. The formation of pores also involves the interaction among them. The growth competition results in a self-organized process and adjusts the relative position of adjacent pores, thus ordered hexagonal pore array can be formed [38].

![Fig. 3.1. (a) A Schematic of the vertical cross section of the porous alumina membrane formed on top of an aluminum substrate. The gray material is aluminum and the light blue part is the porous alumina. The curved layer at the bottom of each pore is the barrier layer. (b) SEM image of the porous alumina template (top view). The scale bar represents 200nm.](image)

Anodization parameters such as voltage, current density, electrolyte temperature and composition are all adjustable and can be tuned for fabrication of suitable template with desired distribution, size and length of the pores. Generally speaking, the size of the pores and the distance between the pores (pitch of the pore array) both get larger as the anodization voltage increases.[39] The pore shapes and regularity may also be affected by the applied voltage. Furthermore, for different electrolytes, the optimum condition of temperature, electrolyte concentration for generating a uniform and thick membrane varies accordingly. In our fabrication, we chose 40V working voltage together with 0.2M
oxalic acid in ice water bath since such a combination of parameters gives us required pitch, pore size (therefore the correct metal filling ratio) and regular pore shape.

With optimized parameters, high purity (99.9995%) aluminum foil was first mechanically polished and degreased with acetone, then put into 0.2M oxalic acid as anode for the first anodization step. The oxidized layer was then removed in a mixture of H₃PO₄ and H₂CrO₄. The first anodization leaves a regular array of dips on the metal surface. The regularity is determined by the self-organizing mechanism during the anodization process. Since the development of the nanopores in AAO templates is guided by the appropriate texture of the surface at the initial stage of anodization, a better ordered nanopore array will be generated in the second anodization. Both steps were performed in an iced water bath. In such a two step anodization process, pore sizes and the distances between the pores in the final template are much more controllable and uniform[38].

After the anodization process, the porous alumina layer has formed on top of the thick aluminum metal slab. The sample is then immersed in a saturated solution of Hg₂Cl₂ in order to remove the residual aluminum. Another commonly used method is to soak the sample in mixed solution of CuCl₂ and HCl. Both methods worked well during our fabrication process. The barrier layer at the bottom of the template was then removed in diluted H₃PO₄ at room temperature. The quality of nanopore openings after barrier layer removal is very critical for future silver nanowire deposition, as discussed in more details in section 3.3.

3.2 Electrochemical deposition of Ag nanowires in AAO template

Nanowires of different metals and semiconductors can be fabricated in the pores of this template membrane. It can be done with a variety of methods such as electrochemical deposition, evaporation, sol–gel method, chemical vapour deposition (CVD), melt or solution deposition and electroless deposition[40]. The electroplating method is the most straightforward way for many metal nanowire growth, including silver. After barrier layer removal, a silver seed layer was deposited (EB3, BOC Edwards) on top of the template and then connected to a cathode. Electrochemical plating process was followed inside electrolyte containing AgNO₃, nitric acid and L-tartaric acid, in order to grow silver nanowires in the nanopores of the template.

It has been reported that the growth rate of nanowires usually is much faster close to the edge of the sample compared to the center part[41]. We also observed the same trend in our fabrication process. When the longer nanowires grow out of the pores, they will start to conglomerate at the surface and form a block of silver metal, as shown in Figure 3.2.
The overgrown silver on the surface were removed by mechanical polishing. Note that the polishing process should not stop until all the short nanowires show up, otherwise there will be widely distributed hollow pores in the sample, which are defects that cause strong random scattering of light.

![Fig. 3.2. Cross sectional view of an AAO template after silver nanowire growth using electrochemical plating method. (a) The center part of the sample. (b) Close to the edge of the same sample in (a), the boundary between the nanowire filled and empty parts can be seen. The nanowires grow faster at the edge than the center part and overgrown silver forms a block on top of the sample. The scale bars represent 10μm.](image)

### 3.3 Improvement of uniformity in nanowire metamaterial

The bottom-up method using the self-organized porous template greatly reduces the fabrication time and makes very fine and high aspect-ratio nanostructures achievable. On the other hand, materials made with such methods are usually not so uniform in the pore sizes, shapes and lattice regularity as those fabricated with top-down approaches, which makes the fabrication of materials with good optical quality a great challenge. In order to improve the optical performance, it is critical to create pore arrays with high uniformity. First, the optical response of the metamaterial is dictated by the filling ratio of the metal nanowire in the dielectric matrix, as we have shown in the theory. The non-uniform size of the pores will cause the fluctuation of the effective permittivity throughout the material, resulting in a material property deviated from design. Second, non-uniformity is also reflected in the thickness of the barrier layer formed at the porous alumina/aluminum interface during the anodization. As mentioned above, we used phosphoric acid to remove the barrier layer and make the pores open channels for nanowire formation. With ununiform barrier layer thickness, it is impossible to find a universally optimum etching depth. In order to make sure every pore is opened, we have to increase the etching time, which usually results in the unexpected widening of pores that opens earlier. Figure 3.3 gives atomic force microscope images of the template
surface morphology after removal of the barrier layers, which clearly show the dependence of barrier layer opening uniformity on the uniformity of the whole array. In order to optimize the uniformity, a two-step approach was applied as we have emphasized previously. In Fig. 3.3(a) the pores are not well ordered and the opening of barrier layer is highly ununiform. With extended first anodization time, the ordering of the nanopore array can be improved, which is also reflected in the uniform opening sizes of the barrier layer, as shown in Fig. 3.3(b).

![Figure 3.3](image)

Figure 3.3, atomic force microscope images of the template bottom surface morphology after removal of the barrier layers. The two samples are both fabricated using two-step anodization approach. First anodization time is (a) 5 hours and (b) 24 hours, respectively. The scale bars represent 200nm and the false color bar represents 100nm height range.

Different pore diameters and barrier layer opening sizes lead to different ion transportation rates during the electro-deposition process, which may result in very short nanowire or even no nanowire in some pores. The pores without nanowire are optical defects in the material, which induce unexpected scattering and create artifacts in the imaging process. Figure 3.4 are 3-dimensional simulation results showing the scattering effects caused by a single missing nanowire in a nanowire array. The configuration is the same as our experiment. A slit is cut through the silver seed layer. Light with wavelength 660nm was incident from bottom of the structure. Fig 3.4(a) is the result without any defect, while one nanowire is missing (pointed out by the yellow arrows) in both (b) and (c). When light is transmitted through the nanowire composite, a missing nanowire causes strong distortion of the field distribution. Even when the missing nanowire is not in the slit region (Fig 3.4(c)), the scattering is so substantial that optical measurement will result in a false field distribution. Fig. 3.5 gives the samples fabricated with different uniformity (by varying the time for the first anodization), which clearly show the difference in defect density. Note that most defects occur at locations where the self-organized lattice is not well ordered.
Figure 3.4, 3-dimensional simulation of light transmission through the anisotropic sample. The sample is a slab made of nanowire/AAO composite. The nanowires are along vertical direction. Incident light with 660nm wavelength is illuminated on the sample through a 600nm slit cut in the silver layer covering the bottom surface of the slab. (a) Nanowire array without any missing nanowire; (b) and (c) Nanowire array with one missing nanowire each, whose position is pointed out by a yellow arrow.

Fig. 3.5, SEM images of two nanowire samples with different uniformity. It is clear that the pores in (a) is much less ordered than those in (b) and therefore more defects can be found in it. The scale bars in both images represent 500nm.

Besides the two-step anodization method, pre-pattern methods [42-45] are expected to reduce these optical perturbation caused by the material non-uniformity, since they can provide AAO templates with extremely narrow distribution on lattice spacing, pore size, and as well as thickness of the barrier layer. With the help of the fabulous uniformity of template fabricated by pre-pattern methods for the following electroplating process, the reduction of missing nanowires and the precise control of the nanocomposite in the anisotropic metamaterials are then possible to be obtained.

Here, we choose focused-ion-beam (FIB) direct-write technique[43], because of its effective guidance on the growth of high-aspect-ratio long-range-ordered nanochannel arrays and its flexibility on defining the tunable lattice-spacing and exact position of
every pore in the template. A commercial 50 KeV Ga FIB with a diameter of ~10nm and beam current of 10 pA is employed to create arrays of hexagonally close-packed concaves on polished high purity Al surfaces. In the same principle as the two-step anodization method, the concaves will then induce the growth of ordered nanopores in the later anodization process. Given that the surface texture is compatible with the natural parameters for the self-ordering, the long-range-ordered nanopore array architecture can be expected to grow at the loci dictated by the pre-patterns.

Fig 3.6(a) shows SEM image of the FIB pre-patterned Al film, while (b) is the nanopore array guided by the surface texture. Silver nanowire grown in FIB pre-patterned template after anodization and barrier layer removal creates a nanowire array with ideal order and high uniformity, as shown in Fig 3.6(c). Defects caused by missing nanowire have been substantially reduced. Defect density is typically less than 0.05% for samples with pitch ~ 110nm and nanowire diameter ~ 50nm. Notably, defects occur almost only at few locations where the lattice is imperfect, which are negligible compared to the defects found in self-organized nanochannels on AAO. Therefore, the FIB pre-patternning of Al facilitates of the fabrication of long-rang ordered AAO nanochannel arrays, which can be used as templates for growing arrays of nanowires exhibiting negative refraction without detrimental interference originated from defects on the arrays.

As the final step, a 1μm wide slit was etched through the silver seed layer using a Focused Ion Beam system (FIB, Strata 201XP, FEI), for the convenience of optical characterization. It can confine the light beam width within certain propagation distance so that we are able to identify the direction of the refracted beam as will be discussed in next chapter. Such a slit can also serve as a 1D object in order to demonstrate the imaging ability of slab lenses made of the nanowire metamaterials[46].

**3.4 Conclusions**

In this chapter, the principles and technical details of the bottom-up fabrication approach
of nanowire metamaterials are discussed. Self-organized porous alumina template provides a convenient way for nanowire metamaterial fabrication and its feature sizes meet the requirement for optical negative refraction demonstration. Silver nanowires can be efficiently grown inside the nanopore array with electroplating method. A very critical issue in controlling the optical property of nanowire metamaterial is its uniformity. We have developed techniques in order to improve the uniformity and reduce the defect density in the sample.
Chapter 4

Experimental Demonstration of Negative Refraction and Slab Lens Imaging

4.1 Near-field Scanning Optical Microscopy (NSOM)

An NSOM system is used in the optical characterization of nanowire metamaterials. It can reach a high resolution that is beyond the diffraction limit of the visible light used in the imaging process and the scanning mechanism allows it to map the electromagnetic field distribution at specific locations either at the near field of sample surface or in the 3D space.

For any optical imaging method, the information of an object is carried by the light radiated from it. The information about the size and shape of an object is contained in various wave vectors of light. Small $k$ values correspond to large shapes and large $k$ values represent fine structures. However, for most media, the range of $k$ values that are allowed to propagate is limited. For example, Let us consider the dispersion relation of air,

$$k_n^2 + k_i^2 = \frac{\omega^2}{c^2}$$

where $k_n$ is the component normal to the surface of the object and $k_i$ is tangential to the surface, $\omega$ is the frequency of light, $c$ is the speed of light in air. In order to resolve very fine features on the object, $k_i$ needs to be very large, when $k_i > \omega / c$, the value of $k_n$ will be imaginary, which means a wave exponentially decaying along the direction normal to the object surface. Consequently, information about such fine structures cannot be detected in the far field.
In order to resolve the details beyond the diffraction limit, many different approaches have been proposed and demonstrated including NSOM. The basic idea of NSOM is to use a very sharp tip to scan the near field of the object, the evanescent near field signal can be coupled out with certain techniques. There are two major types of NSOM systems. One is apertured NSOM which uses a fiber tip with a sub-wavelength opening at the end of tip to collect light, the other is apertureless NSOM which uses a sharp metal tip or dielectric tip to scatter near field signals and collect them in the far field. In both types, the tiny structures at the end of the probes provide a broad spectrum of k values and couple the evanescent signals into propagating waves and make them detectable.

![Figure 4.1, Schematic NSOM setup for optical characterization of silver nanowire metamaterial. (BS: beam splitter, L: tube lens, M: mirror, O: objective, P: polarizer.) The incident angle 1 is tuned by adjusting the position of the laser diode (D) with a one-dimensional stage (S). The inset illustrates a cross-sectional review of the light propagation of TE mode (beam #2) and TM mode (beam #3) inside the metamaterial.](image)

Practically the resolution of a NSOM system is limited by the size of the aperture (aperture NSOM) or the tip end (apertureless NSOM) rather than the working
wavelength, therefore, resolution of 50nm or even higher may be obtained by a NSOM system although it is using visible light.

4.2 Negative refraction of visible light

An aperture NSOM system is applied for demonstration of the negative refraction and slab lens imaging of nanowire metamaterials, as schematically illustrated in Fig. 4.1. The metamaterial slab comprising vertical aligned nanowires is mounted on the stage of the NSOM system. The slits cut through the seed layer are illuminated by a laser beam at variable incident angles. The transmitted light was mapped by a tapered optical fiber tip at the top surface of the metamaterial, and then guided to a photo-detector. All data are collected by a computer on which the light field distribution on the sample surface or even in the 3D space can be recovered.

The incident angle of the light was controlled by altering the position of the incident laser beam into the objective lens using a linear stage. The incident angle \( \theta \) is determined by the equation \( \theta = \arctan(x/f) \), where \( x \) is the shift of the beam and \( f \) is the focus length of the objective used to illuminate the sample. A polarizer was used to select TE and TM mode of incident light. When the polarization is parallel or perpendicular to the beam shift, TM or TE mode is excited inside the metamaterial respectively. We marked the center position of the transmitted beam under normal illumination as a reference. The lateral displacement of the beam \( x' \) at the output surface was determined by comparing the center position of the beam with respect to the reference. The refraction angle inside of the material \( \theta' \) was consequently extracted by \( \theta' = \arctan(x'/t) \), where \( t \) is the sample thickness.

The NSOM probe used to detect the output light is an optical fiber that was tapered and bent 90° by a CO2 laser beam. The tip apex was coated with 100nm thick aluminum using e-beam deposition (Edwards EB3 E-beam Evaporator). Subsequently, the tip was milled using focused ion beam milling (FIB, FEI Strata 201 XP) to generate a sub-100nm aperture at the probe apex. When positioned in close proximity to the sample surface with an AFM scanner (Bioscope, Digital Instruments), the light from the sample can be collected to form an image with sub-diffraction resolution.

Fig 4.2(a) is a schematic showing the light path of a negatively refracted light in our experiments. A slit is cut on the 250nm thick Ag film. A light beam at 780nm wavelength is transmitted through the slit and refracted to the negative direction at the air/metamaterial interface. Fig. 4.2(b) is the combined results of refracted light spot for
different incident angle. The horizontal axis represents the lateral displacement of the output light. The output beam of normally incident light is set as the reference point and marked as zero on the axis. The vertical axes are the sines of various incident angles. When $\theta$ is negative, normal refraction behavior dictates that the output beam has a positive displacement. However, it is clearly shown in the upper half of the figure that TM polarized light beams behave in the opposite way, which shows negative refraction. In a control experiment, TE polarized light beams were positively refracted as recorded in the lower half of Fig. 4.2(b). The group refractive indices of the metamaterial are shown to be $-4.0$ and $2.2$ for TM and TE light, respectively. The phase refractive index of the metamaterial remains positive, in contrast to that of left-handed metamaterials. Furthermore, negative refraction also occurs at the output interface of the sample, which leads to focusing effect and forming an image of the slit at a distance from the output surface which will be discussed in the next section.

Taking the material property from experimental data ($\varepsilon_{\text{Al}_2\text{O}_3} = 2.4$ and $\varepsilon_{\text{Ag}} = -35.0+2.0i$) at the wavelength of 780nm, the calculated effective permittivities perpendicular and parallel to the wires are $4.92+0.03i$ and $-8.82+0.6i$, respectively. (Notice the permittivity of $\text{Al}_2\text{O}_3$ here is slightly smaller than the value of crystallized $\text{Al}_2\text{O}_3$ in reference[47], which is mainly attributed to the process of porous alumina fabrication.) With these effective material properties, we can analytically obtain the refraction angle of Poynting vectors for transverse magnetic (TM) and transverse electric (TE) waves. The analytical results are compared with the experimental data in Fig. 4.3(a), showing good agreement.

We also performed the same measurements for 660nm wavelength light. Negative refraction was also found, as shown in Figure 4.3(b), which justified the broad band of the indefinite property of the nanowire metamaterials.
Figure 4.3, (a) The dependence of refraction angles on incident angles and polarizations at 780-nm wavelength. The negative refraction occurs for broad incident angles. The experiment data agree well with calculations (solid curves) using the effective medium theory. (b), (c) Negative refraction has been observed for TM polarized light at both 660nm and 780nm wavelengths. Control experiments show that TE polarized light is still positively refracted.

4.3 Imaging visible light with nanowire metamaterial slab lens

As proposed by Vesalago in the 1960’s, materials with the ability of negatively refracting light can be made into a slab lens. Here we show that a slit object on the surface of the nanowire metamaterial slab can form an image outside the lens due to the negative refraction[46].
Fig. 4.4, Cross sectional view of the light profile in the xz plane which is perpendicular to the slit. y-axis is parallel to the slit. Incident light is propagating in z direction. (a) Focusing of TM polarized light. The light distribution in the space has been recovered by combining all the optical signals obtained by NSOM in each point at different heights. The noise level is higher than for TE wave due to higher loss and less transmission of TM wave comparing to TE wave. (b) NSOM measurement result of TE polarized light. The beam diverges after passing through the slab lens. No focusing effect is observed. The interference fringes are different from the simulation result due to the limitation of sample quality, NSOM resolution and sensitivity. (c)(d) Numerical simulation results for TM (c) and TE (d) polarized light in the cross sectional plane using commercial software (CST Microwave Studio). The lower part of (c) and (d) is the slab lens, where the nanowire array is shown. The upper part is air. The colors from blue to red in the simulation results represent increasing amplitude of electric component of the waves. The inset shows the cross cuts of the normalized intensity distribution at the focus point (Blue –experiment, Red - simulation). The unit of the horizontal axis is micrometer. (a), (b), (c) and (d) have the same scale bar.
We used a 4μm thick slab with a 600nm wide slit, cut through the gold seed layer, being the object. The slit was illuminated with a He-Ne laser at 633nm, where the polarization of the incident light can be selected by a linear polarizer. The transmitted light was mapped by NSOM in various distances from the output surface, using a tapered optical fiber coated with chromium as the NSOM tip. The tip is fabricated in the same way as described in the previous section. A xyz AFM scanner was used to control the tip position so light in any point of interest in the 3D free space can be detected, which enables us to study the detail of the light profile at various distances from the output surface of the metamaterial slab. The optical setup is the same as shown in Fig. 4.1.

Figure 4.4(a) shows the cross sectional view of the light profile in the plane perpendicular to the slit. The light distribution in the space has been recovered by combining all the optical signals obtained by NSOM in each point at different heights. The bottom of the image is the output surface of the metamaterial slab. The light transmitted through the slit has been spread out into 1.5μm wide at output surface. However, due to the transition from indefinite material to that with normal dielectric properties, the light divergence inverts into convergence at the metamaterial-air interface. Consequently, the 600nm slit is retrieved as an 800nm wide line at the image plane, which is about 1.7μm away from the interface. Based on the focus position, we can estimate an effective (group) index of refraction for the slab lens to be -2.2. Since the nanowire material shows negative refraction ability over a wide range of frequencies[26], the lensing phenomena can also be achieved for a broad spectrum.

Numerical simulations using commercial software (CST Microwave studio) were conducted to verify the lensing action in the metamaterial slab. The parameters of the simulated structure are similar to those of the actual material properties with ε = 2.4 for the Al₂O₃ [30],[31] and ε = -19.4+0.7i for Ag [32] at wavelength of 633nm. The simulation results, shown in Fig. 4.4(c) reveal a 0.8 um wide focused spot at 2 um distance, similar to our experimental result. The inset in the picture gives the cross cuts of the intensity distribution at the focus point. The simulation result is consistent with the experiment. Also shown in this figure is the light propagating inside the metamaterial slab, which cannot be detected by the NSOM in our experiment. Incident light from the slit at the bottom gets diffracted, then re-focused after the refraction at the slab/air interface, just as shown in Fig. 1(b)

We note that the lensing action presented in this work is diffraction limited. Although the anisotropic metamaterial has the ability to support the propagation of high k component much larger than k₀ (the wave vector of light in free space), those high k components are lost when the light is coupled back into the air, unlike the designs that enhance the evanescent waves[48],[49]. The propagating light in air can only carry those components that are smaller than k₀, therefore, the focus point is diffraction limited no matter how
narrow the original slit is. In order to break the diffraction limit, the imaging process needs to be done inside the indefinite material or at the near field of its surface. In Chapter 6 we will discuss about a possible approach.

It is worth pointing out that the focusing effect is polarization dependant. Since the hyperbolic iso-frequency contour only applies to the TM mode of light, transverse electric (TE) light cannot be focused by the metamaterial slab in the way described above. As a control experiment, we have measured TE-polarized wave emerging from the metamaterial slab. The experimental result is shown in Fig. 4.4(b) and simulation result shown in Fig. 4.4(d). The light beam kept going broader and no focusing effect is observed.

4.4 Conclusions

Based on the indefinite permittivity and the unique hyperbolic dispersion of the nanowire metamaterials, broad-band and wide angle negative refraction has been demonstrated using an aperture NSOM system. A major application for materials with negative refraction ability is in the field of imaging. Hence a slab lens was made using such nanowire metamaterial and its imaging ability has been demonstrated experimentally.
Chapter 5

Three-Dimensional Deep Subwavelength Optical Naoncavities of Indefinite Metamaterials

5.1 Miniaturization of optical cavities

An optical cavity confines light in a limited space by resonant recirculation. The resonant superposition of the light wave effectively enhances the electromagnetic field inside the cavity and allows concentration and storage of electromagnetic energy. A direct consequence of the field enhancement is stronger light-matter interaction. Therefore, optical resonant cavities have been widely used in different fields for light emission and detection applications.

An ideal cavity would confine light without any loss and would have resonant frequencies at precise values. However real cavities can never be perfect and the deviation from ideal condition is quantitatively described by the cavity $Q$ factor, which is proportional to the confinement time in units of the optical period. When an optical cavity approaches the ideal condition, the $Q$ factor goes to infinity. The resonant frequency spectrum of an optical cavity is also size-dependent, as an analogue to the classical resonators such as the tuning fork. Microscale cavity volume ensures that resonant frequencies are more sparsely distributed throughout this spectrum than they are in a corresponding “macroscale” resonator[50].

Like electronic devices, there is a great demand on the miniaturization of optical cavities for both scientific research and technology development purposes. Optical microcavities and nanocavities with both high quality factor $Q$ and small modal volume $V$ are important for the enhancement of light-matter interaction[51],[52]. The strong light confinement and long photon lifetime in these high-$Q/V$ optical cavities lead to lots of studies of fundamental optical physics and integrated nanophotonics applications, such as
Purcell factor in spontaneous emission enhancement, strong coupling in cavity quantum electrodynamics[53],[54], enhancement of optical nonlinearities[55],[56], and optomechanics[57],[58].

With the help of surface plasmons, which has unique dispersion relation supporting high $k$ vectors that correspond to ultrashort wavelengths, nanocavities with subwavelength mode volume have been demonstrated recently, such as plasmonic WGM microdisks[59], and one-dimensional plasmonic Fabry-Pérot cavities[60]. The Q/V ratio is still quite high although the Q is relatively low due to the Ohmic loss in metal [59].

In optical dielectric cavities, total internal reflection (TIR) plays an important role for photon confinement. For example, in whispering gallery mode (WGM) cavities, optical waves are confined with continuous TIR along the periphery of the cavities to reach ultrahigh Q factors, which are limited by the surface roughness of the sidewalls[61],[62]. In photonic crystal cavities, the photon is confined by both Bragg reflection and TIR[63],[64]. By engineering the momentum ($k$-) space distribution of cavity modes through roughness reduction (WGM modes) or fine tune the cavity geometries (photonic crystal cavities), the radiation leakage inside the light cone of air in TIR can be substantially suppressed to achieve remarkable high radiation Q factors[64],[65]. Although the Q factors can be ultrahigh for dielectric cavities, the physical sizes of cavities are much large than the wavelength in order to confine photon effectively. The fundamental limit to the size of the dielectric cavities results from the optical mode cutoff. Therefore the volumes for dielectric cavities are diffraction limited and are always larger than single cubic wavelength ($\lambda/n$)$^3$, where $\lambda$ is the free space wavelength and n is the refractive index with a value limited by the currently available dielectrics (for example, for silicon $n = 3.48$ at 1.55 $\mu$m).

The invention of metamaterials brought new perspective on how light can be manipulated, which permits the realization of many novel functionalities. In this chapter, we propose a new concept to confine photon in three-dimensional truly nanoscale optical cavities based on omnidirectional TIRs in indefinite metamaterials. The unique photon confinement mechanism based on the high $k$ components in indefinite metamaterials breaks the limitation of cavity size and permits to create nanocavities with both high Q/V ratio and broad bandwidth.

5.2 Indefinite optical nanocavity

In previous chapters it has been demonstrated that materials with indefinite permittivity can be realized by meticulously designed metamaterial structures. Figure 5.1 shows a typical iso-frequency contour of the propagating light inside materials with indefinite
The indefinite permittivity of the material allows the propagation of very large k component which cannot propagate in air and natural dielectrics. Ideally, the hyperbolic curve allows k to be infinitely high, implying a media with no frequency cutoff for the light propagating in it. Such material allows us to create a nano-cavity with deep sub-wavelength sizes in all three dimensions.

![Diagram](image)

Figure 5.1, (a) Uniaxial indefinite materials are anisotropic material with permittivity and/or permeability tensors whose elements are not all with the same sign. Indefinite permittivity has been realized in nanowire system[26] and multilayer system[49]. (b) Isofrequency contours of light with 1.5um wavelength in vacuum. The inner and outer circles are the contours in air and in silicon respectively. The hyperbola (black curves) is the contour in the indefinite material.

The special dispersion contour also leads to the strong confinement of optical waves inside indefinite materials. Consider an interface between indefinite material and air, boundary condition dictates that the k component tangential to the interface must be conserved across the interface. However, for propagating waves in indefinite material with wave vectors much larger than that in the air ($k_0$), their tangential components are so
large that, on the light cone of air, the components normal to the interface must be an imaginary value, i.e., the wave will be total internally reflected back by the interface and there is no matching propagating mode in the air (Fig. 5.1(b)). More significantly, at an indefinite material/air interface parallel to z axis, no mode can be found inside the leaky region as defined by the matching tangential component with the iso-frequency contour in the air. Therefore, a three-dimensional entity with properly oriented facets can act as a cavity in which light will be total internally reflected at all faces and propagate only inside the cavity. There could be various designed geometries to realize such 3D cavities, for example, a cube with 2 faces perpendicular to z axis and 4 faces parallel to z axis, or a hexagonal cylinder with its side walls parallel to z axis.

Due to the symmetry of the permittivity tensor, it is convenient to use tetragonal shaped cavity for further study (shown in Fig. 5.1(a)). A tetragonal cavity has 8 vertices. At each vertex, 3 faces perpendicular to each other merge and form a retro-reflector. The retro-reflector reverses the direction of the wave vector of any incident light. So light inside the cavity is reflected back and forth by pairs of such reflectors. And because all the reflections are total internal reflection, the cavity is formed with very little radiation loss only due to the scattering from the cavity edges. Similar to the Fabry-Pérot cavity formed by two mirrors, the requirement for any eigenmode supported inside the tetragonal cavity is that the roundtrip phase of optical wave after being reflected by a pair of opposite retro-reflectors must be an integer multiple of $2\pi$,

$$k \cdot L + \Delta \phi = 2n\pi$$ (5.1)

where $k$ is the magnitude of the wave vector, $L$ is the light propagation length, and $\Delta \phi$ is the phase shift associated with the TIRs occur at the pair of retro-reflectors, $n$ is any integer which defines the mode order.

Light is reflected by pairs of retro-reflectors and there are 4 different pairs of such reflectors in a tetragonal cavity. Therefore the resonating modes are formed by 4 pairs of oppositely propagating waves.

$$\vec{H}(\vec{r}) = \sum_i \vec{H}_i \exp(\vec{k}_i \cdot \vec{r} + \phi_i), \quad \vec{E}(\vec{r}) = \sum_i \vec{E}_i \exp(\vec{k}_i \cdot \vec{r} + \phi_i)$$ (5.2)

where $i$ is the index for 4 pairs of optical waves with different orientations and $\phi_i$ represent the extra phase associated with the $i$th optical wave.

The optical modes can be simplified into the form of standing waves as

$$E_i(x, y, z) = A \sin(k_i x - \frac{\phi_x}{2}) \cos(k_i y - \frac{\phi_y}{2}) \cos(k_i z - \frac{\phi_z}{2});$$
\[ E_y(x,y,z) = A \cos(k_x x - \frac{\varphi_x}{2}) \sin(k_y y - \frac{\varphi_y}{2}) \cos(k_z z - \frac{\varphi_z}{2}) \]

\[ E_z(x,y,z) = A \cos(k_x x - \frac{\varphi_x}{2}) \cos(k_y y - \frac{\varphi_y}{2}) \sin(k_z z - \frac{\varphi_z}{2}) \] (5.3)

if the origin point is set to be at arbitrary vertex point of the cavity. Similar expressions can be found for \( E_y \) and \( E_z \). \( \varphi_x, \varphi_y, \varphi_z \) represents the phase shift associated with the TIR at interfaces perpendicular to \( x \) (\( y, z \)) axis, which can be calculated as

\[ e^{i\varphi_{x,y}} = \frac{a - b}{a + b}, \] (5.4)

where \( a = \frac{k^2_0 - k^2_z / \varepsilon_z}{k_{x,y}}, \quad b = \frac{k^2_0 - k^2_z}{k'_{x,y}} \), \( k_0 \) is the wave vector in vacuum and

\[ k'^2_{x,y} = k^2_0 - k^2_z - k^2_y. \]

For certain wave vector \( k \), the size of the cavity in \( x, y, z \) directions respectively are

\[ L_x = \frac{l \pi + \varphi_x}{k_x}, \quad L_y = \frac{m \pi + \varphi_y}{k_y}, \quad L_z = \frac{n \pi + \varphi_z}{k_z}, \] (5.5)

where \( l, m, n \) are integers for the mode orders in three directions, respectively. Eq. 5.5 is consistent with Eq. 5.1.

The above modes are very similar to those in a classic cubic dielectric cavity with sizes not less than the wavelength scale (\( \lambda / n \)). However, in indefinite materials, the cavity size \( L \) can be extremely small due to the large \( k \) supported, for realizing truly nanoscale cavities which support 3D deep subwavelength optical modes as shown in Figure 5.1.

Quality factor is an important property for resonant cavities. Because of the spatial dispersion and high \( k \) components in all three dimensions, a typical indefinite cavity with size less than 100nm in all 3 dimensions has very low radiation loss due to the strong confinement of optical field. The radiation quality factor \( Q_{rad} \) larger than \( 10^4 \) is achieved based on the simulation without considering the material loss. For comparison, a metal nanoparticle with the same size and shape can only achieve \( Q_{rad} \) about a few hundred (without material loss). For the cavities in indefinite material, since the optical modes are confined by TIRs from all faces, the major radiation loss is induced by the scattering from the sharp cavity edges. High \( k \) components cannot propagate from bulk indefinite material into air if the interfaces are infinitely large, due to the fact that such high \( k \) components are not supported in air and can only exist as evanescent modes.
However, the sharp cavity edges will scatter the optical waves with high $k$ ($>>k_0$) and generate additional $k$ components located in the light cone of air ($<k_0$), which will result in the radiation loss.

The quality factor of a cavity can be obtained as $Q = \frac{2\pi n_{\text{eff}}}{\alpha \lambda}$. The energy loss due to the radiation of the cavity mode by the sharp edges can be estimated from k-space field distribution[66] as $\alpha_{\text{rad}} \propto k^{-3}$. On the other hand, $n_{\text{eff}} = k / k_0$. Therefore, we can expect a extraordinary cavity behavior $Q_{\text{rad}} \sim k^4$, which means that the radiation quality factor is actually increasing when the cavity size shrinks (larger $k$ means the wave can be confined in a smaller cavity). Such behavior has been proved by numerical simulations as we will show in the next section.

### 5.3 Nanocavity with nanowire metamaterials

As a particular example, the concept of this kind of nanocavity can be realized in the indefinite materials demonstrated in metal nanowire system. The permittivity tensor elements along ($\varepsilon_p$) and perpendicular to ($\varepsilon_v$) the optical axis can be estimated from effective media theory as we have discussed in Chapter 2,

$$
\varepsilon_p (\varepsilon_v) = p \varepsilon_m + (1-p) \varepsilon_d \\
\varepsilon_v (\varepsilon_x = \varepsilon_y) = \varepsilon_d \frac{(1+p)\varepsilon_m + (1-p)\varepsilon_d}{(1-p)\varepsilon_m + (1+p)\varepsilon_d}
$$

(5.6)

where $p$ is the filling ratio of metal, $\varepsilon_m$ and $\varepsilon_d$ are the permittivity of metal and dielectric, respectively. Figure 5.2(b) is the dispersion relation calculated from full wave simulation (Microwave Studio). The bright curve shows the propagating modes inside a bulk metamaterial made of silver nanowire array in alumina matrix (shown in Fig. 5.2(a)). The figure shows the first Brillouin zone of the $k$ space determined by the periodicity of nanowires. Just like any other periodic structures, as we have discussed in the Introduction section, the nanowire array diffracts waves with wavelengths comparable to the period of the array and forms Brillouin zone in the momentum space. The curve is bended close to the edge of the first Brillouin zone, due to the Bragg diffractions. The dashed lines are asymptotic lines for the hyperbola with permittivity components derived from the effective media theory. It is clear that for $k$ values not too close to $\pm \pi/a$, the effective media theory is a good approximation to the nanowire system.
Figure 5.2. (a) Schematic of the nanowire metamaterial which possesses indefinite permittivity. (b) Isofrequency contour of the nanowire metamaterial in the plane parallel to the nanowires inside the first Brillouin zone defined by the period of nanowire array. The bright spots represent the allowed propagating modes inside the bulk metamaterial. The red curve is one branch of the hyperbolic isofrequency contours calculated from effective media approximation. The dotted lines are the theoretical asymptotics of the hyperbola and the white circle in the center represents the isofrequency contour of light in air. The curves formed by simulation data bend and become flatter close to the Brillouin zone boundary due to Bragg diffraction effect. The data were obtained from full wave simulation of the silver nanowire array embedded in Al₂O₃ matrix at 300THz. (c) Schematic of the perspective view of the 3D isofrequency contour, which is formed by the rotation of hyperbolic cross-section contour around the optical axis.

For a real material the hyperbolic relation is only valid in a limited k-region, which can still easily support the propagation of k components at least one order higher than that in the air. Simulation results proved that a cavity made of nanowires array can serve as a 3D deep subwavelength nanocavity. Figure 5.3 shows the E_z field distribution cross sections of the eigenmodes inside a nanocavity with 4×4 nanowire array (as illustrated in Fig.5.2(a)), which has the size of 80nm × 80nm × 104nm. Fig. 5.3(a)-(d) are the fundamental to forth

Figure 5.3. Cross-sectional view of E_z field distribution from simulation results of different orders of modes inside a 3D subwavelength cavity made of indefinite metamaterials. (a) Perspective view of the cavity containing 4×4 silver nanowire array. The gray plane across the center of the cavity is where we obtain the field distribution in (b)-(e). (b), (c), (d) and (e) are (1,1,1), (1,1,2), (1,1,3) and (1,1,4) modes, respectively. The nanowires are clearly shown. Inside the cavity there is a 4×4 nanowire array.
order modes in z-direction, respectively \((l = 1, m = 1, n = 1, 2, 3, 4, \text{ where } l, m, n \text{ are mode orders defined in Eq.} 5.5)\). The field outside the cavity are all evanescent and do not cause the radiation leakage. Note that these eigenmodes are confined inside the cavities very well, even with wave vector \(k\) close to the first Brillouin zone boundary, where there is some deviation of \(k\) value between the nanowire systems and the effective media approximation (as shown in Figure 5.2b). It means that the period of nanowire system is not necessarily much smaller than the wavelength inside the material to approximate the effective media. For example, in Fig. 5.3 the wave vector component in x-y plane is about 1/3 of the first Brillouin zone size defined by nanowire period.

Figure 5.4, Cross-sectional view of \(E_z\) field distribution similar as those in Fig. 2, but in cavities containing different lattices of nanowires. (a) Perspective view of the cavity containing 6x6 silver nanowire array. The gray plane across the center of the cavity is where we obtain the field distribution in (b) and (c). (b) and (c) are fundamental and 1st order modes for 6x6 nanowire array. (d) Perspective view of the cavity containing hexagonal silver nanowire array. The gray plane across the center of the cavity is where we obtain the field distribution in (e) and (f). (e) and (f) are fundamental and 1st order modes for hexagonal nanowire array inside a tetragonal cavity. The field distribution is slightly asymmetric because of the symmetry mismatch between the hexagonal lattice and the tetragonal cavity.

Note that the high \(k\) modes inside the nanowire cavity are not because of local resonance effect of individual silver nanowire (localized surface plasmon resonance), but rather homogenized indefinite properties, which is manifested by the fact that the modes are
determined by the filling ratio, not the detailed configuration (arrangement) of nanowires. Figure 5.4 shows the simulation results for cavities with different arrangement of nanowires but the same metal volume filling ratio. Fundamental and second order modes are shown for 6×6 square arrays and a hexagonal array. It is clear that the field distributions of the eigenmodes for different arrangement of nanowires are almost identical, which indicates that the cavity modes are depended on the filling ratio of nanowires with the validity of effective media approximation.

Figure 5.5, Resonating k values compared to the isofrequency contour of the bulk nanowire metamaterials. The black curve is the hyperbola calculated using effective media approximation. Red points are peak k values obtained by Fourier transform the field distribution inside various sized cavities all resonating at 200THz.

A remarkable feature of indefinite material is its strong spatial dispersion, which is reflected by the large variation of k magnitudes at a fixed frequency as shown by the iso-frequency contour in Fig. 5.1 and Fig. 5.2. An interesting consequence of such property is that indefinite material cavity with the same resonant frequency may have large size variations. Fig. 5.5 shows that the fundamental modes can be confined in nanocavities with substantially different sizes and various wave vectors, which have the same metal filling ratio and same resonant frequency (at 200THz, 1.5um wavelength in vacuum). In the same material, eigenmodes with same mode order and same resonant frequency can be confined within completely different mode volumes, which is due to the broad tunability of wave vectors in IM. Such extraordinary behavior has never been achieved in any other kinds of optical cavities, to our best knowledge. The data points are slightly deviated from the theoretical curve, which is because that the effective
permittivity of the cavity is not exactly the same as the bulk material due to its finite size.

Figure 5.6 is the simulated $Q_{\text{rad}}$ values as a function of $k/k_0$ (or cavity size $V$) for the fundamental modes resonating at 200THz. From the calculated $Q_{\text{rad}}$ values, we found a relation of $Q_{\text{rad}} \propto k^{4.0}$, which is consistent with the theoretical predictions we made in the previous section. As the size decreases, the resonating $k$ becomes very large and faraway from the leaky region where $k$ values represent those propagating modes in air, therefore, the coupling between the resonating mode and propagating modes outside the cavity gets weaker and weaker. From this perspective, such behavior can be expected for most sub-wavelength cavities. In fact, enhanced quality factor with decreasing device size has been noticed for deep sub-wavelength antennas for telecommunication applications.

![Graph showing $Q_{\text{rad}}$, $Q_{\text{Ohmic}}$, and $Q_{\text{tot}}$ as a function of cavity volume.](image)

Figure 5.6, Quality factor values obtained from full wave simulation of various sized cavities with indefinite permittivity. Black dots represent the $Q$ values in cavities neglecting the material losses. Red dots are $Q$ values obtained in cavities considering full material losses. The dashed line is the theoretical estimation of the quality factor based on the material loss only.

Mode volume is another very important factor for modern micro- and nano-cavities. The effective modal volume is usually defined in terms of the electrical field energy density in the cavity as follows

$$V_u = \frac{1}{\max\{W(\vec{r})\}} \iiint W(\vec{r}) d^3\vec{r}$$

(5.7)
where \( W(\vec{r}) = \frac{1}{2} \left[ \text{Re} \left\{ \frac{d}{d\omega} \{ \varepsilon(\vec{r}) \omega F(\vec{r}) \} \right\} \right|_{E(\vec{r})^2 + \mu F(\vec{r})^2} \) is the electromagnetic energy density.

It has been found that achievement of small mode volume is usually accompanied with sacrifice of Q values for most cavities, i.e., Q decreases when V gets smaller. Our indefinite cavity behaves in the opposite way. For the same resonant frequency and same mode order, we found that the quality factor actually increases as V shrinks.

In our indefinite cavity, the mode volume can be as small as \( 0.3 \times 10^{-3} \lambda^3 \). In lossless case, we can achieve \( Q > 10^4 \) and \( V < 10^{-3} \lambda^3 \), we will be able to achieve a figure of merit \( \lambda^3 Q/V > 10^7 \). Such a high value may lead to various types of new applications.

In a cavity made of real materials, material loss is not negligible and is the major factor that restricts the actual quality factor. The total quality factor Q is determined by both radiation loss and Ohmic loss.

\[
\frac{1}{Q_{\text{tot}}} = \frac{1}{Q_{\text{rad}}} + \frac{1}{Q_{\text{Ohm}}} \tag{5.8}
\]

\( Q_{\text{tot}} \) and \( Q_{\text{Ohm}} \) are also shown in Fig.6 for indefinite cavities. \( Q_{\text{Ohm}} \) can also be estimated by \( \frac{2\pi n_{\text{eff}}}{\alpha \lambda} \), where \( \alpha \) is the attenuation factor caused by the material loss and \( n_{\text{eff}} \) is the effective index defined as the ratio between resonating wave vector and free space wave vector (\( k/k_0 \)). Calculation shows that \( n_{\text{eff}}/\alpha \) is nearly constant inside indefinite cavities with different sizes, therefore, the \( Q_{\text{Ohm}} \) is almost the same for different cavities which limits the \( Q_{\text{tot}} \) around 30. Although the total quality factor does not increase dramatically as shown in the lossless case, it maintains the value for cavities with different sizes, which means that the \( Q/V \) ratio will increase significantly as the cavity is shrunk and can reach the value above \( 10^5 \). Recently, compensation of the optical frequency losses in the metals by gain media has been proposed and successfully demonstrated[67-69]. Amplification and even lasing condition has been achieved. Furthermore, scheme of directly reducing metal losses has also been proposed[70]. The high Q and small V indefinite cavity can be realized with material loss compensated or reduced to achieve \( Q/V \) at the order of \( 10^8 \). These nanocavities have deep subwavelength photon confinement and high \( Q/V \) ratio, together with low Q, which indicates a broad operation bandwidth.
5.4 Nanocavity with multilayer metamaterials

Nanowire metamaterial is not the only way to achieve indefinite material properties. Another widely used design is the metal/dielectric multilayer structure, which is also a uniaxial anisotropic material. The effective permittivity elements parallel to ($\varepsilon_p$) and perpendicular to ($\varepsilon_v$) the optical axis can be calculated by[71]

$$
\varepsilon_p(\varepsilon_x = \varepsilon_y) = p\varepsilon_m + (1-p)\varepsilon_d
$$

$$
\varepsilon_v(\varepsilon_z) = \frac{\varepsilon_m\varepsilon_d}{(1-p)\varepsilon_m + p\varepsilon_d}
$$

(5.9)

z axis is defined to be perpendicular to the multilayers. (as shown in Fig. 5.7). Similar to the nanowire case, $\varepsilon_p$ is negative while $\varepsilon_v$ remains positive over a large frequency range from visible to infrared. Hyperbolic iso-frequency contour can also be achieved although the 3D structure of the contour is different from the nanowire structure, as shown in Figure 5.8. Nevertheless, large k values are still accessible and a 3D deep subwavelength nanocavity can be made from multilayer metamaterials. Figure 5.7b and 5.7c show the field distribution cross sections of fundamental mode and second order mode in such a cavity.

Figure 5.7, Indefinite permittivity can also be achieved in metal/dielectric multilayer system. (a) Schematic of the metal/dielectric multilayer cavity. (b) and (c) Full wave simulation results of $E_z$ field distribution inside an indefinite cavity made of multilayers. The figures show the fundamental mode (b) and 2nd order mode (c).
5.5 Conclusions

In conclusion, we have designed a resonant cavity with deep subwavelength size in all 3 dimensions by using indefinite materials. Such materials have two major advantages in constructing a nano cavity. First is the existence of large $k$ modes in IM with relatively low frequency due to the unique dispersion of EM waves in IM, therefore helps the realization of an extremely small 3D nano-cavity. Second, the large $k$ values of the resonant states are far away from the “leaking region”, reducing the possible coupling between the cavity modes and plane waves. In addition, the iso-frequency contours of IM and air has no overlap along certain direction, which forbids the existence of leakage modes in one or two dimensions and hence greatly reduces the radiation loss of the cavity, so as to increase the radiation $Q$ factor dramatically. Although the total $Q$ factor is limited by the material loss, the $Q/V$ ratio is still quite high due to the extremely small cavity size.

The unique features of IM cavity allow a very simple and compact design for the cavity and a fairly high $Q$ may be achieved if the material loss can be reduced or compensated.
Traditional micro/nano cavities usually require a large auxiliary structure to confine the propagation of light although the mode volume itself is small, e.g., the photonic crystal defect mode cavity uses a photonic crystal structure that is sometimes hundreds of times larger than the cavity to form a band gap structure in momentum space. Whereas for IM cavity the free-standing cube itself confines the light well.
Chapter 6

Anomalous Diffraction in Nanowire Metamaterials

6.1 Diffraction and iso-frequency contours

Diffraction is a symbolic property of waves. To lowest approximation the interaction of electromagnetic waves is described by ray tracing (geometrical optics). The next approximation involves the diffraction of the waves around the obstacles or through the apertures with a consequent spreading of the waves[72]. A propagating wave can be decomposed into a linear combination of a series of waves that form a set of complete orthogonal basis. Spherical waves and plane waves are most widely used sets. Spherical waves are used in Huygens-Kirchhoff theory of diffraction[72]. Calculations based on Fourier transforms take plane waves as the bases. In the latter case, the behavior of the diffraction of waves can usually be illustrated in the momentum space. The analysis of the material dispersion in momentum space conducted in the previous chapters provided us a powerful tool in the study of diffraction behavior of light in indefinite nanowire materials. In this chapter we show that light is anomalously diffracted in the nanowire metamaterials.

Figure 6.1 shows the iso-frequency contours of electromagnetic waves with different frequencies in an isotropic media, e.g., air. The contours are circles in these materials, as discussed previously. The black circle represents the contour for lower frequency and the red circle with larger radius represents higher frequency waves. The region shaded by cyan color represents the spacial frequency band of an object on x-axis. Only those waves whose lateral (x) components are in this region are allowed to transmit through. From the definition of the group velocity of waves, the Poynting vector or the direction of the energy flow is always normal to the iso-frequency contours. As indicated by the arrows on the contours in Figure 6.1(a), for the same aperture, the diffraction angle increases as the frequency of light decreases, since the curvature radius of the contour becomes smaller. Figure 6.1(b), (c) show the diffraction of light with 750nm wavelength
and 1.5μm wavelength respectively by a 4μm wide aperture. For such an aperture, the pass band can be divided into multiple sub-bands and the diffraction pattern contains higher order beams. Since most of the diffracted energy is in the zeroth order beam, we consider only the zeroth order diffraction spread angle. The diffracted light spread angle for 1.5μm is much wider than the shorter wavelength case. Similar behavior can be found in most natural materials including anisotropic ones.

![Diagram](image)

**Fig. 6.1.** (a) Iso-frequency contours for different wavelengths in the same isotropic media. The black circle represents the contour for lower frequency and the red circle with larger radius represents higher frequency waves. The region shaded by cyan color represents the spacial frequency band of an object on x-axis. The black and red arrows represent the directions of light diffracted by the object for different wavelengths. (b) Plane wave of light with wavelength 750nm gets diffracted by a 4μm wide aperture. (c) Plane wave of light with wavelength 1.5μm gets diffracted by the same aperture as in (b). The diffraction angle is much larger for longer wavelength.

However, the diffraction of light in nanowire metamaterials follows different rules. As shown in Figure 2.2, for TM polarized light over a broad frequency band from visible to infrared, the permittivity components perpendicular to the nanowires and parallel to the nanowires have opposite signs, therefore, the iso-frequency contour is hyperbolic at long wavelength limit. The values of $\varepsilon_p$ and $\varepsilon_v$ can be calculated from equations 2.1, from which we can see that $\varepsilon_p$ is much more sensitive to the change of the permittivity of metal inclusions than $\varepsilon_v$. Figure 2.2 shows that the $\varepsilon_p$ value decreases rapidly and
becomes more negative when the frequency gets lower, which is a direct consequence of the strong permittivity dispersion of silver, while $\varepsilon_r$ value is relatively stable. Therefore, the iso-frequency contour for lower frequency light is much “flatter” as shown in Figure 6.2.

Again, we study the pass band representing an object. The arrows in Figure 6.2 show the direction of the energy flow for different components of waves. For the same $k_x$ value, the first derivative of the iso-frequency contour for lower frequency has a smaller magnitude, therefore, the diffracted wave with such $k_x$ value has smaller diffraction angle compared to high frequency wave. In general, as the frequency of the propagating wave decreases, the diffraction spread angle also gets narrower. Such anomalous diffraction behavior is opposite to that of the diffractions in normal materials.

![Fig. 6.2, Schematic iso-frequency contours for light with different wavelengths in nanowire metamaterials and in air. The region shaded by cyan color represents the spatial frequency band of an object on x-axis. The black and red arrows represent the directions of light diffracted by the object for different wavelengths. Diffraction in nanowire metamaterial manifests an anomalous frequency dependence.](image)

**6.2 Simulation and Experimental observation of anomalous diffraction**

3D full wave simulation has been done using commercial software COMSOL Multiphysics. As shown in Figure 6.3, a slab of metamaterial composed of silver hexagonal nanowire array embedded in alumina template was covered with 300nm thick silver layer at the bottom. A 300nm wide slit, served as the object for diffraction study,
Fig. 6.3, Finite element simulation results showing the anomalous diffraction phenomena inside nanowire metamaterials. The radius of the silver wire, the lattice constant, and the length of the wires are 30nm, 110nm and 1.5μm, respectively. Plane waves of light propagating upwards get diffracted by a 300nm wide slit cut through the 300nm thick silver layer at the bottom of the metamaterial slab. Working wavelengths are (a) 633nm, (b) 780nm and (c) 980nm respectively. Longer wavelength light has less energy loss and substantial fraction of the beam is reflected back. The false color scale has been adjusted accordingly to show the width of the central beam only.
was cut through the silver layer. Incident light with wavelengths at 633nm, 780nm and 980nm respectively transmits through the slit and gets diffracted. The simulation results clearly show that the diffraction angle gets smaller when the working wavelength gets longer. Such anomalous diffraction behavior agrees well with our theoretical predictions.

Experimental verification of such anomalous diffraction was carried out with an apertureless NSOM system, which has been introduced in section 4.1. The nanowire metamaterials were fabricated using the FIB pre-patterning approach described in Chapter 3, the same as in the experiments demonstrating the negative refraction and slab lens imaging. A 2μm thick slab of nanowire metamaterial is prepared by focused ion beam milling. 300nm wide slits were cut through 450nm thick gold layer at the bottom of the slab. In order to show the anomalous frequency dependence for the diffraction angle, the outgoing light pattern at the top surface of the slab is scanned by the NSOM system. By measuring the width of the pattern for different frequencies, we will be able to compare their diffraction angles.

The measured results for 633nm, 808nm and 980nm working wavelengths are shown in Figure 6.5(a)-(c) respectively. The horizontal axes represent the lateral distances along the direction perpendicular to the slits. The vertical axes represent the measured near field light intensity. Despite the significant noise signal, the central peaks give the profile of fundamental beams at the top interface. We fit the results with Gaussian curves and obtained the width of the patterns for different wavelengths. As concluded in Figure 6.5(d), the pattern width reduced from 1.2um for light with 633nm wavelength to about 500nm for 980 nm wavelength, which agrees our theoretical predictions well.
Fig. 6.5, (a)-(c) NSOM measurement results at the top surface of the nanowire metamaterial slab for
working wavelengths of 633nm, 808nm and 980nm respectively. The horizontal axes represent the lateral distances along the direction perpendicular to the slits. The vertical axes represent the measured near field light intensity. (d) Compiled figure of widths for diffracted light beam at different wavelengths.

The ripples on the right side of the figures are attributed to noise generated by the NSOM system because they only appear on one side and cannot be removed after rotating the sample by 180 degrees. Improvements of the NSOM system are ongoing and the noise will be suppressed to give more clear results for the diffracted beam width.

Another unique property of the hyperbolic dispersion is that it allows the propagation of waves with very large $k$ values. In fact, deep subwavelength focusing and imaging have been investigated[49],[73]. For normal materials, the diffraction is limited to objects larger than half wavelength of light. For smaller objects the Fourier transform of the object forms a band wider than the iso-frequency contour of the light, therefore the diffraction spread angle is wider than $\pi$ (or $2\pi$ solid angle) and some of the large $k$ information has been lost. That is also why $4\pi$ microscopy can improve the resolution. However, for indefinite materials, the iso-frequency contour is not limited to a narrow band. The hyperbolic contours allow the propagation of very large $k$ waves, although in real structures like nanowire metamaterials, there is an upper limit corresponding to the first Brillouin zone determined by the period of the nanowire array. Consequently, the diffraction in indefinite materials is not limited by half wavelength of light which means that diffraction pattern can be observed for objects much smaller than the traditional limit. As illustrated in Figure 6.2, the pass band is beyond the coverage of the iso-frequency contours in air. Some of the large $k$ information cannot be carried by the light and the diffracted light spreads in all the upper half space. On the other hand, in nanowire metamaterials the whole pass band is covered by the iso-frequency contours and the diffracted light is limited in a certain angle range.

Furthermore, the Brillouin zone size is determined by the nanowire array structure, no matter what frequency the wave has. Hence large $k$ value electromagnetic wave components, which carry high resolution information can always propagate in the metamaterial, even when the frequency gets lower, which corresponds to a larger wavelength in free space. As discussed previously, the diffraction in the nanowire metamaterial has an anomalous relationship with the frequency of the propagating waves. Therefore, the diffracted light from a deep subwavelength aperture may form a nearly collimated beam with subwavelength width, since the light carries large $k$ information. Such a beam can be used for high resolution optical imaging that is not restricted by the diffraction limit.
6.3 Conclusions

The flatter iso-frequency contours at longer wavelengths are not an intrinsic property for indefinite materials, but the consequence of strong dispersion of metals inside the nanowire metamaterials. This feature results in an anomalous diffraction behavior, i.e., the diffraction spread angle becomes smaller when the wavelength of light increases, which is opposite to the diffractions in normal dielectric materials. With the indefinite property of supporting large k waves, the width of diffracted beam may be smaller than the diffraction limit and lead to applications like sub-wavelength imaging and lithography.
Chapter 7

Surface Plasmon Interference

7.1 Surface Plasmons

Surface plasmon polaritons (SPPs) refer to electromagnetic waves that are bound to a Metal/dielectric interface[74]. Since the pioneering work of Ritchie in the 1950s[75], the fundamental SPP properties have been extensively studied and widely applied in a number of important applications such as surface plasmon resonance sensing[76],[77] and imaging[78],[79], surface enhanced Raman scattering[80],[81], surface-enhanced second harmonic generation[82-84], etc. The recent advancement in nanoscale fabrication techniques has given rise to even more fascinating applications in superimaging beyond the diffraction limit[48],[49],[85],[86], subwavelength electromagnetic wave guiding[87-90], plasmonic lithography[91-95], plasmonic ruler[96],[97], optical negative refraction[26], as well as cancer treatment by metallic nanoparticles[98],[99], which has remarkably extended and transformed the horizon of the field of plasmonics.

Although strictly speaking SPPs are the collective electron oscillations associated with electromagnetic waves at the metal/dielectric interface, their existence can also be understood from classical electrodynamics[74]. If the metal and dielectric materials are both semi-infinite, from the boundary condition, the dispersion relation of SPs can be determined as

\[
d_{m} \epsilon_{m} + d_{e} \epsilon_{e} = \omega^2 c^2
\]

where \( d_{m} \) is the wave vector of the surface plasmon, \( \omega \) is its frequency and \( c \) is the speed of light in vacuum. \( \epsilon_{m} \) and \( \epsilon_{e} \) are the permittivities of the metal and dielectric material, respectively. Since the strong dependence of the metals’ permittivities on
frequency, Eq. 7.1 dictates the frequency-dependant dispersion relationship of the surface

Fig. 7.1. (a) Dispersion curve for SPs at the interface between bulk silver and air. (b) The dispersion for the SP modes on a 20nm thick silver film surrounded by air.
plasmons at an isolated interface between metal and dielectric.

Fig. 7.1 shows the typical dispersion curve calculated using evanescent wave transmission method[100]. Fig. 7.1(a) is the dispersion curve for single mode SPs at the interface between semi-infinite silver and air, and (b) is the dispersion for the SP modes on a 20nm thick silver film surrounded by air. When two metal/dielectric interfaces get close to each other, the SP modes on these two interfaces are able to interact with each other and change their general behavior. New combined modes will form and finally change the dispersion property of the SPPs[101].

From the dispersion curve we can clearly see two new modes which are different from the original modes at either of the two single interfaces. They are usually referred to as anti-symmetric mode (top curve) and symmetric mode (bottom curve) based on their field distribution. A very interesting phenomenon is that the right-hand part of the dispersion curve of anti-symmetric mode bends to negative slope. Note that the group velocity of a propagating wave is defined as \( \frac{d\omega}{dk} \), which is exactly the slope of the dispersion curve. Therefore the negative slope of the dispersion curve indicates a negative group velocity. It can be proved that the net power flow of SPPs along the interface is opposite to the phase propagation direction when the group velocity is negative, which should be taken into account when exciting SPPs. Here we focus on another interesting aspect of this dispersion, i.e., for a certain range of frequencies, one frequency corresponds to two different wave vector magnitudes, which means that monochromatic incident light may couple to two different modes of SPPs. Beats may be formed by such surface plasmon modes with the same frequency.

### 7.2 Beats formed by surface plasmon waves with the same frequency

The field confinement of surface plasmons in a two dimensional (2D) world have triggered a lot of efforts to study its generation, propagation and interaction[88], which has also been termed as 2D optics. Many 2D counterparts to classical 3D optics have been realized for SPPs. Light sources, mirrors, waveguides, prisms and filters[102-106] of SPPs offer people enough elements to play with light in the 2D world. 2D optics will not only fulfill our curiosity, but also bring us more opportunities to manipulate and make use of light. Applications include the focusing of SPPs[107],[108], the nanolithography based on the interference of SPPs which will be discussed in the next section and the beats formed by two surface plasmons propagating on thin metal films.

Beats originate from the interference between two waves with slightly different frequencies or wave vectors or both. The difference in the frequency or wave vector leads
to the phase difference in propagation, thus at certain time points and spatial positions, there are constructive interference while some others destructive. A lower frequency/longer wavelength (compared to those of either mode that builds up the beat) envelope will form on the profile of the waves. The frequency and wave vector of the envelope is determined by those of the two beating waves. Hence if we can get the information of the envelope, the difference in wave vectors and frequencies may be obtained. On the other hand, the shape of the envelope can be controlled by tuning the difference in wave vectors or frequencies.

![Diagram](image)

Fig. 7.2. (a) Schematic picture of the system we are studying. (b) The electric field beat pattern of SPs excited from left bottom using ATR. The horizontal black line under the film (in the region marked “Air”) is there for convenience of calculation, not a physical boundary. (c) The cross sectional view of field distribution of $E_x$ at a distance of 10nm above the silver film.

Commercial software COMSOL Multiphysics which is based on finite element algorithm is used in the simulation. An attenuated total reflection (ATR) set up is adopted to excite the surface plasmons on the silver film in air. In order to get enough propagation length to observe the beats, we reduced the imaginary part of the silver permittivity, which determines the loss of the metal, by 100 times in the simulation. The permittivity of the dielectric material is 2.6 to enable the coupling to both SP modes. The silver film thickness is 20nm and the air gap between the film and the underneath ATR prism is 80nm. We also removed the dielectric material under the part far from the excitation.
position to reduce the radiation loss, as shown in Fig. 7.2(a) and 7.2(b). In Fig. 7.2(b), 7.3, 7.4(a), 7.5 and 7.6(a), a horizontal black line remains under the film at the top boundary of removed dielectric region. It is there for convenience of calculation, not a physical boundary. The boundary condition of the whole system is set to be open.

Figs. 7.2(b) and 7.2(c) are simulation results at the vacuum wavelength 319.5nm. Only Ex component (along the direction in which the SPs are propagating) is shown. Two Gaussian beams with the same frequency are irradiated onto the silver film from the dielectric material beneath it. Their incident angles are carefully chosen in order to excite the two different modes corresponding to this frequency. Due to the total internal reflection, the evanescent field is generated above the dielectric top surface and is resonantly coupled to SP modes. We chose frequencies very close to the maximum of the anti-symmetric mode dispersion curve so that the difference in k is not too large, hence the beating effect is more clear. From Fig. 7.2(b) the difference in k can be calculated directly from the data, \( \Delta k = 2.3 \times 10^6 \text{m}^{-1} \). Also shown are the cross-sectional results of Ex at a distance of 10nm above the silver film, which clearly demonstrate the beating effect.

From the beat patterns we can also tell the ratio of field amplitudes between the two beating waves. If they have the same amplitudes, there will be clear nodes in the pattern. In other cases, the wave with larger amplitude will be dominant and weaker wave simply modifies the amplitude of the dominant wave. In either case, we can calculate the amplitudes of the two beating waves in a simple way: the maximum value of the beat amplitude represents the constructive interference, hence is the sum of the two amplitudes, while the minimum position represents the destructive interference and gives the difference between the two amplitudes. With the above method, one can always get the exact value of the beating waves’ amplitudes. It is a very useful way to extract information from experimental data.

The above beating effect can hardly be detected in experiments because their envelopes are not stationary in time. We excited the two beating waves at the same point and made their group velocity at the same direction. However, one of the two components of the beat has an opposite group velocity compared to its phase velocity, hence the two beating waves have opposite phase velocity. From simple mathematics we find that the envelope is not independent of time t.

\[
Ae^{i(k_1x-\omega t)} + Be^{i(k_2x-\omega t)} = e^{i\frac{k_1+k_2}{2}x-\omega t} \left( Ae^{i\frac{k_1-k_2}{2}x} + Be^{i\frac{k_2-k_1}{2}x} \right)
\]

The first factor on the right side of the equation is time dependent and the second factor is time independent. The second factor has a period of \( |k_1 - k_2| / 2 \). When \( k_1 \) and \( k_2 \) are in opposite directions, \( |k_1 - k_2| >> |k_1 + k_2| \). So the first factor has a much longer wavelength,
thus represents the envelope and it is dependent on time. In order to get a stationary envelope, \( k_1 \) and \( k_2 \) should be in the same direction, so that \( |k_1 - k_2| \ll |k_1 + k_2| \), and the second factor turns to be the envelope. We tried to put ATR set up at two ends of the silver film, excite the two waves at different positions and get the pattern in Fig. 7.3.

![Fig. 7.3. Upper panel: the electric field beat pattern of SPs excited from both ends of the silver film using ATR. Lower panel: The corresponding energy density distribution.](image)

The simulation results agree well with previous analysis. Such beats turns to be very non-classical. Traditional beats are formed by waves propagating in the same direction. But in our case one of the beating waves has opposite group velocity and phase velocity, which makes the beat more like a standing wave. We call it standing-wave-like beats. They are different than standing waves in the sense that it is the envelope, not the wave itself is stationary.

Beating SPPs can also be excited with other methods. For example, Fig. 7.4(a) shows the SPPs excited from a slit on the silver film. Because the slit can add a broad band of wave vector components to the incident light, two SPP modes corresponding to this frequency are simultaneously excited. Beats were automatically formed on both sides of the slit. Fig. 7.4(b) is again the value of \( E_x \) at the cross section 10nm above the metal surface. The high bump in the center is actually the electrical field of the incident and scattered light. It is obvious that the efficiency of coupling from the light to SPPs is not so high. We intentionally make the beam slightly deviate from the center of the slit. Hence the beat on the left of the slit behaves a little different from that on the right. The general efficiency and the efficiencies for different wave vectors vary while the incident position changes. Using the method mentioned above, one can find out the amplitude for each wave and thus get the coupling efficiency for either of them.
In addition to the beat between two anti-symmetric modes with different group velocity, similar behavior exists between one symmetric and one anti-symmetric mode with the same frequency. From Fig. 7.1(b) one can see that in the relatively low frequency region, there are always two modes, one symmetric, one anti-symmetric, corresponding to one frequency. Because of their different k values, they may also form spatial beats. To demonstrate the above beating effect, a working frequency at 666.2THz, which corresponds to the free space wavelength 450nm, and a silver film that is 40nm thick were selected. This time the real loss of the materials from experimental data were applied. Again, propagating waves were coupled into SPPs via ATR method. Fig. 7.5 shows the energy density of the two SPPs that were excited at the left bottom side. Since at the wave length used here, both modes have positive group velocity, we do not need to excite them at different positions as in the high frequency case discussed at the beginning. The beat here is quite special compared to the previous ones in the sense that the profile of the energy density has no mirror symmetry with respect to the film, i.e., it has different node position at different sides of the film. However, this property will not affect the experimental observation because the methods of detecting SPPs, e.g., NSOM (Near-field Scanning Optical Microscopy), fluorescent dies, are usually along only one side of the film.
From a practical point of view, the beat described here has advantages over the first configuration. In the former case, in order to have two modes with same frequency but different $k$ that can form beat in space, not in time, we worked at the vicinity of the top of the silver film dispersion curve, where the loss of the system is so high that it becomes not practical to observe such beat patterns in real experiments. The lowered loss in our simulation could be an evidence. While in the latter configuration significantly long propagation length was shown in the calculations even with real loss of silver, which means there is no fundamental obstacle for the observation of these beats in experiments. Once the two modes have wave vector close to each other, they can be excited by a single light beam due to imperfect collimation. Therefore, a high probability of observing such phenomena could be expected. The time averaged energy density distribution shows that the pattern has a much larger length scale than the wavelength of the excitation, which indicates that its observation is not restricted by the diffraction limit. We may detect the pattern even in far field. These temporally stable patterns are helpful to determine the modes that exist on the metal surface. Similar to the beating phenomena in many other physical systems, one can use them to determine the difference of wavelength of the modes involved, and even relative amplitudes.

With the stability of spatial pattern and much longer period than the SPP wavelength, the beating behavior of SPPs can be studied using NSOM. The introduction of a NSOM tip will affect the beat pattern. However, the detected signal can still show essential property of the beat phenomena. Here we present our simulation of SP beats detection by adding a dielectric waveguide coated with aluminum (similar to an actual NSOM tip) close to the metal surface. Since our system is invariant along $y$ direction, the waveguide is actually a slab instead of a cylinder, but it still gives a qualitative sense of what can be seen from the NSOM. The thickness of the waveguide is 100nm which is a typical size for NSOMs. Since the waveguide is sub-wavelength, the EM wave with 450nm wavelength cannot propagate inside it. So we only calculated the power flow through the aperture of the dielectric slab. Fig. 7.6(b) shows the relative power flow into the NSOM along the propagation direction on the metal surface in a range from the maximum output to the minimum output position. One can see that the pattern could be strongly disturbed by the NSOM tip. However, the signal detected by the tip has no big difference from the actual field distribution. A Max/Min contrast of around 40 is obtained, which is sufficient to tell the beat pattern in experiment.
7.3 Surface plasmon interference lithography

A light beam in three-dimensional (3D) free space can be converted into a two dimensionally (2D) confined SPP wave as long as the momentum mismatch between them is compensated by a coupling element. The sacrifice of dimensionality, however, results in extraordinary “optical frequency but X-ray wavelength” property, i.e., an SPP wavelength much smaller than that of the excitation light, as well as strong electromagnetic field enhancement in the SPP near-field[74]. As a straightforward consequence, converting free space light into SPPs on a planar surface should lead to devices or applications that possess higher spatial resolution and higher near-field energy density. Hence a precise yet flexible design of surface structures on a metallic film to couple the free space light into various SPPs and to guide their propagation is on demand. Here we present a general scheme to manipulate SPP interference patterns by designing the surface structure shape and controlling the wavelength of the excitation light beam. We demonstrate lithographic pattern formation to exemplify the strength of this design[109].

Fig. 7.6. (a) The energy density distribution of the same structure as in Fig. 5, but with the existence of a NSOM tip. (b) Relative power flow into the NSOM along the propagation direction on the metal surface.
A typical SPP dispersion curve based on the above equation is illustrated in Figure 7.7(a). Since the wave vector of the SPP is always larger than that of the light in the surrounding media at the same frequency (i.e., smaller wavelength of SPPs), a momentum compensation coupling mechanism is necessary to excite the SPPs. A grating is considered as one of the best SPP couplers because it can provide an additional discrete wave vector in a very efficient way. Sharp edges of a slit can also be used to excite SPPs, where the light diffracted from the corner gains very broad band wave vectors; the interface will automatically select the components with matched wave vector with SPPs and support their propagation[110],[111], (see also Figure 7.7b). Although the nonresonant nature of this process will reduce the coupling efficiency, these simple structures will drastically reduce the complexity of sample fabrication.
Fig. 7.8, Simulation a-c and experimental results e-g using a 100 nm thick aluminum plate with various edge/slit shapes: (a, e) triangle; (b, f) square; (c, g) pentagon. The side lengths are 2, 2, and 1.5 μm, respectively in (a-c). The excitation light had angular polarization in all the simulations. The scale bars in all of the AFM images represent 500 nm. The side lengths of the triangle, square, and pentagon structures used in the experiment are 2, 2.5, and 2μm, respectively.

Since SPPs are essentially two dimensionally confined on a metal-dielectric interface, their interference patterns can be controlled by arranging different 2D geometries of the slits. The slits that formed various shapes were obtained by focused ion beam (FIB, FEI Strata 201 XP) milling (slit openings are about 150 nm wide) in an aluminum film deposited on the quartz wafer. The SPPs will be excited by the slit in all samples. The aluminum thickness is 100 nm. Subsequently, a 15 nm thick OmniCoat (MicroChem, refractive index is 1.57) layer was spun on the samples to increase the adhesion between
aluminum and exposed photoresist. Finally, a negative near-UV photoresist (SU-8) was spun on the top of the OmniCoat. A single collimated i-line beam from a mercury lamp ($\lambda = 365$ nm) is used to generate all these patterns with exposure time typically less than 10 s, corresponding to a dose of around 18 mJ/cm$^2$. After the development, the topography of the recorded features was measured by an atomic force microscope (AFM, Dimension 3100, Veeco).

Figure 7.8a-c show simulated SPP interference patterns with three geometries. Obviously, not only periodic but also quasi-periodic and even more complicated 2D patterns can be realized. The lithography experimental results (see Figure 7.8e-g) clearly show the formation of different interference patterns predicted by simulations.

Compared with the pattern formation by free laser beam interference, one obvious advantage of SPP interference is the higher resolution as we discussed above. In addition, SPP interference requires a much simpler setup. To achieve a complex laser interference pattern, multiple laser beams have to be very precisely directed and controlled by complicated optics. As for SPP interference in our case, all of the complicated optics can simply be replaced by slits/edges with well-designed shapes and only one excitation beam is required.

7.4 Conclusions

In summary, we used numerical simulations to study the beats between two different thin film SP modes with the same frequency, including the beats between anti-symmetric modes with positive and negative group velocities and those between symmetric mode and anti-symmetric mode SPs. Beating with the existence of a NSOM tip was simulated to clarify the possible deviation of experimentally detected signal from actual field distribution. Possible applications of beating phenomena were also discussed.

SP modes with different wavelengths but the same frequency can be excited on a thin metal film and form beats. Such SP beats have the potential of being applied in highly integrated optical circuits as interferometric modulators. Switches, or even logic gates may be realized by using beating effect. And a great advantage of using such beats is that they are on the same metal film, hence the fabrication of complicated 3 dimensional structures is not needed. Furthermore, by choosing different working frequency, the difference in wave numbers of two beating modes can be controlled, leading to certain tunability with the same metal device.

Surface plasmons interference has also been applied in 2D lithographic pattern formation. Slits cut through the metal films provide a precise yet flexible design of surface
structures on the films to couple the free space light into various SPPs and to guide their propagation. Various kinds of high resolution 2D patterns were generated by interference lithography based on the SPPs excited from the slits. Further control of the slits positions may potentially provide the ability of lithography of more complicated 2D patterns.
Chapter 8

Summary

In the field of optics/photonics, the pursuit of smaller device but faster performance and the ability to manipulate light at will has led to many fascinating discoveries. Specifically, the invention of metamaterials has greatly enriched our scientific toolbox. New phenomena such as negative refraction of light, perfect lens, and more science fictional invisible cloaks have been demonstrated based on the very concept.

In this dissertation, I have presented my research on light propagation and imaging in indefinite materials, which are a unique type of metamaterials. The principal components of indefinite materials’ permittivity and/or permeability tensors are not all with the same sign. Such strong anisotropy can be realized using artificial photonic structures, for example, metal nanowire array embedded in dielectric matrix or metal/dielectric multilayer structures.

In order to achieve a uniform optical property, typical feature size of the photonic structure should be much smaller than the wavelength of light. For optical wavelengths, such structures should be at nano-scale. Fabrication of such nano-structures with high throughput and low defect ratio is a great challenge. Bottom-up approach based on electrochemical deposition of metal in self-organized porous alumina template provided us an efficient way to realize nanowire indefinite metamaterials.

Associated with the unique hyperbolic dispersion relation of the indefinite metamaterials are many abnormal optical properties, such as negative refraction of visible light, 3D deep subwavelength confinement of light and anomalous diffraction.

Unlike isotropic materials, the iso-frequency contours for anisotropic materials are not circular any more; therefore the direction of Poynting vector in anisotropic materials is not in the same direction as the wave vector. For indefinite material, deviation between the two vectors is even more substantial and results in the negative refraction of energy.
flow at the interface between indefinite material and normal material. An important application of negative refraction is to create a slab lens for imaging purposes. Moreover, due to the strong dispersion of metal inclusion in the nanowire metamaterials, light experiences anomalous diffraction, i.e., for longer wavelength of light, the diffraction angle gets smaller, which is inverted behavior comparing to normal dielectric materials. With the help of NSOM system, we have successfully demonstrated the above phenomena.

Another consequence of the hyperbolic dispersion is that indefinite material allows the propagation of modes with wave vector much larger than those in vacuum or normal dielectric materials. A direct application of this property is that light can be confined in a cavity that is much smaller than its wavelength. For a fixed frequency, the wave vector can be tuned in the range of more than one order of magnitude, therefore, the size of the cavity for the same resonant frequency and same mode order can be greatly different. Furthermore, the volume dependence of radiation induced quality factor of such a cavity behaves oppositely to traditional dielectric micro-cavities. Q increases while the size of the cavity shrinks. Such properties have been verified by FDTD simulations.

Also presented in the dissertation was my research work on the interference of surface plasmons. Beats of surface plasmon and lithography based on 2D surface plasmon patterning were shown.

With the help of metamaterials, transformational optics is getting more and more practical. Fine control of light propagation becomes a reality. New optical devices that are not possible with traditional materials may be created, and greatly enhance our ability in scientific research and technology development. Specifically, better control of light propagation may be applied for energy harvest purposes, which is a possible research direction I will explore in the future. Such innovations will have great impact on human life.

As another very important research direction in photonics, nanoscale optical cavity has attracted much attention and will lead to many different applications such as strong light-matter interaction, nano-scale laser device and its integration with on-chip optical circuits. We will try to fabricate nanocavities made of indefinite metamaterials and demonstrate their unique behavior and explore the potential applications of such cavities.

With the development of science and technology our understanding of nature is quickly expanding. Yet the more we learn, the more we learn how little we know. In the exploration of the vast unknown territory of science, we are touching a world at smaller, faster and more complex scales. I am honored to be able to get involved in some of the most exciting discoveries. And I am sure there will be many more down the road.
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