ABSTRACT

Kang, Mi Sun. Mid-Infrared Localized Surface Plasmon Resonance of Indium Tin Oxide Nanostructures. (Under the direction of Stefan Franzen).

In this thesis we investigate the phenomenon of surface plasmons on patterned surfaces of conducting thin films. The interaction of electromagnetic radiation with the electrons of a thin film made of a conducting metal oxide (CMO) can result in a surface plasmon resonance (SPR). However, patterned surfaces give rise to two optical phenomena known as localized surface plasmon resonance (LSPR) or capacitive plasmon resonance (CPR). LSPR is the optical phenomenon of the interaction of light with nano-scale objects. CPR is from a perpendicularly interaction to the surface between surface plasmon and incident light in a very thin film, i.e. with a thickness less than the skin depth of the conducting material. Surface plasmons (SP) are collective electronic oscillations of electrons which are induced by electromagnetic wave at the interface between and conductor and a dielectric. SP couple with incident light to form a surface oscillation known as a surface plasmon polariton (SPP), which can propagate along the surface of the conductor-insulator interface. Then, SPPs can be excited by either electrons or photons and the excitation is measured or observed as a SPR. Specially, on a nanoscale patterned surface or in a nanoparticle sample, the excitations of SPPs are detectable as LSPR. The shapes, sizes, or properties of the conducting materials can be controlled to give rise to a variety of LSPR signatures. Therefore, the lithographic techniques, which are able to make patterns or shapes on the micro- to nano-scale, have been also received attention in photonic applications. Many researchers, until now, have focused on noble metals such as gold and silver as plasmonic materials. Gold (Au) and silver (Ag) are well known for their plasmonic absorption in the ultraviolet and visible regions. Despite the
fact that this is a well-developed field of investigation there are many fundamental aspects that cannot be studied with the noble metals: First, it is not possible to make a film that is thinner films than the skin depth of the noble metal. For example, Ag has a skin depth of less than 5 nm in the IR-region, but it is not possible to make a smooth film of Ag with that thickness due to the formation of islands. The island formation of both Au and Ag arises because of the high surface free energy. Ag films tend to react with impurities, which makes it difficult to handle. Au is far from a pure plasmonic material because of intense inter-band transitions. For these reasons, we have sought a new material for study of SPR phenomena. CMOs have proven to be a suitable alternative material. CMOs also show plasmonic phenomena in near-IR and even mid-IR. Thus, the optical phenomena can be observed using Fourier-transform infrared technology. Furthermore, CMOs are tunable and their optical properties can be controlled based on doping materials, deposition conditions, etc. This thesis shows that CMOs also have the potential for use in lithographic applications.
Mid-Infrared Localized Surface Plasmon Resonance of Indium Tin Oxide Nanostructures

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

Chemistry

Raleigh, North Carolina

2016

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Mi Sun Kang was born on June 27th, 1979 to Eung-seok Kang and Jung-hee Kim in Seoul, Korea. She graduated from Inha University with Bachelor degree and from SungKyunKwan University with a Master of Science degree in Physics department. She learned the way of the scientific thinking during Bachelor degree and studied solid state physics in SungKyunKwan University. To be specific, she analyzed the lattice of multiferroic materials via neutron scattering and X-ray scattering methods and investigated magnetic characteristics of multiferroic materials. At the same time, she studied Iron oxide nanoparticles as contrast medium for MRI and by studying that, she was interested in the biophysics. Later, she met Dr. Stefan Franzen who is the professor of the physical chemistry division in Chemistry department at North Carolinas State University. Dr. Franzen has studied plant viruses, dehaloperoxidase, and plasmonics. After several times of the intensive scientific discussions with Dr. Franzen, Mi Sun has joined his group since August, 2010 and focused on the research of plasmonics with the surface of Indium tin oxide films via surface plasmon resonance or localized surface plasmon resonance methods in the mid and near infrared regions of the electromagnetic waves.
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CHAPTER 1 INTRODUCTION

Studies of nano-scale structures have grown enormously in every scientific area for three decades.\textsuperscript{1} Semiconductor technology has had a great impact on mankind for the past five decades. More recently, nanotechnology has exerted a strong influence on as the recent developments in semiconductor technology.\textsuperscript{2-4} Nanotechnology is divided into two aspects. The first is manufacturing technologies to have high productivity, uniformity, and quality while reducing expense at the same time. These efforts have accelerated the development in the semiconductor technology. The second aspect is for the development of a fundamental understanding and characterization of nano-scale phenomena. These studies have included new and interesting materials research in areas such as optical response in metallic nanostructures, which has led to methods for enhancing resolution beyond the classical optical limit. The field of optoelectronics focuses on the study of electronic devices, which are capable of controlling or detecting light across the electromagnetic spectrum from the X-ray to the infrared region. Plasmonics is a research field that has optoelectronic applications, specifically because of recent developments of nanotechnology.\textsuperscript{1, 5-7} The applications of this research can be seen in diverse areas of optoelectronics such as optical devices\textsuperscript{8}, light emitting or receiving devices\textsuperscript{9}, display panels, data storage devices, or biomedicine\textsuperscript{10-12}, which span the past three decades\textsuperscript{13}.

Plasmonics is a field of study focused on how an electromagnetic (EM) field interacts with the conductive electrons at the surface of metals or conductors. It is of interest to push beyond the limits of the traditional plasmonic materials of noble metals such as Au and Ag both from a materials perspective and in order to study effect of EM radiation in areas of the
spectrum outside of the UV-vis. In this thesis we have explored plasmonic phenomena of conducting metal oxide (CMO) films and the patterns of CMO films in the near- and mid-IR spectral regions. This field of study has industrial applications, for instance, in lithography or optical data storage.\textsuperscript{14-16} The term of surface plasmon amplification by simulated emission of radiation (SPASER) also emerged in 2003 in a study by Bergman and Stockman\textsuperscript{17,18} and high harmonic generation can be enhanced by plasmons as well.\textsuperscript{19} During last 20 years, the consideration of surface plasmons has greatly increased, as can be seen on the number of the publications in the field of SPR and related phenomena.\textsuperscript{20} For example, Dr. Takahara and his group published a paper about one-dimensional (1D) optical waveguides to guide thin optical beams in the nanometer range in 1997.\textsuperscript{21} In 1998, Dr. Ebbesen and his coworkers announced the interaction between plasmons and electronic excitations on the metal surface of the periodically patterned film, and the interaction made extraordinary optical signals in transmission (surface plasmon resonance).\textsuperscript{22} However, the entire field has been dominated by Au and Ag until recent new research began to increase the repertoire of materials available for SPR research.

In our research group, Prof. Franzen has published a series of papers demonstrating the observation of SPR on CMOs such as indium tin oxide (ITO), zinc oxide (ZnO), or Cadmium oxide (CdO). Prof. Franzen and our group had predicted and calculated the phenomena related in the material properties since 2002.\textsuperscript{23,24} The first demonstration of SPR on a CMO thin film was published in 2006 using ITO thin films.\textsuperscript{25} ITO, which has been the most widely studied CMO for SPR measurements, is chemically stable, relatively easy to deposit and to process using lithography techniques. Although we have recently shown that CMOs with higher
mobility than that of ITO that can be used create narrow bandwidth plasmonic thin films, ITO still has the advantages of ease of processing and chemical stability, which make it a useful material for proof-of-concept experiments.

In this thesis surface plasmon resonance on patterned ITO films were studied based on previous research by former group members showing SPR on ITO thin films.\textsuperscript{23-28} The various patterns of ITO thin films are made by nanosphere lithography and photolithography methods. Localized surface plasmon resonance (LSPR) and capacitive plasmon resonance (CPR) are shown in the reflective spectra on the surface of the patterns by interacting with mid- or near-IR waves. LSPR and CPR are optical resonances on small features comparing to the wavelength of incident light and thinner films than skin depth of the materials, respectively. These phenomena are novel. There have been no previous patterned surfaces made of ITO or other CMOs. The optical phenomena observed are also novel and there are many questions that have not yet been fully explored. The dissertation is divided into four main parts: First, theoretical considerations for understanding surface plasmon resonance on conducting metal oxide films are discussed. Second, manufacturing and characterization parts of the various patterned surfaces with two different lithographic techniques are described. The third part consists of a presentation of the measurements on the patterned films in near-IR and mid-IR regions, which is the major focus of the research. The last part of the thesis discusses applications in which self-assembled monolayers (SAM) are deposited on the surfaces of cadmium oxide films and characterizations of these SAMs are presented.
CHAPTER 2 THEORETICAL BACKGROUNDS

2.1 Plasmon and polaritons

2.1.1 Surface waves

The concept of a plasma was introduced by Langmuir to describe an ionized gas in the 1920s. Many types of plasma have been developed by laser applications and, advances of high energy physical techniques for plasma acceleration.\textsuperscript{1,29} There are various types of plasma: a hot plasma is also called a thermal plasma produced by atmospheric arcs, sparks and flames.\textsuperscript{30} One of other types is a cold plasma in which the ions is not able to have thermal motion, the example of the plasma is the Earth’s ionosphere.\textsuperscript{31} An ultracold plasma is also one example that is produced at temperature as low as 1K, thus experiments on this type of plasma are carried out in vacuum.\textsuperscript{32} Our interest, however, has been focused on plasma on conducting surfaces, driven by ordinary light sources. Understanding surface wave is the first step to understand the formation of plasma on a surface of conducting films. By the term of surface wave, we mean that a wave propagates along the interface from one medium upon another one that is interacted with the boundary between two media. Figure 2.1(a) shows the electric polarization called a transverse electric (TE) wave, in which the electric fields oscillate perpendicular the plane of incidence. Figure 2.1(b) shows the order case, known as the magnetic polarization called a TM wave. The magnetic field is perpendicular to the plane of incidence in this wave. The TE and TM wave incidents from the first media to the second are both reflected (with an angle $\theta_1$) and refracted (with $\theta_2$) partly (see Figure 2.1).
2.1.2 The effective permittivity and permeability

First of all, let us introduce the definitions of the permittivity and permeability, which are fundamental too much of the following description. They can be expressed as:

\[
\varepsilon = \varepsilon_0 \varepsilon_r \quad \text{and} \quad \mu = \mu_0 \mu_r
\]

(2.1)

where \( \varepsilon_r \) and \( \mu_r \) are the relative permittivity and the relative permeability.

In SI unit, \( \varepsilon_0 = 8.85 \times 10^{-12} \ [\text{As}^{-1} \text{m}^{-1}] \) and \( \mu_0 = 4\pi \times 10^{-7} [\text{Vs}^{-1} \text{m}^{-1}] \)

In vacuum, \( \varepsilon_r = \mu_r = 1 \).

In a certain medium, we have to introduce other physical quantities \( \vec{P} \) and \( \vec{M} \), which are so-called the electric polarization and the magnetic polarization, respectively.

We now get

\[
\vec{P} = N \vec{p} \quad \text{and} \quad \vec{M} = N \vec{m},
\]

(2.2)

where \( \vec{p}, \vec{m} \), and \( N \) are the electric, magnetic dipole moments, and the number of atoms, respectively. Therefore, the electric and magnetic flux densities are shown by the combinations of two fields and two polarizations such as
\[ \vec{D} = \varepsilon_0 \vec{E} + \vec{P} \quad \text{and} \quad \vec{B} = \mu_0 \vec{H} + \vec{M}. \quad (2.3) \]

These electric and magnetic flux densities in equation (2.3) may often use in Maxwell equations in a medium. In a linear dielectric material, the electric polarization is directly proportional to the applied electric field when the field is not too strong.

\[ \vec{P} = \varepsilon_0 \chi_{\text{electric}} \vec{E} = N \alpha \vec{E} \quad (2.4) \]

where \( \chi_{\text{electric}} \) is the electric susceptibility and it depends on the microscopic structure of the dielectric material and \( \alpha \) is the atomic polarizability. By substituting equation (2.4) into equation (2.3), and then we obtain

\[ \vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon_0 \vec{E} + \varepsilon_0 \chi_{\text{dielectric}} \vec{E} = \varepsilon_0 (1 + \chi_{\text{dielectric}}) \vec{E} = \varepsilon_0 \varepsilon_r \vec{E} \quad (2.5) \]

In the correlation between \( \vec{P} \) (polarization in a unit volume) and \( \vec{p} \) (polarization in an atom), we understand that \( \vec{P} \) is a macroscopic quantity and \( \vec{p} \) is a microscopic quantity. This fact is also directly linked to a discrepancy in the definition of the electric fields. In equation (2.4), the electric field of \( \varepsilon_0 \chi_{\text{electric}} \vec{E} \) is macroscopic but the electric field of \( N \alpha \vec{E} \) indicates the electric field for a certain atom (microscopic). To properly understand the polarization of matter, we define the local electric field as.

\[ \vec{E}_{\text{loc}} = \vec{E}_{\text{ext}} + \vec{E}_{\text{dipole}} \quad (2.6) \]

Let us assume the simplest case, which is a small sphere (radius is macroscopically small enough. According to ref. 26, which is “Introduction to electrodynamics” by Griffiths, the radius of the small sphere is still 1000 times larger than a molecule). The electric field can be calculated by a simple formula for the charges far away as equal to \( \vec{P} / 3 \varepsilon_0 \). So Equation (2.6) is changed:
\[ \vec{E}_{loc} = \vec{E}_{ext} + \frac{\vec{P}}{3\varepsilon_0} \]  

(2.7)

However, the polarization is proportional to the local electric field, \( \vec{P} = N\alpha \vec{E}_{loc} \). From Equations (2.7), we can obtain

\[ \vec{P} = \vec{E}_{ext} \frac{N\alpha}{1 - \frac{N\alpha}{3\varepsilon_0}} \]  

(2.8)

We are able to define \( \varepsilon_{eff} \) as

\[ \vec{D} = \varepsilon_{eff} \vec{E}_{ext} = \varepsilon_0 \vec{E}_{ext} + \vec{P} \text{ and } \varepsilon_{eff} = \varepsilon_0 + \frac{N\alpha}{1 - \frac{N\alpha}{3\varepsilon_0}} \]  

(2.9)

Alternatively, we can also obtain the correlation between the atomic polarizability and the relative permittivity and it is expressed as (\( \varepsilon_{eff} = \varepsilon_0 \varepsilon_r \)):

\[ N\alpha = 3\varepsilon_0 \frac{\varepsilon_{eff} - \varepsilon_0}{\varepsilon_{eff} + 2\varepsilon_0} = 3\varepsilon_0 \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \]  

(2.10)

Equation (2.10) is called the **Clausius-Mossoti** formula. If we substitute the index of refraction for the dielectric function according to \( \varepsilon_r = n^2 \) we call the corresponding equation the **Lorentz-Lorenz** formula, which is used in optics.

On the other hand, from the Newton’s basic equation

\[ m \left( \frac{dv}{dt} + \frac{v}{\tau} \right) = eE \]  

(2.11)
where \( v \) is the velocity, \( E \) is the electric field and \( t \) is time. A relaxation time for damping is also expressed by \( \tau \). From (2.11), \( v \) has the general solution of the following equation:

\[
v = \frac{e}{m} \frac{E}{i\omega + \frac{1}{\tau}}
\]

(2.12)

And the current density is expressed by

\[
J = Nev = \frac{Ne^2\tau}{E} \frac{E}{1 + i\omega\tau}
\]

(2.13)

In addition, equation (2.13) may be written as \( J \equiv \sigma E \), where the quantity \( \sigma \) is defined in the equations below:

\[
\sigma \equiv \frac{\sigma_0}{1 + i\omega\tau} \quad \text{and} \quad \sigma_0 \equiv \frac{Ne^2\tau}{m}
\]

Here, \( \sigma_0 \) is called the electrical conductivity.

2.1.3 Maxwell’s equations

2.1.3.1 Maxwell’s equations in vacuum

In this section, we introduce Maxwell’s equations in vacuum since these four formulas are essential for understanding any process that involves electromagnetic waves. More to the point, to understand SPR phenomena in matter, Maxwell’s equations in matter are solved with boundary conditions. Therefore, the understanding of the equations in vacuum is necessary.

\[
\vec{\nabla} \cdot \vec{E} = \frac{1}{\varepsilon_0} \rho
\]

(2.14)

\[
\vec{\nabla} \times \vec{B} = 0
\]

(2.15)
\[ \vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \] (2.16)

\[ \vec{\nabla} \times \vec{B} = \mu_0 \vec{J} \] (2.17)

Three of the expressions have their own names. Equations of (2.14), (2.16), and (2.17) are called Gauss’ law, Faraday’s law, and Ampere’s law, respectively. (Equation (2.15) does not have any name), but it is an important statement that a magnetic monopole does not exist in nature. Actually, James Clerk Maxwell suggested another formulation with only two formulas rather than four expressions. He understood that all electromagnetic laws are derived from two four-dimensional vector potentials (so-called electric and magnetic potential) given by:

\[ \vec{B} = \vec{\nabla} \times \vec{A} \] (2.18)

\[ \vec{E} = -\vec{\nabla} \phi - \frac{\partial \vec{A}}{\partial t} \] (2.19)

Where, \( \vec{A} \) and \( \phi \) are the electro-magnetic potential and the electric potential, respectively. However, vector potentials were not measurable physical quantities at the time that Maxwell proposed and therefore the four formulas in Equations 2.14-2.17 have become the standard presentation. On the other hand, Ampere’s law (equation 2.17) has a fatal contradiction that a curling vector field does not diverge. In this case, the divergence of the static current is zero, but Ampere’s law does not give the correct result when a current is disconnected or changed such as occurs in a capacitor. Therefore, Maxwell has solved this charge accumulation issue at two surfaces of a capacitor by adding one part in equation 2.17, which is called the displacement current (the time derivation of the electric field).
\[
\vec{\nabla} \times \vec{B} = \mu_0 \vec{J} + \mu_0 \varepsilon_0 \frac{\partial \vec{E}}{\partial t}
\]

(2.20)

The interpretation of equation (2.20) is that a changing electric field can generate a magnetic field. Eventually, this interpretation was experimentally observed by Hertz.\(^{34}\)

**Figure 2.2** The electrical circuit with capacitor that the current in the circuit is disconnected.

We can introduce the electromagnetic waves derived from Maxwell equations in vacuum. Where we assume that there are no electric currents or charges, Maxwell equations are given as:

\[
\vec{\nabla} \cdot \vec{E} = 0
\]

(2.21)

\[
\vec{\nabla} \times \vec{B} = 0
\]

(2.22)

\[
\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}
\]

(2.23)

\[
\vec{\nabla} \times \vec{B} = \mu_0 \varepsilon_0 \frac{\partial \vec{E}}{\partial t}
\]

(2.24)

By using equation (2.21) and (2.22) and we multiply \(\vec{\nabla} \times\) to equation (2.23) and (2.24), we can obtain:
\[ \nabla^2 E = \mu_0 \varepsilon_0 \frac{\partial^2 E}{\partial t^2} \]  
(2.25)

\[ \nabla^2 B = \mu_0 \varepsilon_0 \frac{\partial^2 B}{\partial t^2} \]  
(2.26)

These two independent time and space second derivative equations, which are the equations of traveling wave, are called wave equations.
2.1.3.2 Maxwell’s equations in a dielectric medium

In the previous section, Maxwell’s equations in a vacuum (differential forms) were introduce and the use of these equations to generate a wave equation was discussed. In this section we will further consider the application of Maxwell’s equations in matter. In order to describe the equations properly in matter, all charge distributions should be reflected. Moreover, free electrons or bound charges in matter will be re-distributed due to the applied and magnetic fields. Bound charges and free electrons in matter are spontaneously re-distributed or re-oriented when an electric field or a magnetic field is applied to the material. Among those physical quantities in matter such as the electric polarization ($\vec{P}$), magnetic flux density ($\vec{M}$), the bound charge density ($\rho_b$), and the bound current density ($\vec{J}_b$), we can find two famous relations which are express as:

\[ \rho_b = -\nabla \cdot \vec{P} \]
\[ \vec{J}_b = \nabla \times \vec{M} \]

In substance, $\rho_b$ and $\vec{J}_b$ occur an electric field and a magnetic field as a charge density and a current density, respectively. In addition, they are linearly proportional to an electric field and a magnetic field.

\[ \vec{P} = \varepsilon_0 \chi_e \vec{E} \]
\[ \vec{M} \propto \vec{B} \]

(2.27)

In equation (2.27), $\vec{M}$ is just proportional to $\vec{B}$ since we con conventionally use $\vec{H}$ instead of $\vec{B}$. Finally, two displacement fields (electric and magnetic fields) can be introduced:
\[
\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}
\]
\[
\mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M}
\]

Therefore, we can re-rewrite Maxwell’s equations, for application inside a material
\[
\nabla \cdot \mathbf{D} = \rho_f
\]
\[
\nabla \cdot \mathbf{B} = 0
\]
\[
\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}
\]
\[
\nabla \times \mathbf{H} = \mathbf{j}_f + \frac{\partial \mathbf{D}}{\partial t}
\]

Where \(\rho_f\) and \(\mathbf{j}_f\) are the charge density and the current density, respectively. They should be distinguished from the bound charge density and the bound current density.

2.1.4 Electromagnetic waves

From Maxwell’s equations in medium, we can obtain a wave equation which is given by:
\[
\nabla \times (\nabla \times \mathbf{E}) = \nabla \times \left( \frac{\partial \mathbf{B}}{\partial t} \right) = -\frac{\partial}{\partial t} (\nabla \times \mathbf{B})
\]

\[
-\nabla^2 \mathbf{E} + \nabla (\nabla \cdot \mathbf{E}) = -\frac{\partial}{\partial t} (\mu \mathbf{j}_f + \varepsilon \mu \frac{\partial^2 \mathbf{E}}{\partial t^2})
\]

\[
-\nabla^2 \mathbf{E} + \nabla \left( \frac{\rho_f}{\varepsilon} \right) = -\mu \frac{\partial \mathbf{j}_f}{\partial t} - \varepsilon \mu \frac{\partial^2 \mathbf{E}}{\partial t^2}
\]

\[
\therefore \nabla^2 \mathbf{E} - \varepsilon \mu \frac{\partial^2 \mathbf{E}}{\partial t^2} - \sigma \mu \frac{\partial \mathbf{E}}{\partial t} = \nabla \left( \frac{\rho_f}{\varepsilon} \right)
\]
The name of equation (2.31) is the inhomogeneous wave equation about the electric field.

For the case of vacuum, \( \rho_f = 0, \vec{J}_f = 0, \varepsilon = \varepsilon_0, \) and \( \mu = \mu_0; \)

\[
\therefore \nabla^2 \vec{E} - \varepsilon_0 \mu_0 \frac{\partial^2 \vec{E}}{\partial t^2} = 0
\]

The equation is so-called “homogeneous wave equation”. This equation was derived at the end of Section 2.1.3.1 (equation 2.25) above. One of the possible solutions is

\[
\vec{E} = E_0 e^{i(\vec{k} \cdot \vec{x} - \omega t)}
\]

which represents a plane wave travelling in the direction of the wave vector \( \vec{k} \) with frequency \( \omega \). When we substitute this plane wave obeys the homogeneous wave equation, one famous relation can be obtained to find the velocity of the electromagnetic wave:

\[
\frac{\omega}{k} = \frac{1}{\sqrt{\mu_0 \varepsilon_0}}
\]

Where \( \frac{\omega}{k} = \nu \) is called the dispersion relation. The speed of electromagnetic wave traveling is given by the group velocity. In particular, the speed of electromagnetic waves in a vacuum is

\[
c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}} = 2.997 \times 10^8 \text{ m/s}
\]

Thus, Maxwell’s equations predict that electromagnetic radiation has oscillating electric and magnetic fields that propagate at a speed of light in vacuum. There is an attenuation of this speed when an electromagnetic wave propagates in a dielectric medium.
2.1.5 The Fresnel equations

The Fresnel equations are derived at the boundary of two materials to describe the propagation of electromagnetic waves across the interface. When the two surfaces are both insulators the incident waves from one medium to another have both reflected and refracted waves at the boundary of the two media (see Figure 2.1). The light moves from a medium 1 with refractive index \( n_1 \) to a second medium 2 given the refractive index \( n_2 \). The Fresnel equations predict the ratio of the refracted and reflected light relative to the incident light based on Maxwell’s equations with appropriate boundary conditions. The assumptions for the Fresnel equations are that the both media are flat and homogeneous. As an incident light a plane wave is assumed and distinguished \( p \)- and \( s \)-polarized light. To find the reflection and transmission coefficients with the polarized lights, we chose TM waves to calculate (in Figure 2.1 (b)). Dispersion relation is essential if there is to be a wave propagating in the medium.

First, we examine the details with the \( p \)-polarized waves (TM mode) in two layers.

Note that we are using the definition of the \textbf{positive H-field} direction in Figure 2.1 (b)

I. Define magnetic field:

\[
\vec{H}_i = H_i \hat{y} \exp\{i(k_i \cdot r - \omega t)\} \\
\vec{H}_r = H_r \hat{y} \exp\{i(k_r \cdot r - \omega t)\} \\
\vec{H}_t = H_t \hat{y} \exp\{i(k_t \cdot r - \omega t)\}
\]  

(2.32)

II. Define wave vector:

\[
\vec{k}_i = -\hat{x}k_1 \sin \theta_1 + \hat{z}k_1 \cos \theta_1
\]
\[ \vec{k}_r = -\hat{x}k_1\sin\theta_1 - \hat{z}k_1\cos\theta_1 \quad (2.33) \]

Under the phase matching condition at the interface between medium 1 and 2, (see Figure 2.1 (b))

\[ \vec{k}_t = -\hat{x}k_1\sin\theta_1 + \hat{z}k_{2z} \quad (2.34) \]

On the other hand, the phase matching condition is shown in the following equation. This condition holds at the point where the incident, reflected, and refracted waves meet:

\[ (\vec{k}_t \cdot \vec{r} - \omega_i t) = (\vec{k}_r \cdot \vec{r} - \omega_r t) = (\vec{k}_t \cdot \vec{r} - \omega_t t) \quad (2.35) \]

\[ (\omega_i = \omega_r = \omega_t) \]

III. If the tangential fields must be continuous across the boundary then the phase factors must be equal across the interface:

\[ \frac{c^2}{\omega^2} (k_x^2 + k_z^2) = \varepsilon \quad (2.36) \]

From equation (2.36),

\[ \varepsilon_1 = \frac{c^2}{\omega^2} k_1^2 = |\varepsilon_1|e^{i\phi_1} \quad (2.37) \]

Then, from equations (2.37), the relevant angle is 0 to 180 degrees,

\[ \therefore k_1 = \frac{\omega}{c} \sqrt{\varepsilon_1} \quad (2.38) \]

After taking the square root in equation (2.38), the angle range should be 0 to 90 degrees.

Again, from equation (2.36), the second layer is assumed to be in air
\[ \varepsilon_2 = \frac{c^2}{\omega^2} (k_1^2 \sin^2 \theta_1 + k_{2z}^2) , \text{and } \varepsilon_2 = 1 \]  
(2.39)

\[ \therefore k_{2z} = \frac{\omega}{c} \sqrt{1 - \varepsilon_1 \sin^2 \theta_1} \]  
(2.40)

Using Ampère law (the equation 2.41), get the electric fields from the equations of (2.32) and (2.33).

\[ \nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{J} + \frac{1}{c} \frac{\partial D}{\partial t} \text{, and } D = \varepsilon E \]  
(2.41)

The Ampère law (2.41) is expressed into different form which is below:

\[ \mathbf{k} \times \mathbf{H} = -\frac{\omega\varepsilon}{c} \mathbf{E} \]

\[ \therefore \mathbf{E} = -\frac{c}{\omega\varepsilon} \mathbf{k} \times \mathbf{H} \]  
(2.42)

Then, put (2.32) and (2.33) equations into equation (2.42)

\[ \mathbf{E}_i = (\hat{x} \cos \theta_1 + \hat{z} \sin \theta_1) \frac{ck_1}{\omega \varepsilon_1} H_i e^{ik_1(x)x} \]

\[ \mathbf{E}_r = (-\hat{x} \cos \theta_1 + \hat{z} \sin \theta_1) \frac{ck_1}{\omega \varepsilon_1} H_r e^{ik_1(x)x} \]

\[ \mathbf{E}_t = (\hat{x} k_{2z} + \hat{z} k_1 \sin \theta_1) \frac{c}{\omega \varepsilon_2} H_t e^{ik_{2z}(x)x} \]  
(2.43)

Where in the equation (2.35), \( \mathbf{k}_i \cdot \mathbf{r} = k_{1(x)}x + k_{1(y)}y + k_{1(z)}z \)

and because \( k_{1(y)} = 0 = z \), \[ \therefore \mathbf{k}_i \cdot \mathbf{r} = k_{1(x)}x \]
IV. Equating only the x-direction with equation (2.43).

This calculation is done along the boundary, \( z = 0 \) and \( t = 0 \).

\[
\frac{ck_1 \cos \theta_1}{\omega \varepsilon_1} (H_i - H_r) = \frac{ck_2}{\omega \varepsilon_2} (H_i - H_r) = \frac{ck_2}{\omega \varepsilon_2} H_t
\]

(2.44)

where \( k_1 \cos \theta_1 = k_{1z} \). Here, define the refractive index, \( n \) (it will be verified in the next section from the dispersion relation)

\[
\frac{ck_{1z}}{\omega} = n_{1z}, \text{ and } \frac{ck_{2z}}{\omega} = n_{2z}
\]

(2.45)

Put the equation (2.45) into the equation (2.44):

\[
\frac{n_{1z}}{\varepsilon_1} (H_i - H_r) = \frac{n_{2z}}{\varepsilon_2} H_t
\]

(2.46)

And initial assumption: \( H_i + H_r = H_t \)  

(2.47)

\[
\frac{H_i - H_r}{H_i + H_r} = \frac{\varepsilon_1 n_{2z}}{\varepsilon_2 n_{1z}}
\]

(2.48)

Define the reflection coefficient \( r \) and transmission coefficient, \( t \)

Then, rearrange the equation (2.47) and (2.48),

\[
\frac{H_r}{H_i} (= r) = \frac{\varepsilon_2 n_{1z} - \varepsilon_1 n_{2z}}{\varepsilon_2 n_{1z} + \varepsilon_1 n_{2z}}, \quad \frac{H_t}{H_i} (= t) = \frac{2 \varepsilon_2 n_{1z}}{\varepsilon_2 n_{1z} + \varepsilon_1 n_{2z}}
\]

(2.49)

V. Reflection and transmission coefficients

While \( r \) and \( t \) coefficients are ratios of electric field amplitudes, we define \( R \) and \( T \)
as the ratios of reflected and transmitted powers, respectively to the incident power in Figure 2.3.

\[ R \equiv \frac{P_r}{P_i} \quad \text{and} \quad T \equiv \frac{P_t}{P_i} \quad (2.50) \]

Then, according to Energy conservation, \( P_i = P_r + P_t \)

\[ \therefore 1 = R + T \quad (2.51) \]

To verify equation (2.49) by satisfying equation (2.50), use Poynting vector (= \( \vec{S} \)),

\[ \vec{S} = \frac{1}{\mu_0} \vec{E} \times \vec{B} = c^2 \varepsilon_0 \vec{E} \times \vec{B} \]

Where \( \vec{E} = E_0 \cos(\vec{k} \cdot \vec{r} - \omega t) \) and \( \vec{B} = B_0 \cos(\vec{k} \cdot \vec{r} - \omega t) \). Therefore,

\[ \vec{S} = \frac{1}{\mu_0} \vec{E}_0 \times \vec{B}_0 \cos^2(\vec{k} \cdot \vec{r} - \omega t) \quad (2.52) \]

Furthermore, the radiant flux density (=I [W/m^2]) is defined by the equation (2.52)

\[ I = < S >_T = \frac{c \varepsilon_0}{2} E_0^2 = \frac{c}{2 \mu_0} B_0^2 \quad (2.53) \]

Within a linear, homogeneous, isotropic dielectric, the equation (2.53) is becoming the following equation:

\[ I = < S >_T = \varepsilon \nu < E^2 >_T = \frac{\nu}{\mu} < B^2 >_T \quad (2.54) \]
Figure 2.3 Reflection and transmission of an incident beam [Reprinted with permission from Figure 4.47 in Ref. Hecht, Eugene (2002). Optics (4th ed.). Addison Wesley]

From equation (2.50) in Figure 2.2,

\[ R \left( \equiv \frac{P_r}{P_i} \right) = \frac{I_r}{I_i}, \quad \text{and} \quad T \left( \equiv \frac{P_t}{P_i} \right) = \frac{I_t}{I_i} \]

From equation (2.53) and (2.55),

\[ R = \frac{I_r}{I_i} = \frac{\nu r}{2 \mu r} B_{0r}^2 \cos \theta_r \left( \frac{H_{0r}^2}{H_{0i}^2} \right) \cdot \left( \frac{\mu_r}{\mu_i} \right) \]

\[ T = \frac{I_t}{I_i} = \frac{\nu t}{2 \mu t} B_{0i}^2 \cos \theta_i \left( \frac{C}{n_i} \right) \mu_i H_{0i}^2 \cos \theta_i \left( \frac{H_{0t}^2}{H_{0i}^2} \right) \]

Then,

\[ R + T = \left( \frac{H_{0r}^2}{H_{0i}^2} \right) \cdot \left( \frac{\mu_r}{\mu_i} \right) + \frac{n_i \mu t}{n_t \mu i} \cos \theta_t \left( \frac{H_{0t}^2}{H_{0i}^2} \right) \]

Put equation (2.49) into equation (2.56),
\[ R + T = \left( \frac{\varepsilon_i n_{iz} - \varepsilon_i n_{tz}}{\varepsilon_i n_{iz} + \varepsilon_i n_{tz}} \right)^2 \left( \frac{\mu_r}{\mu_i} + \frac{n_i \mu_t \cos \theta_t}{n_t \mu_i \cos \theta_i} \left( \frac{2 \varepsilon_i n_{iz}}{\varepsilon_i n_{iz} + \varepsilon_i n_{tz}} \right)^2 \right) \]

\[ = \left( \frac{\varepsilon_i n_i \cos \theta_i - \varepsilon_i n_t \cos \theta_t}{\varepsilon_i n_i \cos \theta_i + \varepsilon_i n_t \cos \theta_t} \right)^2 \frac{\mu_r}{\mu_i} + \frac{n_i \mu_t \cos \theta_t}{n_t \mu_i \cos \theta_i} \left( \frac{2 \varepsilon_i n_i \cos \theta_i}{\varepsilon_i n_i \cos \theta_i + \varepsilon_i n_t \cos \theta_t} \right)^2 \]

\[ = \frac{\mu_r}{\mu_i} \left( \frac{\varepsilon_i n_i \cos \theta_i - \varepsilon_i n_t \cos \theta_t}{\varepsilon_i n_i \cos \theta_i + \varepsilon_i n_t \cos \theta_t} \right)^2 + \frac{n_i \mu_t \cos \theta_t}{n_t \mu_i \cos \theta_i} \left( \frac{2 \varepsilon_i n_i \cos \theta_i}{\varepsilon_i n_i \cos \theta_i + \varepsilon_i n_t \cos \theta_t} \right)^2 \]

(2.57)

In the second part in equation (2.57),

\[ \frac{n_i \mu_t \cos \theta_t}{n_t \mu_r \cos \theta_i} \left( \frac{2 \varepsilon_i n_i \cos \theta_i}{\varepsilon_i n_i \cos \theta_i + \varepsilon_i n_t \cos \theta_t} \right)^2 \]

\[ = \frac{n_i \mu_t \cos \theta_t}{n_t \mu_r} \frac{4 \varepsilon_i^2 n_i^2 \cos \theta_i}{(\varepsilon_i n_i \cos \theta_i + \varepsilon_i n_t \cos \theta_t)^2} \]

\[ = \frac{n_i^2 \mu_t \varepsilon_i}{n_t^2 \mu_r \varepsilon_i} \frac{4 \varepsilon_i \varepsilon_i n_i n_t \cos \theta_i \cos \theta_t}{(\varepsilon_i n_i \cos \theta_i + \varepsilon_i n_t \cos \theta_t)^2} \]

\[ = \frac{4 \varepsilon_i \varepsilon_i n_i n_t \cos \theta_i \cos \theta_t}{(\varepsilon_i n_i \cos \theta_i + \varepsilon_i n_t \cos \theta_t)^2} \]

(2.58)

This is because

\[ \mu_r = \mu_i, \quad \text{and} \quad \mu_t \varepsilon_t = \frac{1}{v_t} = \frac{n_i^2}{c^2}, \quad \mu_i \varepsilon_i = \frac{1}{v_i} = \frac{n_i^2}{c^2}, \]

We put the equation (2.58) into (2.57) then, equation (2.57) is expressed by the following equation,

\[ \therefore R + T = \frac{\mu_r}{\mu_i} \left[ \left( \frac{\varepsilon_i n_i \cos \theta_i - \varepsilon_i n_t \cos \theta_t}{\varepsilon_i n_i \cos \theta_i + \varepsilon_i n_t \cos \theta_t} \right)^2 + \frac{4 \varepsilon_i \varepsilon_i n_i n_t \cos \theta_i \cos \theta_t}{(\varepsilon_i n_i \cos \theta_i + \varepsilon_i n_t \cos \theta_t)^2} \right] \]

\[ = 1 \]
Therefore, the equation (2.17) satisfies equation (2.19). Summarizing, the coefficients for reflection and transmission are found with TM wave (= p-polarized wave):

\[
\frac{H_r}{H_i} (= r_p) = \frac{\varepsilon_2 n_{1z} - \varepsilon_1 n_{2z}}{\varepsilon_2 n_{1z} + \varepsilon_1 n_{2z}}, \quad \frac{H_t}{H_i} (= t_p) = \frac{2 \varepsilon_2 n_{1z}}{\varepsilon_2 n_{1z} + \varepsilon_1 n_{2z}}
\] (2.17)

Then, the coefficient with TE wave (= s-polarized wave) will be:

\[
\frac{H_r}{H_i} (= r_s) = \frac{\varepsilon_1 n_{1z} - \varepsilon_2 n_{2z}}{\varepsilon_1 n_{1z} + \varepsilon_2 n_{2z}}, \quad \frac{H_t}{H_i} (= t_s) = \frac{2 \varepsilon_1 n_{1z}}{\varepsilon_1 n_{1z} + \varepsilon_2 n_{2z}}
\] (2.59)

From the coefficients in equation (2.17) and (2.59), the probabilities are shown by the square of these equations.

\[
R_p \equiv r_p^2 = \left(\frac{\varepsilon_2 n_{1z} - \varepsilon_1 n_{2z}}{\varepsilon_2 n_{1z} + \varepsilon_1 n_{2z}}\right)^2, \quad T_p \equiv t_p^2 = \left(\frac{2 \varepsilon_2 n_{1z}}{\varepsilon_2 n_{1z} + \varepsilon_1 n_{2z}}\right)^2
\]

\[
R_s \equiv r_s^2 = \left(\frac{\varepsilon_1 n_{1z} - \varepsilon_2 n_{2z}}{\varepsilon_1 n_{1z} + \varepsilon_2 n_{2z}}\right)^2, \quad T_s \equiv t_s^2 = \left(\frac{2 \varepsilon_1 n_{1z}}{\varepsilon_1 n_{1z} + \varepsilon_2 n_{2z}}\right)^2
\] (2.60)

The reflectance and transmittance of equation (2.60) are drawn in Figure 2.4. In the graph of Figure 2.4, the index of refraction, \(n_1\) and \(n_2\) are 1, and 1.5, respectively.
Assume an unpolarized EM wave is incident on the surface between two media which are transparent, and if the incident angle is equal to the specific incident angle, the reflected light will become plane polarized light. The specific angle that produces this result is called Brewster’s angle in Figure 2.4. Since the incident and reflected angles are the same, the sum of incident (or refracted) angle and transmitted angle is 90°.

\[ \theta_i + \theta_t = 90^\circ \]

Using Snell’s law with the Brewster’s angle (\( \theta_i = \theta_B \)),

\[ n_1 \sin \theta_B = n_2 \sin (90 - \theta_B) = n_2 \cos \theta_B \]

Then, from equation (2.61), the Brewster’s angle is following.

\[ \theta_B = \arctan \left( \frac{n_2}{n_1} \right) \]
Again when the light goes from the first medium with the smaller refractive index \((n_1 > n_2)\) to the from the second medium with larger refractive index than the first one, from Snell’s law,

\[
sin\theta_i = \frac{n_2}{n_1} \sin \theta_t
\]  

(2.62)

To find critical angle \((\equiv \theta_c)\) that is defined when \(\theta_t = 90^\circ\) in equation (2.62). Then,

\[
\theta_c = \theta_i = \arcsin \left( \frac{n_2}{n_1} \right)
\]  

(2.63)

From the equation (2.63), when the incident angle is larger than the critical angle, the every incident lights are reflected into the first medium (no transmitted light) and it is called total internal reflection (TIR). When TIR occurs, even though there is no transmitted light from the original medium, some of the light can penetrate into the second medium as a damped or evanescent wave. In the case where both dielectric media 1 and 2 are insulators the evanescent wave decays exponentially across the boundary in medium 2 (also labeled t for transmitted).

As a matter if convenience, assume that a plane wave is in \(xz\) plane in Figure 2.1. The wavevector will be

\[
\vec{k}_t = k_t \sin \theta_t \hat{x} + k_t \cos \theta_t \hat{z}.
\]  

(2.64)

In addition, since \(n_1 > n_2\), from equation (2.62)

\[
sin \theta_t = \frac{n_1}{n_2} \sin \theta_1 > 1
\]  

(2.65)

On the other hand,

\[
\cos \theta_t = \sqrt{1 - \sin^2 \theta_t} = i\sqrt{\sin^2 \theta_t - 1}
\]  

(2.66)
According to the assumption with the equations of (2.64), (2.65), and (2.66)

\[
\bar{E}_t = E_0 \exp\{i(k \cdot \vec{r} - \omega t)\}
\]

\[
= E_0 \exp\{i(xk_t \sin \theta_t + zk_t \cos \theta_t - \omega t)\}
\]

\[
= E_0 \exp\{i \left( xk_t \sin \theta_t + zk_t i \sqrt{\sin^2 \theta_t - 1} - \omega t \right)\}
\]

\[
= E_0 \exp(-\kappa z) \exp\{i(kx - \omega t)\}
\]

(2.67)

where

\[
\kappa = \frac{\omega}{c} \sqrt{(n_1^2 \sin^2 \theta_i) - n_2^2} = k_2 \sqrt{\sin^2 \theta_i - \left(\frac{n_2}{n_1}\right)^2}
\]

and

\[
k = \frac{n_1 \omega}{c} \sin \theta_i = k_1 \sin \theta_i
\]

According to equation (2.67), the evanescent wave propagates along x-direction and attenuates exponentially in both z-directions.

2.1.6 Bulk polaritons in the Drude model

Paul Drude proposed a model to explain conduction of electrons in metals. In the Drude model, electrons in a solid move like the ball in a pinball machine following the Newton’s law in equation (2.12) and (2.13). While the pinball field is due to gravity electrons move in response to an electric field. From the Maxwell’s equation and equation (2.13),

\[
\nabla \times \vec{H} = J + i\omega \vec{D}
\]

The right side of the above equation is also expressed by
\[ J + i \omega \varepsilon E = i \omega \varepsilon_{eff}E, \quad \text{and} \quad \vec{J} = \sigma \vec{E} \]

Therefore,

\[ \varepsilon_{eff} = \varepsilon + \frac{\sigma_0}{i \omega} \frac{1}{1 + i \omega \tau} \quad (2.68) \]

In the low frequency limit, equation (2.68) becomes

\[ \varepsilon_{eff} = \varepsilon - i \frac{\sigma_0}{\omega} \]

In the high-frequency limit, calling \( \varepsilon = \varepsilon_\infty \)

\[ \varepsilon_{eff} = \varepsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2}\right) \quad (2.69) \]

Here,

\[ \omega_p^2 = \frac{Ne^2}{\varepsilon_0 m} \quad (2.70) \]

For a metal, \( \hbar \omega_p \) (bulk plasma frequency) is circa 10 eV (~ 80,655 cm\(^{-1}\) or ~ 0.124 μm).

Equation (2.69) is the dielectric constant of ideal plasma. In addition, the definition of \( \varepsilon_r \) is
able to apply into equation (2.69).

\[ \varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2} \quad (2.71) \]

Again, in the low-frequency limit or for lossy dielectric media we can write the expression
including a damping, \( \gamma_p \).

\[ \varepsilon_r = 1 - \frac{\omega_p^2}{\omega(\omega - i \gamma_p)} = \left\{ 1 - \frac{-\omega_p^2}{\omega^2 + \gamma_p^2} \right\} + i \left\{ \frac{\gamma_p \omega_p^2}{\omega(\omega^2 + \gamma_p^2)} \right\} \quad (2.72) \]
The damping constant, $\gamma_p$, is defined by the reciprocal of the collision time, $\tau$.

\[ \gamma_p = \frac{1}{\tau} \]

**Figure 2. 5** Real and imaginary parts of the dielectric constant of equation (2.72) based on the Drude (or called Drude-Sommerfeld) model for gold. For gold, the constants in equation (2.72) have the following values: $\omega_p = 13.8 \times 10^{15} \text{s}^{-1}$, $\gamma_p = 1.075 \times 10^{16} \text{s}^{-1}$.

The dispersion relation of equation (2.38) is combined with equation (2.71)

\[ k = \frac{\omega}{c} \sqrt{\varepsilon} = \frac{\omega}{c} \sqrt{1 - \frac{\omega_p^2}{\omega^2}} = k_0 \sqrt{1 - \frac{\omega_p^2}{\omega^2}} \]

(2.73)

Equation (2.73) is called the dispersion relation of bulk plasmon polaritons shown in the Figure 2.6 as function of $k/k_p$ with the definition of $k_p = \omega_p/c$. The electromagnetic (EM) wave in vacuum is also plotted as light line ($k = \omega/c$), the dispersion of plasmons has a constant as $\omega_p$. 

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2.1.7 Surface plasmons with TM polarized waves

We can derive Fresnel equations for the propagation of radiation across boundaries that consist of a conductor and an insulator.
Figure 2.7 (a) Schematic of electromagnetic field distribution at the metal and dielectric interface in surface plasmon polariton mode, (b) The electromagnetic field intensities are exponentially decay on the distance away in the both ways from the interface

Surface plasmons (SPs) are collective excitations of the free electrons in a thin metal layer at the interface between two materials which have opposite signs for the real part of the dielectric functions such as a metal and dielectric interface. SPs are excited by a specific polarization (TM wave with a specific frequency depending on the material) resulting in a surface plasmon polaritons (SPPs) shown in Figure 2.7 (a). SPs propagate in a longitudinally along the interface and decay exponentially normal to the interface (in Figure 2.7 (b)). From Figure 2.7 (a), the electric and magnetic fields with TM waves are expressed by

\[
\begin{align*}
  z > 0 & \quad \left\{ \begin{array}{l}
     \vec{H}_m = H_m \hat{y} \exp\{i(k_m \cdot r - \omega t)\} \\
     \vec{E}_m = E_m (\hat{x} + \hat{z}) \exp\{i(k_m \cdot r - \omega t)\}
     \end{array} \right.
  \\
  z < 0 & \quad \left\{ \begin{array}{l}
     \vec{H}_d = H_d \hat{y} \exp\{i(k_d \cdot r - \omega t)\} \text{ at } z < 0 \\
     \vec{E}_d = E_d (\hat{x} + \hat{z}) \exp\{i(k_d \cdot r - \omega t)\}
     \end{array} \right.
\]

(2.74)
And the equations of (2.74) are satisfied Maxwell’s equations (Chap 2.1.3). From Maxwell’s equations (with no current density, \( J_f = 0 \))

\[
\nabla \times \vec{H} = \epsilon \frac{\partial \vec{E}}{\partial t}
\]

and inserted into equation (2.74), then

\[
\begin{align*}
    k_m z H_m y &= \omega \varepsilon_m E_m x \\
    k_d z H_d y &= \omega \varepsilon_d E_d x
\end{align*}
\]

(2.75)

On the other hand, the boundary conditions in Figure 2.7 are the below,

\[
\begin{align*}
    E_{m x} &= E_{d x} \text{ for } E_\parallel \text{ continuity} \\
    H_{m y} &= H_{d y} \text{ for } H_\parallel \text{ continuity}
\end{align*}
\]

(2.76)

When we combine equations (2.75) and (2.76) we obtain

\[
\frac{k_m z}{\varepsilon_m} = \frac{k_d z}{\varepsilon_d}
\]

(2.77)

Equation (2.77) is the condition for the existence of surface plasmons. Meanwhile, the continuities of \( E_\parallel \) and \( H_\parallel \) make a relation of \( k_x \):

\[
k_m x = k_d x
\]

(2.78)

Then, from equation (2.38)

\[
k^2 = \varepsilon_i \left( \frac{\omega}{c} \right)^2 = k_x^2 + k_\parallel^2
\]

(2.79)
where $k_x \equiv k_{mx} = k_{dx}$ and $i$ means the metal and the dielectric in $\varepsilon_i$ and $k_{iz}$. Therefore, equation (2.79) gives us the condition to exist for SPs at the interface between a metal and a dielectric;

$$k_x = k_{SP} = \sqrt{\varepsilon_i \left( \frac{\omega}{c} \right)^2 - k_{iz}^2}$$

(2.80)

After putting equation (2.77) into (2.80), we are able to have the following equation (2.81) called the dispersion relation for SPP.

$$k_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$

(2.81)

Since we know $\varepsilon_m = \varepsilon'_m + i\varepsilon''_m$, equation (2.81) is also expressed by

$$k_x = k'_x + i k''_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$

(2.82)

About z-direction of equation (2.80), combine (2.82)

$$k_{iz}^2 = \varepsilon_i \left( \frac{\omega}{c} \right)^2 - \left( \frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d} \right) \left( \frac{\omega}{c} \right)^2$$

$$k_{iz} \equiv k'_{iz} + i k''_{iz} = \pm \frac{\omega}{c} \sqrt{\frac{\varepsilon_i^2}{\varepsilon_m + \varepsilon_d}}$$

(2.83)
2.1.8 The Airy Equation

The Airy equation provides an analytical description for the reflection and transmission coefficients in a homogeneous material that has a three layers structure. To compare and use Fresnel equations (Chap 2.1.2) the light will be $p$-polarized waves (TM mode) in three-layer.

![Diagram](image)

**Figure 2.8** Geometry of reflection and transmission of a TM wave on three layers with refraction index, $n_1$, $n_2$, and $n_3$, respectively.

For calculations in greater than three layers we cannot use an analytical formula, but rather we need to resort to numerical evaluation of transfer matrices for each later. The three layer equation is useful since the common optical configuration for driving a SPP, known as the Kretschmann configuration, is a three layer geometry. Note that definition of the **positive H-field** direction

I. Define wave vector based on the assumption of the Fresnel equations.

\[
\vec{k}_i = -\hat{x} k_1 \sin \theta_1 + \hat{z} k_1 \cos \theta_1
\]

\[
\vec{k}_r = -\hat{x} k_1 \sin \theta_1 - \hat{z} k_1 \cos \theta_1
\]
Under the phase matching condition at the interface

\[
\vec{k}_{t1} = -\hat{x}k_1 \sin \theta_1 + \hat{z}k_{t1(z)}
\]

\[
\vec{k}_b = -\hat{x}k_1 \sin \theta_1 - \hat{z}k_{b(z)}
\]

II. Define magnetic field

\[
\vec{H}_i = H_i \hat{y} \exp \{i(k_i \cdot r - \omega t)\}
\]

\[
\vec{H}_r = H_r \hat{y} \exp \{i(k_r \cdot r - \omega t)\}
\]

\[
\vec{H}_t = H_t \hat{y} \exp \{i(k_t \cdot r - \omega t)\}
\]

\[
\vec{H}_b = H_b \hat{y} \exp \{i(k_b \cdot r - \omega t)\}
\]

(2.86)

At \(z=0\) and \(t=0\),

\[
\vec{H}_i = H_i \hat{y} e^{ik_i(x)} ; \quad \vec{H}_r = H_r \hat{y} e^{ik_r(x)} ;
\]

\[
\vec{H}_t = H_t \hat{y} e^{ik_t(x)} ; \quad \vec{H}_b = H_b \hat{y} e^{ik_b(x)}
\]

(2.87)

III. Obtain the electric field from Ampere’s law

\[
\vec{E} = -\frac{c}{\omega \varepsilon} \vec{k} \times \vec{H}
\]

\[
\vec{E}_i = (\hat{x} \cos \theta_1 + \hat{z} \sin \theta_1) \frac{ck_1}{\omega \varepsilon_1} H_i e^{ik_i(x)}
\]

\[
\vec{E}_r = (-\hat{x} \cos \theta_1 + \hat{z} \sin \theta_1) \frac{ck_1}{\omega \varepsilon_1} H_r e^{ik_r(x)}
\]
\[ \overrightarrow{E_{t1}} = (\hat{x}k_{t1(z)} + \hat{z}k_1 \sin \theta_1) \frac{c}{\omega \varepsilon_2} H_{t1} e^{ik_{t1(x)}x} \]

\[ \overrightarrow{E_b} = (-\hat{x} k_{b(z)} + \hat{z} \sin \theta_1) \frac{c k_1}{\omega \varepsilon_2} H_b e^{ik_{b(x)}x} \]

(2.88)

Here \( \overrightarrow{k_1} \cdot \vec{r} = k_1(x)x + k_1(y)y + k_1(z)z \), and \( k_1(y) = z = 0 \).

Therefore \( \overrightarrow{k_1} \cdot \vec{r} = k_1(x)x \)

V. Equating only the x-direction

(since that is along the boundary, \( z=0 \) and \( t=0 \))

\[ \frac{ck_1 \cos \theta_1}{\omega \varepsilon_1} (H_t - H_r) e^{ik_{i(x)}x} = \frac{c}{\omega \varepsilon_1} (H_{t1} k_{t1(z)} - H_b k_{b(z)}) e^{ik_{t1(x)}x} \]

\[ \therefore \frac{ck_1(z)}{\omega \varepsilon_1} (H_t - H_r) = \frac{c}{\omega \varepsilon_2} (H_{t1} k_{2(z)} - H_b k_{2(z)}) \]

\[ \therefore H_t - H_r = \frac{\varepsilon_1 n_{2(z)}}{\varepsilon_2 n_{1(z)}} (H_{t1} - H_b) \]

(2.89)

And initial assumption: \( H_i + H_r = H_{t1} + H_b \) \hspace{1cm} (2.90)

From (2.89) and (2.90)

\[ H_{t1} = \left( \frac{\varepsilon_1 n_{2(z)} + \varepsilon_2 n_{1(z)}}{2 \varepsilon_1 n_{2(z)}} \right) H_i + \left( \frac{\varepsilon_1 n_{2(z)} - \varepsilon_2 n_{1(z)}}{2 \varepsilon_1 n_{2(z)}} \right) H_r \]

\[ H_b = \left( \frac{\varepsilon_1 n_{2(z)} - \varepsilon_2 n_{1(z)}}{2 \varepsilon_1 n_{2(z)}} \right) H_i + \left( \frac{\varepsilon_1 n_{2(z)} + \varepsilon_2 n_{1(z)}}{2 \varepsilon_1 n_{2(z)}} \right) H_r \]
\[
\begin{align*}
\therefore \begin{pmatrix} H_{t1} \\ H_b \end{pmatrix} &= \begin{pmatrix} 2\varepsilon_1 n_2(z) \\ \varepsilon_1 n_2(z) - \varepsilon_2 n_1(z) \\ \varepsilon_1 n_2(z) - \varepsilon_2 n_1(z) \end{pmatrix} \begin{pmatrix} \varepsilon_1 n_2(z) - \varepsilon_2 n_1(z) \\ 2\varepsilon_1 n_2(z) \\ \varepsilon_1 n_2(z) + \varepsilon_2 n_1(z) \end{pmatrix} \begin{pmatrix} H_i \\ H_r \end{pmatrix} \\
&= \frac{\varepsilon_1 n_2(z) + \varepsilon_2 n_1(z)}{2\varepsilon_1 n_2(z)} \begin{pmatrix} 1 & -r_{12} \\ -r_{12} & 1 \end{pmatrix} \begin{pmatrix} H_i \\ H_r \end{pmatrix} \\
&= \frac{1}{t_{12}} \begin{pmatrix} 1 & -r_{12} \\ -r_{12} & 1 \end{pmatrix} \begin{pmatrix} H_i \\ H_r \end{pmatrix}
\end{align*}
\]

(2.91)

from two layer Fresnel equations, \( r_{12} \) and \( t_{12} \) are defined by
\[
\begin{align*}
\begin{aligned}
& 12 = \frac{\varepsilon_2 n_1(z) - \varepsilon_1 n_2(z)}{\varepsilon_1 n_2(z) + \varepsilon_2 n_1(z)}, \\
& t_{12} = \frac{2\varepsilon_1 n_2(z)}{\varepsilon_1 n_2(z) + \varepsilon_2 n_1(z)}
\end{aligned}
\end{align*}
\]

(2.92)

In Figure 2.8, on the interface between the second material \((n_2)\) and the third material \((n_3)\) \((xy\)-plane at \(z=d)\), \(H_{t1}\) and \(H_b\) become \(H'_{t1}\) and \(H'_b\), respectively after phasing shift of \(e^{ik_2(z)d}\) and \(e^{-ik_2(z)d}\) from \((xy\)-plane at \(z=0)\).

Therefore,
\[
\begin{align*}
\begin{pmatrix} H'_{t1} \\ H'_b \end{pmatrix} &= \frac{1}{t_{12}} \begin{pmatrix} e^{ik_2(z)d} & 0 \\ 0 & e^{-ik_2(z)d} \end{pmatrix} \begin{pmatrix} 1 & -r_{12} \\ -r_{12} & 1 \end{pmatrix} \begin{pmatrix} H_i \\ H_r \end{pmatrix} \\
\therefore \begin{pmatrix} H'_{t1} \\ H'_b \end{pmatrix} &= \frac{t_{12}}{t_{23}} \begin{pmatrix} 1 & -r_{23} \\ -r_{23} & 1 \end{pmatrix} \begin{pmatrix} e^{ik_2(z)d} & 0 \\ 0 & e^{-ik_2(z)d} \end{pmatrix} \begin{pmatrix} 1 & -r_{12} \\ -r_{12} & 1 \end{pmatrix} \begin{pmatrix} H_i \\ H_r \end{pmatrix}
\end{align*}
\]

(2.93)

From the equation (2.93)
\[
\begin{pmatrix} H_{t2} \\ 0 \end{pmatrix} = \frac{1}{t_{12} t_{23}} \begin{pmatrix} 1 & -r_{23} \\ -r_{23} & 1 \end{pmatrix} \begin{pmatrix} e^{ik_2(z)d} & 0 \\ 0 & e^{-ik_2(z)d} \end{pmatrix} \begin{pmatrix} 1 & -r_{12} \\ -r_{12} & 1 \end{pmatrix} \begin{pmatrix} H_i \\ H_r \end{pmatrix}
\]

\[
= \frac{1}{t_{12} t_{23}} \begin{pmatrix} e^{ik_2(z)d} & -r_{23} e^{ik_2(z)d} \\ -r_{23} e^{-ik_2(z)d} & e^{-ik_2(z)d} \end{pmatrix} \begin{pmatrix} 1 & -r_{12} \\ -r_{12} & 1 \end{pmatrix} \begin{pmatrix} H_i \\ H_r \end{pmatrix}
\]
\[
\begin{align*}
&= \frac{1}{t_{12} t_{23}} \left( \begin{array}{ccc}
e^{ik_2(x)d} + r_{12}r_{23}e^{ik_2(x)d} & -r_{12}e^{ik_2(x)d} - r_{23}e^{ik_2(x)d} & \frac{H_i}{H_r} \\
-r_{12}e^{ik_2(x)d} - r_{23}e^{ik_2(x)d} & r_{12}r_{23}e^{ik_2(x)d} + e^{ik_2(x)d} & \end{array} \right) \\
\therefore \frac{H_{t2}}{H_i} &= \frac{e^{-ik_2(x)d}}{t_{12} t_{23}} \left[ (e^{2ik_2(x)d} + r_{12}r_{23}) - (r_{12}e^{2ik_2(x)d} + r_{23}) \frac{H_r}{H_i} \right] 
\end{align*}
\]
\[ (2.94) \]
\[
\therefore 0 = \frac{e^{-ik_2(x)d}}{t_{12} t_{23}} \left[ -(r_{23}e^{2ik_2(x)d} + r_{12}) + (r_{12}r_{23}e^{2ik_2(x)d} + 1) \frac{H_r}{H_i} \right] 
\]
\[ (2.95) \]

from equation (2.95),

\[
\frac{H_r}{H_i} (\equiv R_{123}) = \frac{r_{23}e^{2ik_2(x)d} + r_{12}}{r_{12}r_{23}e^{2ik_2(x)d} + 1} 
\]
\[ (2.96) \]

To find \( T_{123} \), put the equation (2.96) into equation (2.94),

\[
\frac{H_{t2}}{H_i} (\equiv T_{123})
\]
\[
= \frac{e^{-ik_2(x)d}}{t_{12} t_{23}} \left[ (e^{2ik_2(x)d} + r_{12}r_{23}) - \frac{(r_{12}e^{2ik_2(x)d} + r_{23})(r_{23}e^{2ik_2(x)d} + r_{12})}{(r_{12}r_{23}e^{2ik_2(x)d} + 1)} \right] 
\]

After reduction to common denominator of a square bracket, equate the numerator.

Then,

\[
\therefore \frac{H_{t2}}{H_i} (\equiv T_{123}) = \frac{t_{12} t_{23}e^{ik_2(x)d}}{(r_{12}r_{23}e^{2ik_2(x)d} + 1)} 
\]
\[ (2.97) \]

2.2 Grating plasmon resonance and localized plasmon resonance
In 1902, Wood discovered that the optical spectrum of reflection gratings have unexpected narrow bright and dark bands.\textsuperscript{39, 40} Moreover, he reported that the bands had consistent differences that depended on the polarization of the incident light. In his report, only $p$-polarized light was able to make the bands which were called “anomalies” by Wood because the bands could not be explained through ordinary grating theory. Later, the anomalies were again studied with $p$-polarized light which is the incident light was parallel to the surface. On the other hand, with the $s$-polarization of incident light which is perpendicular to the surface of the EM waves, there were no anomalies in spectrum. In 1907, Rayleigh published two papers. In these papers, he suggested possible explanations\textsuperscript{41, 42}: a scattered light comes tangentially out to the grating at a wavelength that is corresponding to the passing-off of a higher order region in a spectrum. Therefore, his theory is related in the following grating formula:

$$\sin(\theta_n) = \sin(\theta) + \frac{n\lambda}{d}$$ \hspace{1cm} (2.98)

where $\theta$ is the incident angle, $\theta_n$ is the angle of diffraction at the $n_{th}$ order, $\lambda$ is the wavelength, $d$ is the groove period, and $n$ means $n_{th}$ order from the grating. Figure 2.9 shows the relation between the incident angles and the wavelength from equation (2.98) and (2.99).

$$\frac{n\lambda}{d} = -\sin(\theta) \pm 1, \hspace{1cm} n = \pm1, \pm2, \pm3 \ldots$$ \hspace{1cm} (2.99)
Figure 2.9 The spectra of Wood’s anomalies. The numbers on the top of the graph is the wavelength in nanometers divided by a factor of 10. The numbers on the left side mean the angles of incidence.\textsuperscript{39, 40} Reprinted by permission from Taylor & Francis Ltd: p. 397 in the Ref. 8.

2.3 Conducting metal oxide materials

Conventionally, the noble metals, Au and Ag, provided the most frequently used source for both SPR and LSPR because of their intense plasmon bands in the visible region of the electromagnetic spectrum.\textsuperscript{43} Au and Ag have the surface plasma frequencies at 2.5 eV and 3.9
eV, in the visible and near-UV spectrum, respectively. On the other hand, semiconductor films of conducting metal oxide (CMO) have transparency, chemical stability, and plasma frequencies in the mid-infrared (IR) spectral region. Recently, scientists have made various kinds of CMO films including indium tin Oxide (ITO) for SPR and several types of ITO nano-structure for LSPR. Since the carrier density of ITO is lower than that for noble metals, (\(10^{21}\) vs. \(10^{23}\) e\(^{-}/\text{cm}^{3}\), respectively) the plasma frequency for ITO is observed in the IR spectral region. Use of IR light has the potential for higher sensitivity for analyte detection increase because of the larger interaction volume accessible to the IR evanescent wave. ITO films can be also used by combining with silicon in several types of devices since silicon is transparent in the IR region. Moreover, the carrier density of ITO films can be controlled depending on the annealing conditions, so the plasma frequency of ITO is adjustable in IR spectrum. Another advantage of ITO thin films is that they provide new opportunities for adlayer surface chemistries. Because the material, local dielectric properties, shape, and size of nanoparticles play important roles for LSPR, most researchers have made nanoparticles by using lithographic fabrications to control the size or shape of their samples, or some of them made ITO nanostructure via chemical methods those are easier than the lithographic fabrication but they are usually sitting on the films in a random way.
CHAPTER 3 TECHNIQUES

3.1 Nanosphere lithography

To make micro- or nano- patterns or materials, there are two major approaches, called the “top-down” and the “bottom-up” methods. A top-down method refers to a way to scale down from films or bulk materials to the micron or nanometer length scale like someone carving a statue out of a big piece of rock. Lithographic tools such as electron beam, X-ray, photo- or ion beam-lithography as optical sources that can shave away the bulk material to produce specific patterns are top-down approaches. Lithography tools have been developed to permit patterning of a desired design onto a surface from submicron resolution to a few 100 microns depending on the usage of the optical lights as a source. However, the cost of the lithographic tools and the required clean room environment of the top-down method is high. The physical limit is also decided by the source of the optical light for lithographic tools. For example, one expects that sub-10 nm resolution is the limit for electron beam lithography in the ideal condition. On the other hand, the bottom-up method is started from simple structures, such as molecules or nanoparticles to complex structure. The method allows smaller geometries than a pattern from photolithography. In addition, the bottom up method is easier and more economical than top-down method. One example of this approach is self-assembly method to build regular arrays on a surface using covalent or noncovalent bonds without guidance from outside source. The bottom-up method is cheap and applying in a large area at one time. However, it is difficult to control matter to give the same regularity and repeatability that is possible with top down methods. Therefore, surface is liable to have a greater number
of defects using bottom up methods. In addition, positioning and shape control for nanostructures is not possible to the same extent as can be achieved with top down methods.

Nanosphere lithography (NSL) was introduced as a simple approach that has the potential to overcome these weaknesses of both top-down and bottom-up methods. NSL is an inexpensive technique that permits one to fabricate homogenous arrays with sub-microns or nano-size particles dispersed over a large area, and it has the both advantages of top-down and bottom-up methods. The method is implemented in steps: First, mask preparation using regular colloids and second, deposition of a functional material onto the mask. The first step consists of mask preparation and is related to self-assembly method in bottom-up approach. The second step involves deposition of a conductor, semi-conductor or other functional material onto the colloidal arrays, which is similar to lithography used in top down approaches. Therefore, in 1980’s, H. W. Deckman’s research group introduced the method as natural lithography. Later, The term was renamed by R.P. Van Duyne’s research group in the 1990’s into NSL and in the paper, they analyzed single layer (SL) and double layer (DL) experimentally and theoretically with Ag, Au, Cr, CaF₂, and CoPc colloidal (shown in Figure 3.1).
For the first step, which is mask preparation, one deposits a colloidal suspension onto a cleaned surface or one uses a spin-coater to spread the colloidal suspension uniformly over the surface. Upon drying the colloidal layer, the particles are formed with a hexagonal-close-packed (HCP) monolayer or double layer, spontaneously. The well packed arrays are used as a mask to deposit a desired material only onto the selected areas of the surface. After deposition, the removal of the mask uses the next procedure which is to remove the colloidal layer by sonication in an appropriate solvent. This procedure is called ‘lift-off’. Then, the pattern of a targeted material remains, on the regions of the surface, which were not covered with the mask (in Figure 3.2). The details of the experiments in our group will be presented below in section 3.1.2.
3.1.1 Preparation of a mask using colloidal spheres

Poly(methyl methacrylate) (PMMA) spheres which are approximately 1 μm in diameter were synthesized using a dispersion polymerization method with a poly(12-hydroxystearic acid) stabilizer. The PMMA spheres were dispersed in cyclohexane with a concentration of 12 wt% and the colloidal solution was spun cast onto a BK7 glass substrate at 1000 rpm for 60
seconds to produce regular PMMA layers. To find the optimized conditions, the concentration of PMMA colloid solution was used in 12 wt% and 14 wt%, and the rpm of the spin speed were conducted an experiments with 400, 500, 600, 800, 1000, 1200, and 1300 rpm. The PMMA spheres, then, are formed in a HCP layer in places during drying in Figure 3.3. In Figure 3.3, small HCP stacks of the PMMA spheres are formed in the whole surface but the dark blue areas (or lines) are the images of BK7 substrates in Scanning electron microscope (SEM), which means no PMMA spheres in the blue lines.

![Image](image.png)

**Figure 3.3** The microscope image of the spun PMMA spheres on a BK7 substrate. The PMMA spheres are stacked in places and the blue lines are images of a BK7 glass.

We did deposition of ITO on the formation of PMMA spheres in Figure 3.3, and then the results are shown in the SEM images of Figure 3.5. There are two different areas of ITO patterns: the first area is seen brighter than other area because remained ITOs after lift-off process are formed as lines or areas rather than regular patterns (In SEM images, ITO
materials look white while the BK7 substrate is observed as black). About the lift-off procedure, in our experiment PMMA spheres under ITO on the substrate were removed by sonicating in cyclohexane for 30 minutes after the ITO deposition. On the other hand, the other dark areas have regular triangle ITO patterns in Figure 3.5 (b). The ITO triangle patterns in the dark area are formed by the ITO deposition on the double layer of PMMA stacks. Therefore, double layers of HCP stacks of PMMA spheres are required in order to make regular patterns after deposition. To make double layer of PMMA spheres, the second spin is done with the same colloid solution at 1000 rpm for 30 seconds to deposit PMMA spheres in a double layer. The reason for a shorter time for the second application was not to disrupt the order of first layer by application of the cyclohexane of the second trial solution. The SEM image after the second spin is shown in Figure 3.4. The final result images with the double layer PMMA spheres will be shown in Figure 3.6.
Figure 3.4 SEM image of the PMMA spheres’ double layer. The double layers are made by twice spinning with the same colloid solution.

3.1.2 Deposition of Indium-Tin-Oxide (ITO) patterns

ITO was deposited through the bilayer template using room temperature RF sputtering from a 1 inch diameter ceramic target (Kurt J. Lesker, 10 wt % SnO2: 90 wt % In2O3). To deposit ITO thin films, argon was used as the sputter gas and the pressure used during sputtering was 6 mTorr. The distance between ITO target and the substrate was 6 cm and 20 W of 13.56 MHz RF power was used to maintain a plasma. As the first trial, ITO deposition with only a single spin of the PMMA colloid solution (in Figure 3.3) after the whole procedure is shown in Figure 3.5. As mentioned in chapter 3.1.1, the PMMA arrays from the spin-coating process are not a uniform mono-layer. Mono-layers and bilayers are mixed-, unevenly as shown in Figure 3.5.
Figure 3.5 (a) A SEM image of the deposition onto the one spinning of the PMMA colloid solution. (b) The enlarge SEM image of the white retangle in (a). The black areas of (a) and (b) are come from the deposition onto the double layer and the relatively white (bright) areas are from the deposition onto mono layer (in Figure 3.3). ITOs are shown the white and the BK7 of the substrate is shown as black images in SEM.

Therefore, the resulting image of the second trial, in which the surface layers were deposited by depositing the PMMA colloid solution, is shown in Figure 3.6. Even the double layer of PMMA colloids has imperfections. However, the surface ordering is sufficient to produce localized surface plasmon resonance (LSPR) signals from the patterns of ITO on the surface.
Figure 3.6 (a) A SEM image after the whole NSL process, which is chosen to deposit with ITO onto the twice spinning substrate of the PMMA colloid solution. (b) The enlarge SEM image of (a).

To make patterns with a thickness of ~ 20 nm (Figure 3.7 and Figure 3.8), we tried carried out the sputtering for 21 min 50 seconds and 65 minutes 30 seconds as shown in Figures 3.7 and 3.8, respectively. Both two trials made resulted in the same thickness because the double layer would permit the heights of ITO patterns to have approximately 20 nm thickness. The heights of the patterns from mono-layer are over 100 nm to around 150 nm thicknesses.
Figure 3.7 AFM images for height and surface measurements of ITO nanostructures made by the nanosphere lithography method.
3.1.3 Annealing of the patterns with Indium-Tin-Oxide (ITO)

Films of ITO nanostructure were annealed \emph{ex situ} at 500 °C for one hour in a 5 \% H₂/95 \% N₂ atmosphere which is called forming gas in order to produce optimally conducting films. Alternatively the thin ITO films were annealed in O₂ gas to make films that have low conductivity. These were used for comparison of optical signals in the work. The ITO materials we used are made up of 10 wt\% SnO₂ and 90 wt\% In₂O₃. The Tin (Sn) atoms in Indium (In) sites, i.e. Sn doping, creates defects and determines the conductivity of ITO thin films. According to standard Kröger-Vink notation, the defects from Sn doping are following the chemistry equations\textsuperscript{25}:

\[
2\text{SnO}_2 \ (\text{into In}_2\text{O}_3) \rightarrow [(2\text{Sn}^\bullet_{\text{In}})\text{O}^{\prime\prime}_0] + 2\text{O}^\xi \text{O} \ (\text{reaction 1})
\]

\[
[(2\text{Sn}^\bullet_{\text{In}})\text{O}^{\prime\prime}_0] \ (\text{with } (\Delta \text{reduction})) \rightarrow 2\text{Sn}^\bullet_{\text{In}} + 2e^- + \frac{1}{2}\text{O}_2(\text{g}) \uparrow \ (\text{reaction 2})
\]

From reaction 1, SnO₂ is doped into In₂O₃ sites by making neutral complexes, [(2Sn\text{In}^\bullet)O\text{O}^{\prime\prime}_0]. Then, the complex produces Sn ions, two electrons and oxygen gas by reduction, as shown in

\[\textbf{Figure 3.8} \text{ AFM image and height measurement of patterned ITO surfaces.}\]
reaction 2. Therefore, the oxygen partial pressure ($pO_2$) during ITO annealing process is a key factor that governs the release of electrons. The 5 % H$_2$/95 % N$_2$ atmosphere has a calculated $pO_2$ of $10^{-24}$ Torr, and that the $pO_2$ is the proper condition for a high carrier density of ITO material. On the other hand, the annealing of ITO in oxygen gas is an oxidation. Oxidation by annealing in the presence of O$_2$ (even a very small amount) results in the reverse of reaction 2.

3.2 Optical contact lithography

During the past few decades numerous lithographic technologies have been used to produce nanostructures on substrates. In the previous chapter, NSL was described as an example of one of the technologies. It has been shown elsewhere that it is possible to fabricate nano-particles for LSPR applications controlling the size or shape using annealing and other processing. However, photolithography is the most powerful, widespread, and generally used technique for fabrication of micro- or nano-size structures. Two types of photolithography are divided according to how the UV patterning is achieved. The first type of photolithography that we used is called optical contact lithography. In this type, the photomask is directly in contact with a photoresist (PR) layer on a substrate to be exposed to UV light. Similarly, in proximity lithography, a PR layer is exposed to UV light through a photomask held at a distance of 3 to 50 μm. Optical contact (or proximity) lithography is able to make micro- or nano-size structures with 1:1 ratio compared to the features on the photo-mask. More details about optical contact lithography will be in the next chapter. The other type of photolithography is called optical projection photolithography, which uses an optical
projection system to de-magnify the features in the photo-mask onto a PR layer on a substrate to make small patterns of submicron sizes. Therefore, optical projection photolithography has few tens of nanometers in resolution which is higher resolution than the resolution of optical contact or proximity lithography. In addition, because there is no direct contact between a PR and a photo-mask when a de-magnification system is used, the optical projection photolithography does not give any damages to the PR layer. This type of photolithography is able to make desired structures onto a small portion of a substrate. In the research reported in this dissertation, optical contact lithography was used to fabricate nanostructures. There are two types of optical lithography. The type of optical lithography depends on the type of photoresist. These are known as positive and negative photoresist. The detail process will be discussed in the following.

3.2.1 Positive optical contact lithography (Lift-off method)

The positive photoresist is removed from a patterned area exposed to UV light. This removal is possible due to exposure of the surface region to UV light makes the chemical structure of the PR more soluble in the developer solution. In particular, the exposed wafer with positive PR to UV light is developed in a dipping bath to remove the more soluble PR area in the wafer. The solution in the dipping bath is called the developer solution and the process is named development or developing. Sodium hydroxide was originally used as a developer solution, but contamination by sodium ions led to degradation of insulators used in the semi-conducting process. Therefore, tetramethylammonium hydroxide (TMAH) is used due to the fact that it is free of metal ions. The mask has the exact same structures as the
patterns to be washed away by the developer solution after exposure. The process with positive PR is also called lift-off method. The details of the process are shown in Figure 3.9. In the first step, the substrates are cleaned chemically to eliminate organic, ionic, or metallic impurities on the surface. Oxide surfaces such as SiO$_2$ or Al$_2$O$_3$ usually are too hydrophilic for resist adhesion because of the surface OH bonds. Thus, these surfaces are treated by hexamethyldisilazane (HMDS) to promote chemical adhesion and increase hydrophobicity by removing OH bonds on the surfaces. The next step is to spread positive PR on the surface of the substrate via high-speed centrifugal spin coating. The third step is known as the prebake, which is also called soft-baking (the third step in Figure 3.9). Soft-baking is the step used for evaporation of the solvents used during PR coating. The solvents are driven off the surface by heating on a hot plate at 80 to 90° for 1 minute or in a convection oven at 90 to 110° for 20 minutes. The next step consists of mask align and exposure. The photomask is aligned with the substrate and the PR is exposed through the patterns on the mask with UV light. After that, the substrate is soaked into a development solution, and then the PR of the exposed area is removed. The deposition is the next step after development with the desired material which is ITO in our experiments. The desired material for the film deposition is sitting on the whole surface. In the Figure 3.9, see the part in the thin film deposition, and then the desired materials are placed on the PR and on the substrate depending on the patterns after development. Then, the last step is lift-off in which the substrate is soaking into a specific solvent at ultrasonic bath called ultrasonic immersion. Since the method makes the temperature of the solvent increase due to the molecular vibration in the solvent, the temperature should be monitored carefully not to go over to around 60 to 70°. Usually, lift-off
is not able to remove the PR completely, thus plasma ash with O₂ gas is done repeatly. This is known as called strip resist. (Shown in Figure 3.9)

![Positive process (Lift-off)]

3.2.2 Negative optical contact lithography (Etching method)

The negative PR is distinct from positive PR in that the chemical bonds of the negative photoresist are strengthened by the exposure to the UV light in negative PR. Therefore, only
the exposed PR remains on the surface after development and the unexposed region is dissolved during development. For the negative process, deposition with the desired material is the second step right after cleaning procedure of a substrate. The conditions of the cleaning of the substrate in the surface preparation step, apply PR via centrifugal, and prebake process in a convection oven or a on a hot plate are the same as the ways of cleaning, PR coating on the surface, and soft-baking in the positive process, respectively. The detailed procedures of the mask alignment, exposure and development steps are also the identical with those in the positive process except that the specific chemicals for the each steps. The difference in the negative method compared to the positive lithography is the etching process. There are two types of etching ways: a liquid (wet) etching and plasma (dry) etching. Depending on the desired materials below the layer of negative PR, the chemicals for the wet etching and gases for the dry etching are chosen. The chosen chemicals or gases have etched from the patterned PR layer as the uppermost to the desired material thin film layer. The top layer of PR has been patterned after development that means patterned areas of PR are on the desired material thin film layer. On the other hand, in dissolved PR areas the desired material thin film is the top part. Therefore, the etching ratios of the PR layer and thin film layer should be considered differently. Usually, even though PR layer is etched faster than conducting (or metal) thin film layer, PR layers on the patterned areas are remained after etching because the thickness of the PR has much thicker. PR layers from spin coating have over one μm thickness and the thin films have few hundreds nm thickness at the most. Then, the remained PR after etching is removed which is called resist stripper via the same method of lift-off process and plasma ash process with O₂ gas.
Negative process (Etching)

- Substrate preparation
- Deposition of the desired materials (@ thin film)
- Photoresist coating
- Prebake
- Mask Align and Exposure
- UV light
- Mask
- Development
- Etching
- Strip Resist

Figure 3.10 Schematic cross-sectional process flow of negative optical contact lithography.
3.2.3 Optical contact lithography in the Nanofabrication facility (NNF) at NCSU

North Carolina State University has a Nanofabrication facility with a cleanroom environment, which is a combination of class 100 and class 1000 in cleanroom space. A class 100 in space has a maximum number of 1,000 particles per m$^3$ in the air and the sizes of the particles must be less than 0.1 μm. A class 1000 cleanroom has 10,000 particles of less than 0.1 μm sizes in 1 m$^3$ of air. In the NNF, both positive and negative processes are used to make ITO nanostructures. Before explaining the details, the photomask is shown in Figure 3.11. The photomask is an opaque surface in part with specific features that block the UV light by opaque areas and pass the UV light by the transparent areas onto the PR layer on a substrate during the exposure process in photolithography. In our experiments, the opaque areas are made by chrome and represented as the black color in Figure 3.11. The blue and green areas in the middle of the mask are 1.5 and 2 μm features, respectively. The nine sections in the edge area are for 3 μm features including an edge bead removal section (about an edge bead, refer to Appendix A).

By using the negative process (etching method), the first attempt was tried without the edge bead removal step as a test. As mentioned before, the starting step is the substrate preparation, and then deposition of ITO on a BK7 glass. The ITO film is deposited via RF sputtering in Ar gas for 21 minutes and 50 seconds to obtain a 150 nm thickness. Then, the ITO film was cleaned by chemicals in the chemical hood in the NNF. Headway Spinner I is a spincoater for the PR application in the chemical hood. The proper size of a spinner chuck, which holds the sample (film) during spinning on the spincoater as a round shape plank is
applied and the prepared ITO film is set on the chuck in Headway Spinner I (shown in Figure 3.12).

![Figure 3.11](image)

**Figure 3.11** A schematic diagram of the photomask. The black parts are sitting on Chrome to block UV light on a PR layer. The blue areas have 1.5 μm features consisting of holes, pillars, triangles, triangular holes, and cross shapes. The green areas are 2 μm features, and the edge areas have 3 μm features including one section of edge bead removal.
The ITO film was cleaned by acetone, methanol, and isopropyl alcohol (IPA) in the indicated order by application and rotation of the Spinner at 4000 rpm for 60 seconds. HMDS was then applied to the cleaned ITO film during spinning. Immediately after dispersal of the positive PR, S1813 resist, they are spun again at 5000 rpm for 40 seconds (Refer to Appendix B for the thickness of S1813 depending on the spin speed). Then we proceeded to the prebake step. The films were exposed to 115° for 60 seconds on a hot plate in order to evaporate the coating solvent on the PR layer. To be specific, the recommended spinning sequence for PR spread in NNF has three steps: First, increasing spinning speed from 0 to 1000 rpm for 7 seconds with 1500 rpm/sec. The step was needed to spread the PR from center to edge area of a surface. Second, the steady state of spinning speed was 4000 rpm with the ramping rate of 1500 rpm/sec for 40 seconds. The last step is stopping to 0 rpm with a deceleration of -1500 rpm/sec. The first step was effective on 4 or 6 inch wafers. In the small area surface such as
our BK7 glass, the first step makes edge beads higher and larger than in a normal-sized wafer. Therefore, the first step was skipped, and instead we increased the spinning speed from 0 to 4000 rpm with the ramping rate of 2000 rpm/sec for 40 seconds. Then, the substrate was placed on the Karl Suss MA6 Mask Aligner to expose UV light with the photomask for 3 seconds. (Shown in Figure 3.13) The aligned mask is 1.5 μm chrome pillars in the right area from the center.

![Figure 3.13 Karl Suss MA6 Mask Aligner in NNF](image)

The exposed substrate is put into a MF-319 developer solution, which has the composition of 95 % water, 1 % surfactant, and 2.2% tetramethylammonium hydroxide, for 60 seconds. The results from the exposure and development of the PR layer are followed in Figure 3.14. As the figure shown, only the edge area has patterns and the blue area in the middle of the substrate is all just ITO film on a BK7 glass without remaining PR layer. That is because the height of
edge beads makes UV light leak into the blocked area of the photomask. Therefore, the PR layer in the middle exposed into UV light including blocked area by chrome of the photomask and the developer washes away all of the exposed PR layer. The next trial started from the edge bead removal step. The exposure and development times in the main procedure were reduced to 2 seconds and 45 seconds, respectively, still using the 1.5 μm chrome pillar mask, which is located right next to the center. Although, the resulting images from the microscope after development are better than the image without the edge bead removal step (the images are not shown in this thesis), the final SEM images after etching had no features on the surface. They results in a bare BK7 glass surface, which means that the ITO films were completely removed by etching via Reactive ion etching. We assume since our PR layer is not perfectly flat, the UV light beams through the space between the PR layer and the photo mask. It is possible that the uneven PR layer disrupted the contact between the PR layer and the photomask, thus the UV light was exposed to the entire surface to be removed after development. This information is included including some of the trial and error during the photolithography process for completeness to aid any future student who attempts these processes.
**Figure 3.14** The microscope image of the patterned PR layer which only has patterns on edge area. The dark patterns are the PR layer and the blue area is from the ITO film on a BK7 glass.

Therefore, we move on to the larger chrome area, which is the one upper area from the center in the photo mask and the mask is for the 1.5 μm holes with etching process. The process is
the same as previous one: ITO deposition on a BK7 glass, cleaning with chemicals, spread S1813 on the cleaned surface at 4000 rpm spin speed for 40 seconds (the ramping rate is 2000/second), aligning the ITO film surface on the MA6 aligner with the photo mask, exposure UV light for 20 seconds with 30 mWatt power as the edge bead removal steps, 60 seconds for development, realignment into the targeted patterns, exposure for 2 more seconds, and finally development for 45 seconds. The result image after development is shown in Figure 3.15.

![Microscope Image](image)

**Figure 3.15** The microscope image after development with 1.5 μm holes mask.

Cl₂ and BCl₃ gases are used for the etching process via Trion (Reactive Ion Etching machine in the NNF). The following figures are the result of images from SEM and AFM. According to Figure 3.17 and Figure 3.18, nine minutes of etching is the right condition for 150 nm ITO films with Cl₂ and BCl₃ gases. Additionally, some areas seem like squares rather than circles in the surface images of SEM and AFM (shown in Figure 3.16 (b) and Figure 3.18).
Figure 3.16 The SEM images after the etching process: (a) and (b) are etched for 6 minutes and (c) is etched for 9 minutes.
Figure 3.17 The AFM images after 6 minutes etched ITO film (b) is the profiler for the depth of (a)
Next we consider ITO nanostructures made from the 2 μm pillar-patterns. These were attempted using the etching method. Before the trial that led to the 2 μm pillar-patterns, we exposed the UV light on the area of 1.5 μm black circles in blue ground (the one next area in right in the photomask) in Figure 3.11. However, the chrome circles in the mask were not able to block the UV light perfectly. Thus the patterned photoresist after the development process did not have circular forms or even washed away by the developing solution. Therefore, we
attempted to produce ITO films consisting of the 2 μm pillar-patterns. In the photomask of Figure 3.11, the 2 μm circle chrome mask (green based black circle schematic) was used to expose UV light after application of the positive PR on the ITO film surface. Other processes and conditions are the same as the previous one including the edge bead removal step. The etching time was also nine minutes with Cl₂ and BCl₃ gases as used previously.

![SEM images of 2 μm pillar-patterns on the ITO film via the etching method.](image)

**Figure 3.19** The SEM images of 2 μm pillar-patterns on the ITO film via the etching method.
To produce regular pillars, we tried lift-off method with the chrome-hole mask in Figure 3.11 (as one upper square in the middle in the mask, since the black means chrome area the section of blue circles in black ground is the one we used). As mentioned previously, the whole process is essentially the same as the etching method. The difference between etching and lift-off is the order for ITO film deposition. In lift–off method, photoresist is spread on cleaned substrates in photolithography, and then ITO deposition is done after development and before strip resist processes. The patterned ITO film of 1.5 μm pillars are made by the lift-off in Figure 3.20 and Figure 3.21. From the images the pillars have approximately 50 nm length.
Figure 3.20 The SEM images of 1.5 μm pillar patterns of ITO films via lift-off method.
Figure 3.21 (a) The AFM images of Figure 3.20, (b) is the profiler for the depth of (a)

Another pattern attempted is the cross-shapes with eight of protrusive edges. In the photomask, there are three sizes of cross-shapes: 1.5 μm, 2 μm, and 3 μm. Since 1.5 μm patterns have a
difficulty that the UV light beams through the chrome patterns 2 μm of cross-shapes are made by etching method including the edge bead removal step.

**Figure 3.22** The SEM images of 2 μm cross-shape patterns of ITO films. The etching time is 12 min.
3.3 ITO film deposition

Figure 3.23 is one of the previous results from our research group that shows the relation of the carrier densities of ITO films to SPR frequencies in near-IR region from 4200 cm\(^{-1}\) to 11,000 cm\(^{-1}\)\(^{25}\).

![Figure 3.23 IR reflective spectra of R_\parallel/R_\perp measured at multiple incident angles with different carrier concentrations of ITO thin films. n means carrier concentrations: (a) 1.4\times10^{21} \text{ cm}^3, (b) 8.7\times10^{20} \text{ cm}^3, (c) 6.2\times10^{20} \text{ cm}^3, and (d) 3.2\times10^{20} \text{ cm}^3. Red thick lines are spectra measured at the highest angles (~ 52°), and the blue dotted lines are spectra taken at the lowest incident angles (~ 41.5°). The interval of the measurements is 0.7°. This is one figure in the reference 12. [Reprinted with permission from Figure 4 in J. Appl. Phy. 106, 024903 (2009)]^{25}

Making thin films required familiarity with the tools for fabrication, annealing, characterizing, and analyzing films. Unfortunately, the initial attempt to reproduce previous results on four
ITO films did not give the same properties as the published result. Apparently, there are many more variables that should be controlled than were initially expected. For example, previous studies reported the argon gas pressure as a sputter gas during deposition, the distance between the ITO target and a substrate, the RF power, etc. In order to obtain reproducible results based on previous published work it was necessary to reoptimize these conditions. The results of this reoptimization are shown in Figure 3.24. In our experiment, ITO films with a high carrier density and a high mobility have advantages. A high carrier density of ITO materials makes the areas of SPR in wavenumber fit in the near IR region. For example, Figure 3.24 (a) and (b) need lower wavenumber areas for the resonance at the high incident light. The high mobility, by the way has sharp peaks for SPR. Comparing (b) and (d) in Figure 3.24 the peaks in (d) have a narrower half-width of the SPR in 42° of the incident light. Therefore, in our whole experiment, the films are deposited in 6 mTorr Ar gas pressure in Figure 3.24 (c).
Figure 3.24 IR reflective spectra of $R_\pi/R_s$ measured at various incident angles based on different carrier concentrations and mobility which are result from the different sputter pressure of Ar gas for ITO thin films. (a) A film deposited in 7 mTorr as a sputter pressure while deposition has $3.68 \times 10^{20}$ cm$^{-3}$ of carrier concentration and 9.52 cm$^2$ V$^{-1}$ s$^{-1}$. (b), (c), and (d) have 15 mTorr, 6 mTorr, and 4 mTorr as sputtering pressures made the films have $5.24 \times 10^{20}$ cm$^{-3}$, $9.16 \times 10^{20}$ cm$^{-3}$, and $6.56 \times 10^{20}$ cm$^{-3}$ of carrier concentrations and 6.76 cm$^2$ V$^{-1}$ s$^{-1}$, 31.37 cm$^2$ V$^{-1}$ s$^{-1}$, and 32.82 cm$^2$ V$^{-1}$ s$^{-1}$ of mobility, respectively.
CHAPTER 4 CHARACTERIZATIONS OF VARIOUS PATTERNED-ITO STRUCTURES

4.1 Thin film SPR measurement

SPR measurements can be obtained using either the Otto configuration\textsuperscript{62} or the Kretschmann configuration\textsuperscript{63} with total internal reflection (TIR) shown in Figure 4.1.

**Figure 4.1** Diagrams of (a) Otto configuration, and (b) Kretschmann configuration

The Kretschmann configuration is usually used due to its simplicity. The configuration is also applied for biosensing applications and in biological research because it is also quite versatile. One can use a simply flow cell to permit an analyte to come into contact with a biological target molecule immobilized on the surface. As shown Figure 2.6, since the plots of the dispersion of bulk plasmon polaritons and the EM waves do not intersect when the EM radiation propagates in air. However, EM radiation wave passing through a prism has a smaller slope on the plot of the dispersion curve, which leads to an intersection. This signifies the possibility of the incident radiation to drive a SPP on the surface of the thin film. Figure
4.2 shows a sketch of the main optical components in a typical Kretschmann configuration SPR spectrometer. The dispersion relation of light (EM wave) in Chapter 2.1 is

\[ \frac{\omega}{k} = \frac{1}{\sqrt{\mu_0 \varepsilon_0}} \rightarrow k_{EM} = \frac{\omega_{EM}}{c} \]

(4.1)

Figure 4.2 A sketch of the optical components in SPR spectrometer with a typical Kretschmann configuration.

Then, from the equation (4.1) and the equation (2.81) for the dispersion relation of SPP, Figure 4.3 shows that the light or EM wave line and the SPP dispersion relation do not have any intersection. Therefore, the Kretschmann or Otto configurations are needed for the experiments to permit an intersection between the light line and the SPP dispersion curve. When light propagates through a prism its momentum is reduced such that it makes an intersection between the light line and the dispersion of SPP. The intersection signifies the possibility for SPR on the interface between the metal (or conducting metal oxide) surface and
a dielectric material. Equation (4.1) of the EM wave (or called light) line in air is changed due to propagation in a dielectric material with $\varepsilon > 1$ (or $n > 1$). Since the resonance is related with the in-plane component, which is represented by $\sin \theta_i$, the equation (4.1) will be replaced with equation 4.2.

\[
k_x^{(EM)} = \frac{\omega_{EM} \cdot n_{prism} \cdot \sin \theta_i}{c}
\]

(4.2)

In Figure 4.4, we are able to see the intersections depending on the incident angles, and those points represent SPR between SPP and the matching energy from the propagating light in the certain medium.

![Figure 4.3](image)

**Figure 4.3** The EM wave-line and the dispersion of SPP in air (air has the dielectric medium of $\varepsilon=1$) have no intersection in any energy.
Figure 4.4 The SPP dispersion has a intersection with The EM wave-line in a dielectric medium ($n>1$ or $\varepsilon>1$), and the intersection position of the wavevector depends on an incident angle.

In 1971, Kretschmann invented a method to excite an SPP. Kretschmann’s method became widely used since the Otto configuration is difficult to implement. Specifically, it is difficult to control the small air gap between a prism and a metal surface with sufficient uniformity to maintain the appropriate geometry required to drive the optically excite the SPP. In Figure 4.2, the geometry that Kretschamann suggested is shown in the experimental setup in which a thin metal film was deposited on a prism. In our experiments, a matching fluid is used between the film and the prism, so the conducting metal oxide is deposited on a substrate. In addition, we are able to check the resonance by confirming the minimum in the reflectivity curves. The minimum means the loss of lights from the laser to the detector, and it is possibly assumed that the energy from the lights is converted to surface plasmons at the interface. The resonance only occurs with the in-plane component of EM waves. In other words, only $p$-
polarized light is able to excite with SPPs in both configurations. An example of the SPR measurement of the ITO film with $p$-polarized light at $41.5^\circ$ of incident angle is shown in Figure 4.5. The measurement is using the Kretschmann configuration with near IR region. The reason for the $y$-axis having $R_p/R_s$ is that only $p$-polarized light is able to make the resonance, thus dividing by $s$-polarized light removes other effects that is not related in SPR. The optimized condition for deposit ITO film is in Chap 3.3 and SPR measurements for the optimized films are in Figure 3.24.

![Figure 4.5](image)

**Figure 4.5** An example of the experimental reflectivity of ITO film at $41.5^\circ$ of incident angle with the Kretschmann configuration. The SPR is occurred at $6300 \text{ cm}^{-1}$ area in the near IR region.

As explained in Chapter 2, SPR is a well-known optical phenomenon that has electron oscillations at the interface between a metal and a dielectric. For SPR to exist, the real parts of two materials’ respective dielectric constants should have opposite signs. For example, a metal has a negative sign and the environment (air) has a positive sign ($=1$) for the real parts
of the dielectric constants. Figure 4.6 shows representative SPR for the optimized films and nano-patterns of ITO studied in this research. There are two features in the figure: one is a region of 8000 cm$^{-1}$ to 9000 cm$^{-1}$ in the absorption band which is independent on the incident angle in the reflectivity spectra. The other spectral region ranges from 4200 cm$^{-1}$ to 5500 cm$^{-1}$ and has different resonance positions depending on the incident angles. These phenomena are caused by two modes of the plasmonic extinctions, which are perpendicular or parallel oscillations with respect to the interface. The parallel polarized plasmon gives rise to a SPR signal, which has large angle dependence and a wave number range from 4200 cm$^{-1}$ to 5500 cm$^{-1}$. The perpendicularly polarized plasmon results in a capacitive plasmon resonance (CPR) in the region of 8000 cm$^{-1}$ to 9000 cm$^{-1}$. The CPR has a small frequency dependence since it is actually a plasmon absorption band similar to those observed in nanoparticles. Elsewhere these absorption bands are called Localized Surface Plasmon Resonance (LSPR).\textsuperscript{27, 51} To be specific, CPR has been observed when metal films or CMO films have thinner thickness than the skin depth of the materials of the films.\textsuperscript{27} This phenomenon is not localized. However, the resonance is perpendicular to the thin films direction as mentioned before while SPR is parallel to the film and propagated to the same direction. Then, comparing to the analog of LSPR in patterned films or nanoparticles, CPR has been observed in CMO films. Noble metals such as Ag or Au have only possible to have a thicker thickness than their skin depth otherwise they are not able to have a uniform surfaces of the films.\textsuperscript{65} According to a previous paper from our research group, as the incident lights are increased, the absorption bands are shown in the decreased wavenumber. The increasing carrier concentrations also make the SPR
frequency move into the higher wavenumber. The trend is corresponding with equation (2.70) in the Drude model.  

**Figure 4.6** The SPR measurement of the ITO film having a carrier density of $9.16 \times 10^{20} \text{ cm}^{-3}$ and a mobility of $31.37 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ from $41.5^\circ$ to $52^\circ$ increased by $0.35^\circ$ as incident angles. The area of 8000 cm$^{-1}$ to 9000 cm$^{-1}$ is caused from CPR and the deep in 4200 cm$^{-1}$ to 5500 cm$^{-1}$ is from SPR.

### 4.2 LSPR measurement for patterned films

The other way to make resonance between SPPs and EM polarized light is to use a grating coupler. The gratings or defects such as protrusions or corrugations on the surface are able to couple electromagnetic radiation to enhance the energy of the incident light when the light diffracted by the gratings on the surface is tangential to the surface and is not transmitted. These enhancements lead to a localized surface plasmon resonance (LSPR) that has been studied for new applications, which have tracked the development of technologies for the controlled fabrication and manipulation of nanostructures.
LSPR originated from the observation of Wood’s anomalies\textsuperscript{40} and has been more recently focused on the resonance incident light interacting with particles or patterns smaller than the wavelength of the incident light. The idea of LSPR is that the surface oscillation driven by an electric field is confined to the special dimensions of the particles. These small oscillations are called LSPR in shown Figure 4.7.\textsuperscript{51, 54} Since LSPR, like SPR is also very sensitive to any change in index of refraction near the surface, researchers in biological and chemical fields have studied these methods for sensing or other new applications.

\textbf{Figure 4.7} Schematic diagram of LSPR. The free electrons in the nanoparticles are polarized by the EM wave having a larger wavelength than the particle sizes. Net charges are able to exist at the surface of the particles, and the net charge difference plays a role as a restoring force. Various kinds of the particle shapes can make resonance.\textsuperscript{51}

\textbf{4.3 The measurement results of triangle nanopatterned ITO films}

In Chapter 3, SEM images of the ITO nanostructures produced by the NSL method with two close-packed layers of PMMA spheres are shown in Figure 3.6, Figure 3.7, and Figure 3.8.
Application of the NSL method with the PMMA results in a periodic array of ITO features consisting of equilateral triangles with edges from 500 to 800 nm in length. The heights of the ITO triangular features are 8 to 20 nm as measured by AFM (in Figure 3.7 and Figure 3.8). There are several types of the defects in the array, which arise because we have used a simple spin coating method to deposit the PMMA layers as a mask before ITO sputtering. For example, the lower part of the area shown in Figure 3.6 (b) was made by sputtering ITO on a partial monolayer of PMMA. One can see several star shapes that arise from vacancies in the second PMMA layer. There are also some defects, which appear as connections between the patterns because of dislocations of a number of the PMMA spheres. Despite these defects, a majority of the area of these prepared surfaces consists of an array of regular triangular shapes. Van Duyne and co-workers have shown that the nanostructures formed by single and a double layer of NS mask differ. The sizes of the nanopatterns are \(a_{SL}\) and \(a_{DL}\), respectively. \(D\) is the diameter of the NS for the mask.

\[
a_{SL} = 0.233D \\
a_{DL} = 0.155D
\]

(4.3)  (4.4)

The NPs from a single layer mask have a triangular shape, while those produced from a double layer mask have a circular shape. The PMMA spheres used in this work have \(D = 1 \mu m\) and we used a double layer as a mask. Therefore, based on the equation of Van Duyne et al. (Equation 2) \(a_{DL}\) of our NPs should be 155 nm circles. However, in Figure 3.6 and Figure 3.7, the patterns we have are much larger than 155 nm and shapes are triangular rather than circular. The explanation for this apparent discrepancy is that the PMMA particles had shrunk to \(\sim 80\%\) of their original volume since they were desiccated by the cyclohexane solvent used
for spin coating (shown in Figure 3.4). Specifically, the NS appear to have shrunk due to solvent drying as the NS settled on the substrate to form the double layer. Consequently, the size of the vacancies between the PMMS particles increased, which led to a triangular shape observed after sputtering ITO. The interparticle distances ($d_{ip,DL}$)\textsuperscript{54} for the NS double layer mask provides another observable. Despite the differences in size and feature between ours and Van Duyne’s nanostructure, the $d_{ip,DL}$ is the same.

$$d_{ip,DL} = D$$ \hspace{1cm} (4.5)

Since the size of our NS is 1 μm, the value is 1 μm based on equation 4.1, 4.2, and 4.3.\textsuperscript{54,73} This calculated value agrees with the experimental value of 1 μm (in Figure 3.7). Figure 4.8 shows the reflectance spectra of the ratio of $p$-polarized to $s$-polarized light of the patterned ITO film in the Kretschmann configuration. A weak absorption band is observed at circa 6500 cm$^{-1}$. The normalized extinction (or absorbance) is defined as:

$$A = -log \left( \frac{T}{T_0} \right)$$ \hspace{1cm} (4.6)

The band has essentially no angle dependence, which suggests that it is not a surface plasmon polariton. By this we mean that it cannot be driven as a delocalized wave along the interface of the material. In general, for thin file materials, there are two possibilities to explain the observed signal since CMOs can have polarizations that are either parallel or perpendicular to the interface. We have shown elsewhere that the optical response in very thin films is analogous to LSPR in that it is not strongly angle dependent (Figure 4.9). In the limit where the film thickness is less than the skin depth only a perpendicular polarization of incident light
can drive a plasmon. This perpendicularly polarized plasmon is called a capacitive plasmon resonance (CPR).

Figure 4.8 The normalized extinction, recorded at incidence angles ranging at 41.5°, with the spectra of a bare BK7 glass substrate (Figure 4.11) (a) Spectra with the film after annealed in a 5 % H$_2$/95 % N$_2$ (forming) gas, (b) with the film after annealed in O$_2$ gas, (c) annealed in O$_2$ gas with the same film as (a), (d) annealed in a forming gas with the same film as (b).
Figure 4.9 The normalized IR reflective spectra ($R_p/R_s$), which are normalized results of Figure 4.10 by a IR reflective spectra ($R_p/R_s$) of a bare BK7 glass substrate (shown in Figure 4.11). Therefore, measured conditions are the same as Figure 4.8 and Figure 4.10, those are recorded at incidence angles ranging from 41.5° to 52° (from mustard (and red) to violet, respectively): (a) The spectra with the film after annealed in a forming gas, (b) with the film after annealed in $O_2$ gas, (c) annealed in $O_2$ gas with the same film as (a), (d) annealed in a forming gas with the same film as (b).
Figure 4.10 The raw IR reflective spectra \( \frac{R_p}{R_s} \) measured at 41.5° to 52° (blue to red, respectively) as incident angles with 0.35° steps for patterned ITO films: (a) The spectra with the film after annealed in a forming gas, (b) with the film after annealed in O₂ gas, (c) annealed in O₂ gas with the same film as (a), (d) annealed in a forming gas with the same film as (b).
Figure 4.11 IR reflective spectra (Rp/Rs) measured at 42.5° to 52° (pink to yellow, respectively) as incident angles for a bare BK7 glass substrate.

Figure 4.8 (a) results from the ITO nanostructure film annealed in a 5 % H\textsubscript{2}/95 % N\textsubscript{2} atmosphere at 500 °C for one hour to yield mostly electronic compensation of oxygen vacancies resulting in a high free carrier concentration.\textsuperscript{25} The spectra in Figure 4.8 (b) depict the normalized extinction of a nanopatterned ITO film annealed in O\textsubscript{2} gas at 500 °C for one hour to reduce the charge carrier concentration in the film. In this case, unlike (a), we are not able to see the CPR phenomena. With the films for Figure 4.8 (a) and (b), we re-annealed those films in O\textsubscript{2} and 5 % H\textsubscript{2}/95 % N\textsubscript{2}, respectively, at the same temperature and duration as the first annealing conditions. Then, the normalized extinction signal in (a) goes away after re-annealing (Figure 4.8 (c)) and the smooth background of (b) has changed to the spectrum with regenerated CPR extinction at around 6,500 cm\textsuperscript{-1} (Figure 4.8 (d)). Therefore, we can reproducibly control the ITO carrier concentration and the CPR spectra depending on annealing conditions.\textsuperscript{25} To be clear, the raw data are in Figure 4.10, and the graphs which are
normalized by the IR reflective spectra of the BK7 are shown in Figure 4.9. Then, the normalized extinctions in Figure 4.8 are converted from IR reflectivity in Figure 4.9.

Figure 4.12 shows the results of the FDTD simulation in a triangular-lattice of arrays with triangles in Schem 4.1. The geometry for the simulation is used 800 nm equilateral triangles with 20 nm thickness to reproduce the NSL patterns. The plane wave light source is placed below the ITO nanostructure for two reasons (in Schem 4.1): First, to replicate the Kretschmann configuration and second, to avoid the intricacy of the reflection of BK7 from ITO nanostructures. The absorption maximums of incident light angles of 39° and 41° from the simulation results are both at 6211 cm⁻¹ in Figure 4.12. The results confirm the independence on the incident angle. The results correspond with the absorption peaks observed in Figure 4.8. Figure 4.12 depicts the corrected reflectivity which is normalized with the result of only the BK7 substrate from the reflection of the ITO nanostructures on the BK7 substrate. The corrected reflectivities from FDTD simulation are then able to compare directly with the experiment results in Figure 4.8 or Figure 4.9. (Figure 4.13 and Figure 4.14 show simulation results of the ITO nanostructures on the BK7 and only the BK7, respectively).
Figure 4.12 FDTD calculated spectra of equilateral triangles of ITO 800 nm on a side and with a thickness of 20 nm. The graphs are normalized with the results from patterned ITO on BK7 substrates. The incident light source is set below the ITO patterns with incident angles of 39° and 41° to be consistent with the Kretschmann configuration geometry.
**Schem 4.1** Schematic illustration of the FDTD numerical simulation in triangular shape of the ITO patterns. The red-dotted square shows the simulation area.

**Figure 4.13** FDTD calculation results of the patterned-ITO with the incident light angle of 39° and 41° in the Kretschmann configuration. The both absorbance maximum are at 6211 cm⁻¹.
Figure 4.14 FDTD calculation results of BK7 glasses as substrates with incident light angles of 39° and 41° in the Kretschmann configuration.

Figure 4.15 indicates the electric field profiles ($|E|^2$) for various wavenumbers with two different incident angles. Figure 4.15 (a-c) are the intensity distributions of the electric fields at the wavenumber of 2000 cm$^{-1}$ (a), 6250 cm$^{-1}$ (b), and 7143 cm$^{-1}$ (c) with the incident angle of 39°. Figure 4.15 (d-f) are the results with the incident angle of 41°. For the case of the wavenumber of 6250 cm$^{-1}$ (see Figure 4.15 (b) and (e)), we can clearly observe the extremely enhanced electric field intensity due to the CPR and the wavenumber corresponds with the absorption maximums in Figure 4.12.
Figure 4.15 The electric field intensity distributions ($|E|^2$) are shown in the xy plane at the wavenumber of 2000 cm$^{-1}$ (2.0 nm), 6250 cm$^{-1}$ (1.6 nm), and 7143 cm$^{-1}$ (1.4 nm). (a)-(c) are calculated with the incident angle of 39°. (d)-(f) are the results with the incident angle of 41°.

4.4 Discussion of the results of triangle nanopatterned ITO film

The lack of angle dependence of the normalized extinction in Figure 4.8 (and Figure 4.9) suggests that the origin of the optical signal due to the conduction electrons in ITO is attributable either to LSPR or to the CPR, but not to SPR. While the LSPR is a well-known absorption seen in essentially all plasmonic materials with sufficiently small dimensions, the
CPR has only been observed in thin films where the thickness is less than the skin depth of the conductor. Alternatively, the CPR can be observed in a hybrid plasmonic material when there is a mismatch between the plasma resonance frequencies such that one material is a perfect reflector (ideal conductor).\textsuperscript{27} The selection rule in a perfect reflector forbids excitation of any transition parallel to the surface. However, the CPR is polarized perpendicular to the film surface and is allowed in a hybrid material consisting of ITO and a solid Au layer that acts as a reflecting surface. The LSPR is distinct from the CPR in that the LSPR may be polarized along any axis of a nanostructured material or nanoparticle, while the CPR is defined only as a resonance perpendicular to the plane of a conducting film. While the optical extinction spectra in Figure 4.8 peaked at 6,300 cm\(^{-1}\) is in the range of the LSPR of ITO NPs made by Teranishi \textit{et al} with different mole percentages of Sn from 0\% to 30\%,\textsuperscript{45} it cannot be a LSPR in the normal sense since the 20 nm thickness of the features is less than the skin depth of conducting ITO (ca. 120 nm). Because of this it is not possible to drive a surface plasmon polariton parallel to the surface. The fact that the extinction spectra maximum in Figure 4.8 is comparable to the 6,180 cm\(^{-1}\) absorption maximum of 10\% Sn-doped ITO in Ref. 38 is perhaps more a function of the similar in preparation conditions.\textsuperscript{74} The FDTD results of the ITO nanostructures having the absorption maximum at 6,211 cm\(^{-1}\) confirm that the photonic phenomena of the ITO nanoscale features are caused by CPR of ITO. The results obtained for a 20 nm thin-flat ITO film in Figure 4.16 also confirm that the absorption maximum at 6,211 cm\(^{-1}\) is independent of features, and Figure 4.18 that is the FDTD calculation result of ITO-regular triangles of 300 nm as a side length with the thickness of 20 nm validates the independence on the size of the features, as well. The results can be explained with CPR as
the intrinsic characteristics of the ITO film. The films studied here have a charge carrier density of $9.1 \times 10^{20} \text{ cm}^{-3}$, which is significantly lower than films studied previously.\textsuperscript{25} Indeed, the LSPR would be predicted to be in the same range if the nanostructures were thick enough to support a LSPR ($> 120 \text{ nm}$). Unlike the LSPR the CPR is not strongly dependent on the shape of the structure. It is dependent mainly on the charge carrier density, which is determined by the Sn doping and the annealing conditions. It has been shown that the differences in the widths and peak positions of LSPR extinctions depend on the size of NPs for metals, such as Al, Ag, Au, and Cu with the same shapes and thickness.\textsuperscript{73, 75} The result obtained on ITO using NSL confirms our previous hypothesis regarding the nature of the CPR.

![Figure 4.16](image)

**Figure 4.16** FDTD calculation results of a 20 nm thick ITO film with incident light angles of $43^\circ$, $48^\circ$, and $53^\circ$ in the Kretschmann configuration. The absorbance maximum of $43^\circ$ is at 6250 cm$^{-1}$ and the other two maximums of $48^\circ$ and $53^\circ$ are at 6211 cm$^{-1}$. 

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Figure 4.17 FDTD calculation results of a 150 nm thick ITO film with incident light angles of 43°, 48°, and 53° in the Kretschmann configuration. The absorbance maximum of 43° is at 6,329 cm⁻¹, two maximums of 48° show at 6,098 cm⁻¹ and 4,367 cm⁻¹, and the maximum of 53° are at 5,376 cm⁻¹.
Figure 4.18 FDTD calculation result of the patterned-ITO film which are equilateral triangles with a side length of 300 nm at the incident light angle of 39° in the Kretschmann configuration. The both absorbance maximum are at 6,211 cm\(^{-1}\).

The NSL method has sucessfully been applied to the triangular patterns of ITO thin films. The plasmonic nature of the patterned surface is demonstrated by the variation of the carrier concentration through ex-situ annealing in air and in N\(_2\)/H\(_2\) forming gas, respectively. The main message of this study is that the plasmonic absorption peak at circa 6,500 cm\(^{-1}\) is CPR rather than a previously reported LSPR. The observed CPR wavenumber is lower than would be expected based solely on the charge carrier density, which can be explained by the experimental charge carrier density. The existence of a CPR in the film explains the difference in optical signals between the ITO nanostructure produced here and the LSPRs described previously.\(^{54,73}\) This study confirms the concept of a CPR as an optical feature in a film whose thickness is less than the skin depth of the conductor.
4.5 Optical response obtained from 1.5 μm pillars of ITO made via photolithography

In Figure 3.20 and Figure 3.21, 1.5 μm pillar-patterns with 50 nm thickness of ITOs are made via lift-off method. SEM and AFM images are confirmed for the patterns. The patterns are measured in IR reflectivity (R_p/R_s) in near IR region, and the results are compared to IR reflectivity of the triangles’ patterns via NSL. According to the measurement result in Figure 4.19, similar to the results of triangle patterns via NSL, the absorptions at around 6500 cm⁻¹ are shown for all incident angles. As explained before, since the LSPR should have angle dependent and the similarity of the result, we are able to say the result of Figure 4.19 also only have CPR of ITOs. This is because the thickness of the pillars is 50 nm, and this thickness is thinner than the skin depth of ITO films. Therefore, the only perpendicular polarization of incident light is driven and the perpendicular polarized plasmon is CPR.
Figure 4.19 The normalized IR reflective spectra ($R_p/R_s$) of 1.5 μm pillars with 50 nm thickness of ITOs from 41.5° to 52° by 0.7° in near IR region. The normalized are used by IR reflective spectra ($R_p/R_s$) of a bare BK7 glass substrate (Figure 4.11).

4.6 The measurement results of 1.5 μm holes of ITO films via Photolithography

The 1.5 μm holes are made by etching method. Unlike pillars, since chrome-hole mask for 1.5 μm holes has larger area to block UV light than the area to exposure the light the patterns are made successfully. The holes are etched various time durations. Specially, the patterns with six minutes and nine minutes etching time have cleaned and regular holes via SEM images (Figure 3.16). On the other hand, according to AFM images, the depths of holes are different: six minutes etched holes have around 50 nm depths (Figure 3.17) and nine minutes etched holes have 150 nm depths (Figure 3.18). We did deposition of ITOs first for 21 minutes 50 seconds to build a 150 nm thick, and then exposure and etching later. However, for IR reflectivity measurement in near IR region and in mid IR region, the two holes-patterns have
the same results of normalized IR reflectivity except some flaws in low incident angle measurements. In Figure 4.20 unlike pillars or triangles results, one can see the angle dependence of reflectivity. The figure is the results through Kretschmann configuration, the $p$-polarized light interact with the holes and the angle dependence of the plasmon resonances is called LSPR. The $p$-resonance or LSPR shows a blue shift in Figure 4.20.76

**Figure 4.20** The normalized IR reflective spectra ($R_p/R_s$) of the 1.5 μm hole-patterns of ITOs (see Figure 3.16) from 43.5° to 52° by 0.7° in near IR region. (a) The depths of the holes are 50 nm by etching for 6 minutes (see
Figure 3.17). (b) The depths of the holes are 150 nm by etching for 9 minutes (see Figure 3.18). The normalized are used by IR reflective spectra ($R_p/R_s$) of a bare BK7 glass substrate (Figure 4.11).

The reflectivity measurement in mid-IR region via IR-VASE is not used Kretschmann configuration, but measure the reflectivity on the surface of the patterns directly. The IR-VASE emits polarized light and detects the each polarized signals. In Figure 4.21, the reflectivity results of the thicknesses of 50 nm (a) and 150 nm (b) are from $s$-resonance in which $s$-polarized light goes onto the patterned surface and the detector also catches $s$-polarized reflected light. According to Dr. Lodewijks’s research group, $s$-polarized excitation is dominated by longitudinal electric coupling and transverse magnetic coupling.\textsuperscript{76} Here, we are using ITOs material on a BK7 glass to make patterns, thus we can say the longitudinal electric coupling makes LSPR in the region of $5000 \text{ cm}^{-1}$ to $6000 \text{ cm}^{-1}$. The LSPR is also corresponding to the reflectivity (SPR) results in near IR of Figure 4.20. On the other hand, area of $3000 \text{ cm}^{-1}$ to $4000 \text{ cm}^{-1}$ shows CPR with no angle dependence absorption in Figure 4.21 and Figure 4.22. Figure 4.22 shows $p$-resonance of the 1.5 $\mu$m hole-patterns with 50 nm thickness (a) and 150 nm (b) thickness. Since the paper from Dr. Lodewijks says that the $p$-polarized excitation is dominated by longitudinal magnetic coupling and transverse electric coupling,\textsuperscript{76} the $p$-polarized coupling or transverse electric coupling for LSPR is very weak or needed to measure the larger area in wavenumber. Only with the results in Figure 4.22, one cannot sure about the interactions for LSPR.
Figure 4.21 The reflective spectra ($R_s$) of the 1.5 μm hole-patterns of ITOs from 25° to 85° of the incident angles with $s$-polarized light. (a) The depths of the holes are 50 nm by etching for 6 minutes (see Figure 3.17). (b) The depths of the holes are 150 nm by etching for 9 minutes (see Figure 3.18). The region of 3000 cm$^{-1}$ to 4000 cm$^{-1}$ has the absorption from CPR and the region of 5000 cm$^{-1}$ to 6000 cm$^{-1}$ shows LSPR with angle dependence.
Figure 4.22 The reflective spectra ($R_p$) of the 1.5 μm hole-patterns of ITOs from 25° to 85° of the incident angles with $p$-polarized light. (a) The depths of the holes are 50 nm by etching for 6 minutes (see Figure 3.17). (b) The depths of the holes are 150 nm by etching for 9 minutes (see Figure 3.18). The whole region seems to have extremely broad absorption of LSPR in the spectra, but with only these results we are not able to sure for the LSPR.

The cross-shapes patterns with 2 μm on a side (see Figure 3.22) are measured by IR-VASE to research the interaction between the polarized lights and the patterns. Unlike holes, $p$-resonance shows LSPR with angle dependence reflectivity in Figure 4.23 (a) and $s$-resonance very weak interactions in Figure 4.23 (b). The LSPR with $p$-polarized light is in the region of
1500 cm\(^{-1}\) to 3000 cm\(^{-1}\). The difference between the 1.5 \(\mu\)m-diameter holes and cross-shapes with 2 \(\mu\)m on a side which means the total length of the shapes is 6 \(\mu\)m is the way of propagating of the resonance.\(^{76}\)

**Figure 4.23** The reflective spectra of the 2 \(\mu\)m cross shape-patterns of ITOs (see Figure 3.22) from 40° to 72° of the incident angles with \(p\)-polarized light (a) and \(s\)-polarized light (b).
CHAPTER 5 SELF-ASSEMBLED MONOLAYERS

5.1 Self-assembled monolayers on conducting metal oxides

Self-assembled monolayers (SAMs) for the attachment of biomolecules onto the surfaces of thin films have promoted the development of biosensing applications. Specially, SAM technology functionalized alkane thiolates on gold surfaces have received enormous interest for the past 40 years. This is because the functional head groups of molecules coupled with the gold, and the other side as tails are able to stand in parallel to each other giving the possibility of the formation a highly ordered semicrystalline organic thin film.⁵¹,⁷³

5.2 Self-assembled monolayers on cadmium tin oxide

The CdO films are deposited by a pulsed laser deposition (PLD) method based on a sapphire substrate. The sapphire substrate has a refractive index of ~1.6 to ~1.7 depending on the wavelength in mid-IR region. To add self-assembled monolayer hexadecanethiol (HDT, CH₃(CH₂)₁₅SH) and mercaptoundecanoic acid (MUA, HS(CH₂)₁₀CO₂H) were used (Sigma-Aldrich). MUA has a long chain structure, and the molecule has a thiol group (S-H) and a carboxyl group (–COOH) at each sides. The thiol group is able to attach the molecule onto the surface of a CdO film and the carboxyl groups make the surface more hydrophilic, which has advantages to applications in aqueous solutions in the bio-field. CdO thin films were supplied with Dr. Maria’s lab in the Department of Materials Science and Engineering in North Carolina State University. As a first step, CdO thin films were cleaned by UV ozonolysis method to make hydrophilic surfaces and remove adventitious carbons. Then, the CdO thin films were immersed in a solution of MUA or HDT in different concentrations with different
immersion times. Two CdO thin films were used in 1mM and 500 mM concentration of MUA for one hour. On the other hand, three CdO thin films are submerged in 100 mM, 500 mM, and neat solution of HDT for 21 hours, 14 hours, and 18 hours. Measurements of SPR spectroscopy of the CdO thin films before and after adding SAM is taken IR-VASE ellipsometer from Wollam Corp. from 1000 cm\(^{-1}\) to 6000 cm\(^{-1}\) of the mid IR region. The other results are shown in Figure 5.1 for the investigation of the HDT on cadmium tin oxide (Cd2SnO4) are shown in FTIR spectra at an incident angle of 70º. Figure 5.1 shows two reflective spectra of the ratio of p-polarized light to s-polarized light on the same film. Solid line spectrum is measured on cadmium tin oxide with SAMs of HDT and dashed line is for a bare film. The peaks at 2850 and 2918 cm\(^{-1}\) correspond to the vibrational asymmetric and symmetric stretching modes of \(-\text{CH2}–\), respectively.

**Figure 5.1** Reflectance FTIR spectra \((R_p/R_s)\) of HDT on a cadmium tin oxide film (solid line) and a bare cadmium tin oxide (dashed line). The spectrum of the added HDT cadmium oxide has two peaks that indicate an alkane adlayer. [Reprinted with permission from Figure 2 in *Thin Solid Film* 516, 1838-1842 (2008)]

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5.3 Measurement for self-assembled monolayers on nanoparticles

On the other hand, the technology for SAMs has been measured by using LSPR or SPR spectroscopy with silver or gold. For example, one group made Ag nanoparticles via NSL (See Figure 3.1) and measured LSPR spectra in N2 gas (See Figure 5.2a)). In the (a), A indicates the LSPR peak when the Ag nanoparticles before chemical modification and the spectrum of B in (a) is the spectrum of Ag nanoparticles with HDT. There is 40 nm shifts from 564 nm to 604 nm. The red shift is because of the change of the dielectric constant caused by HDT. Figure 5.2(b) indicates the relation between optical measurement and adsorptions of alkanethiols on Ag nanoparticles. This represents the existence of well-packed alkanethiols SAMs on the nanoparticles.

![Figure 5.2](image)

**Figure 5.2** (a) Spectra of UV-vis extinction of Ag nanoparticles in N2 environment: The A line is the spectrum of Ag nanoparticles before treatments and the $\lambda_{\text{max}}$ is 564 nm. The B line is the spectrum of the same nanoparticles but after modification with HDT. The $\lambda_{\text{max}}$ of B is 604 nm. (b) LSPR peak shifts depending on the alkanethiol chain length in N2. [Reprinted with permission in *J. Am. Chem. Soc.* 123, 1471-1482 (2001)]
5.4 Self-assembled monolayers on cadmium oxide

Our group has extensively investigated SAMs on CMO thin films, such as ITO, aluminum doped zinc oxide, CdO, or etc.\textsuperscript{50, 51, 73, 83, 84} As a transparent conducting metal oxide (CMO), cadmium oxide (CdO) has a high mobility and a high charge carrier concentration.\textsuperscript{28} We put SAMs of hexadecanethiol (HDT) and mercaptoundecanoic acid (MUA) on CdO thin films. HDT has thiol as a tail with a long carbon chain structure. The thiol is able to attach Cd in the CdO film surface. The advantage of the molecule is that we used it to add layers on the surfaces of CTO films, previously.\textsuperscript{78} The reflective spectra in mid-IR region for a bare CdO thin film and SAMs of HDT on a CdO thin film are shown in Figure 5.3. The CdO thin film is immersed in 100mM of HDT for 21 hours. While the reflective spectrum of CdO thin film has absorption peak around 3080 cm\textsuperscript{-1}, the added layer on the CdO thin film has the peak at around 2700 cm\textsuperscript{-1}. Due to the shift of the reflective spectra we could know HDT is sitting on CdO film.\textsuperscript{73} Figure 5.4 is also reflectivity spectra at the incident angle of 52\degree of a bare CdO film and HDT SAMs on the CdO film. The difference is the concentration of the HDT solution. The position for the added layer of the absorption peak is around 2860 cm\textsuperscript{-1}. In Figure 5.4, 500mM of the HDT solution is used by adding SAMs for 14 hours.
Figure 5.3 The reflective spectra ($R_p/R_s$) measured at 53° of a CdO thin film (Black line) and HDT SAMs on CdO (Red line). 100mM of HDT solution is used to immerse the film for 21h. The CdO film and the CdO film with added layer have absorption peaks at ~ 3080 cm$^{-1}$ and ~ 2700 cm$^{-1}$, respectively.

Figure 5.4 The reflective spectra ($R_p/R_s$) measured at 52° of a CdO thin film with Black line and HDT SAMs on the CdO film with Red line. 500mM of HDT solution is used to add SAMs on the film for 14h. The CdO film and the CdO film with added layer have absorption peaks at ~ 2860 cm$^{-1}$ and ~ 2700 cm$^{-1}$, respectively.
The other kinds of tail we used to add layer on the film is acid, -COOH function group in MUA. The carboxyl acid makes the surface of a film more hydrophilic that is useful for applications in aqueous solutions such as biomaterials. However, since our CdO films are very sensitive to acid, we use MUA solution as a reference. The conditions of immersion are 1mM MUA solution for 21 hours. The spectra in Figure 5.5 measured at 52°, and the absorption peaks are shown in about 2700 cm\(^{-1}\) and 1900 cm\(^{-1}\) which are analyzed a bare CdO film and MUA added layer on the CdO film, respectively.

![Reflective spectra (R_p/R_s) measured at 52° of CdO thin film with Black line and MUA SAMs on CdO film with Red line.](image)

**Figure 5.5** The reflective spectra (R\(_p\)/R\(_s\)) measured at 52° of a CdO thin film with Black line and MUA SAMs on the CdO film with Red line. 1mM of MUA solution is used to add SAMs on the film for 21h. The CdO film and the CdO film with added layer have absorption peaks at ~2700 cm\(^{-1}\) and ~1900 cm\(^{-1}\), respectively.

### 5.5 The thickness measurement of the self-assembled monolayers on cadmium oxide

Ellipsometry is a well known optical tool for studying dielectric properties of thin films. The technique is also able to characterize roughness, compositions, thickness, electric conductivity
or other material properties of thin films since those properties are sensitive to the optical properties.\textsuperscript{86} Therefore, we have investigated the length of SAMs using Infrared Variable Angle Spectroscopic Ellipsometer (IR-VASE) (made by J.A. Wollam) controlled by WVASE-IR software in the Surface Science Laboratory operated by Dr. Genzer’s group in department of Chemical & Biomolecular Engineering in NCSU. Moreover, X-ray specular reflectivity or called X-ray reflectometry (XRR) is used to study the length of SAMs on the CdO films. To characterize the surfaces or multilayers of thin films, XRR has been used since Professor Lyman G. Parratt suggested the technique in Physical Review paper in 1954.\textsuperscript{87} The X-ray tool we used is in Dr. Maria’s group in the Department of Material Science and Engineering in NCSU. The molecules we attached onto the surface of the CdO film are HDT, MUA, and 6-Mercaptohexan-1-ol (MH) to characterize the length of SAMs. Theoretically, the lengths of MUA and MH are 1.62 nm\textsuperscript{6} and 1.07 nm\textsuperscript{88}, respectively. We made solution with a composition ratio of one-to-one and one-to-three with MUA and MH to control of the density, and to analyze the length of SAMs, 5 nm thickness of CdO thin films are used. The immersion time of the composition of one-to-one solution for the thin CdO film was 40 minutes due to the weakness of CdO films for corrosivity of MUA. However, only three samples gave reasonable results. There are reported in Table 5.1. Other results are obtained reduced lengths after added SAMs shown in Table 5.2. As mentioned, the reasons of the reduced lengths after adding SAMs on the bare films are the sensitivity of the acid in MUA solution of the CdO films. The comparison the case of CdO thin film (6) with CdO thin film (7) in Table 5.2 could be evidence.
Here, the SAMs are attached to the surface of bare CdO films. The confirmations of added SAMs are by measuring SPR, IR reflective spectra, and thickness measurement via ellipsometer. Although the sensitivity in an acid solution of CdO films is a challenge to make regular SAMs on the surface, we have finally built one layer of SAMs to add another molecules on the surface, which is applied to various applications.

Table 5.1 The experimental results from IR-VASE and XRR of bare CdO thin films and added SAMs on the thin films. The thickness of the CdO films is 5 nm.

<table>
<thead>
<tr>
<th></th>
<th>MUA:MH</th>
<th>Immersion time</th>
<th>Length of SMAs (nm) From Ellip.</th>
<th>From XRR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdO thin film (1)</td>
<td>1:1</td>
<td>40 min.</td>
<td>0.946 ± 0.514</td>
<td>1.3</td>
</tr>
<tr>
<td>CdO thin film (2)</td>
<td>1:1</td>
<td>40 min.</td>
<td>2.329 ± 0.417</td>
<td>2.2</td>
</tr>
<tr>
<td>CdO thin film (3)</td>
<td>1:3</td>
<td>24 hour</td>
<td>2.00 ± 0.578</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.2 The experimental results from IR-VASE of the bare CdO films and the added SAMs on the thin films.

After added SAMs, the length differences from the bare films and the added SAMs on the films are the negative numbers which mean the bare films are etched rather added layers.

<table>
<thead>
<tr>
<th></th>
<th>Concent. (mM)</th>
<th>MUA:MH</th>
<th>Immersion time</th>
<th>Length of SMAs (nm) From Ellip.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdO thin film (4)</td>
<td>10</td>
<td>1:1</td>
<td>60 min.</td>
<td>-1.10</td>
</tr>
<tr>
<td>CdO thin film (5)</td>
<td>10</td>
<td>3:1</td>
<td>24 hour</td>
<td>-1.43</td>
</tr>
<tr>
<td>CdO thin film (6)</td>
<td>50</td>
<td>1:1</td>
<td>24 hour</td>
<td>-7.30</td>
</tr>
<tr>
<td>CdO thin film (7)</td>
<td>10</td>
<td>1:1</td>
<td>24 hour</td>
<td>-1.80</td>
</tr>
<tr>
<td>CdO thin film (8)</td>
<td>10</td>
<td>1:0</td>
<td>15 hour</td>
<td>-0.0810</td>
</tr>
<tr>
<td>CdO thin film (9)</td>
<td>10</td>
<td>0:1</td>
<td>15 hour</td>
<td>-0.736</td>
</tr>
<tr>
<td>CdO thin film (10)</td>
<td>10</td>
<td>HDT</td>
<td>15 hour</td>
<td>-1.79</td>
</tr>
</tbody>
</table>
CHAPTER 6 CONCLUSION

ITO deposition on patterned surface has been used to make various patterns via NSL and photolithography methods. The patterned ITO films can be easily handed and stable in the normal experimental conditions. Methods were developed to control it’s the optical properties of the thin film CMO by means of control of the carrier density and mobility. The mobility can be adjusted by altering the sputter gas pressure. In addition, after completion of the patterns of ITO films the carrier concentration can be controlled by post annealing conditions. We confirmed these results in patterned surfaces made using NSL via the plasmonic absorption peaks of the CPR and the LSPR signals. The existence of a CPR in the 20 nm thick triangles of ITOs explains the difference in optical signals between the ITO nanostructure produced here and the LSPRs described previously. It also shows that ITO nanostructures can be subject to tuning that can be used to modulate their optical signals. The other various patterns of ITO films by using photolithography method show LSPR in different absorption peak positions depending on the shapes and thickness. The differences of the shapes and thickness make free charges in the surface of ITOs have different types’ resonance with two other polarized light: p-, and s-polarized lights. This aspect of both LSPR and SPR is crucial for applications of the method. The extension of SPR to CMOs holds new possibilities in terms of the wave length range for detection and materials compatibility for novel device design.
REFERENCES


APPENDICES
APPENDICES

Appendix A: Edge beads

One way of the PR application techniques is a spincoating method via centrifuge, and the thickness of the PR layer is decided by the equilibrium between centrifugal force and the solvent evaporation of the PR. Since we use small and square pieces of BK7 glasses (1.8 × 1.8 cm) not 4 or 6 inch circular (in diameter) wafers, our specimens have edge beads which are residual ridge in PR layer at the edge area. For reference, the heights of edge beads are increased when the radius of a wafer is reduced or in a non-circular wafer. The problem is that the thickness of the edge bead is usually up to 20 to 30 times higher than the thickness of the centers in the specimen. Therefore, when the exposure the PR to UV light via contact optical lithography, the contact between the PR layer on the substrate and the photomask is not stable and leakage phenomena of UV light into the gap on the PR layer are occurred, especially during small features.
Figure A.1 (a) Schematic figure of spin coating method for the PR application technique (b) After finishing the spinning, the edge beads are shown in the edge area of the PR layer.
Appendix B: The positive photoresist, S1813

S1813 has different thicknesses based on the spin speed of the centrifuge. The following figure is come from NNF webpage.\(^{(1)}\)

![](image)

**Figure A. 2** Spin speed curve for S1813 resist using a specific recipe \(^{(1)}\)