

FOURIER TRANSFORM PLASMON RESONANCE SPECTROMETER

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By
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January 2017

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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M.S in Material Science and Nanotechnology

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Nanophotonics is an emerging field of research aiming to control interaction of light with matter in nanometer scale. Electrons localized on metallic nanoparticles generate localized plasmon oscillations with interesting optical properties that can be used for various sensing applications. Spectroscopic sensing using plasmonic particles could provide more detailed information, however it requires bulky spectrometers which limits its applications. In this thesis, a nanometer scale Fourier Transform Plasmon Resonance (FTPR) spectrometer is presented. FTPR spectrometer consists of a nanometer slit-groove or slit-ridge plasmon interferometer with varying optical path. The inherent coherence of the surface plasmons propagating through the sub-wavelength holes yield high contrast spatial interference pattern. FTPR spectrometer converts this spatial interference pattern in to spectroscopic information using Fast Fourier Transform (FFT) algorithm. In our design, there is no need for a bulky dispersive spectrometer or dispersive optical elements. We anticipate that high sensitivity of surface plasmons together with spectroscopic information and nanometer dimensions provides new avenues for plasmonic sensors.

Keywords: Nanophotonics, plasmonics, spectroscopy, FFT

ÖZET

FOURIER TRANSFORM PLAZMON REZONANS SPEKTROMETRESİ

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Malzeme Bilimleri ve Nanoteknoloji, Yüksek Lisans

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Nanofotonik bilimi ışık ile nanometre boyutundaki cisimin etkileşmesini kontrol etmeyi amaçlayan alan olarak bilinmektedir. Nanoparçacıkların üzerindeki elektronların plazmon osilasyon üretmesi ile birlikte ilginç optik özellikleri bir çok sensör uygulamalarında kullanılır. Plazmonik parçacıkları kullanarak ayrıntılı detaylı spektroskopik bilgi edilebilir, ama spektrometrelerin geniş hacimli olması plazmon uygulamalarını sınırılıyor. Bu tezde, Fourier Transform Plazmon Rezonans (FTPR) Spektrometresi geliştirilmiştir. FTPR spectrometre nanometreler büyüklüğünde kesik-oyuk veya kesik-çıkıntı şeklinde ışık yolu değişebilen plazmon interferometre içerir. Değişebilen ışık yolu dolayısıyla, dalga boyundan küçük delikten geçen ışık yüksek kontrastta girişim örüntüsü oluşturmaktadır. Biz ışığın spektroskopik bilgisini elde etmek için plazmonik interferometre kullandık. Bizim spektrometremiz boyutsal girişim örüntüsünü Hızlı Fourier Transform algoritması kullanarak spektroskopik bilgiye dönüştürmektedir. Bizim tasarımımızda, hacimli dağınımlı spektrometreye ya da dağınımlı optik parçalara ihtiyaç duyulmamaktadır. FTPR spectrometresi yüzey plasmonların hassasiyetine ek olarak spektroskopik bilgiyi kullanarak nanometre boyutunda yeni bir sensor olacağını öneriyoruz.

Anahtar sözcükler: Nanofotonik, plazmonik, spektroskopi, FFT

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In dedication to my family

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Chapter 1

Introduction

Surface plasmons polaritons (SPPs) are the collective oscillation of the free electrons at the metal dielectric interface. SPPs are excited by external electric field. When the energy and momentum of external light is matched with the momentum of SPPs, Surface Plasmon Resonance (SPR) is achieved. Resonance condition of this surface mode is highly sensitive to any changes in dielectric medium[1], which makes SPR unique for sensor applications. This uniqueness in SPR sensors grab the attention of many researchers. Various forms of SPR sensors with different excitation and detection methods have been demonstrated. Most common excitation methods such as grating coupling and prism coupling are introduced in 1960s [2]. These methods are widely used for biological and chemical sensing. Besides the superior sensitivity of SPR sensors, the localized electric field on the surface can enhance the detection.

In addition to chemical and biomolecular detection, extraordinary transmission due to SPPs is noticed by Ebbesen et. al in 1998[3]. In their study Ebbesen et al. used subwavelength hole arrays which display very unusual behavior of light transmission. Intensity of light transmitted through the holes was higher than classically predicted light intensity. This was another promising application of SPR in opto-electronics. Many other researchers came up with different types of optical and geometrical corrugations to observe extraordinary transmission. One of the famous corrugation is

bull's eye where subwavelength hole is located at the center of many circular grating grooves with increasing radius[4]. Incident light is coupled with SPPs excited from grooves and travels towards the subwavelength hole. Three times higher transmission is observed through the subwavelength hole than classically predicted transmission of light. Using the same idea with different scheme, where slit and groove pair are fabricated by focused ion beam, very high contrast interferometer devices are built to analyze physiological concentration of glucose[5].

There are three main challenges in the field of SPR sensors, (1) improving the detection sensitivity up to single molecule level, (2) miniaturization of the SPR sensors and (3) spectroscopic detection. Although there is a significant progress for the first two challenges, spectroscopic detection with SPR sensors remains outstanding challenge due to requirement of a dispersive optical elements.

Figure 1.1 shows mechanism of three different spectrometers. Working principle of conventional spectrometer is shown in Figure 1.1 on top. In these types of spectrometers, gratings or prism are used to separate spectrum into colors before measuring their intensity. Second type of spectrometer is shown in Figure 1.1 in the middle path. In this spectrometer, tunable broad band filters are used instead of grating and intensity light passed through each filter is measured individually. Last type of spectrometer mechanism is shown in Figure 1.1 on the bottom. It has totally different working principle comparing to previous ones. In this type of spectrometers, no dispersive optical elements or filters are needed. Broad band light is sent directly to interferometer without being separated. The interferogram fringe patterns which contain information about spectrum are detected by moving the mirror. Taking Fast Fourier Transform of these fringe patterns, spectrum is reconstructed back. Further explanation will be discussed in chapter 6.1.

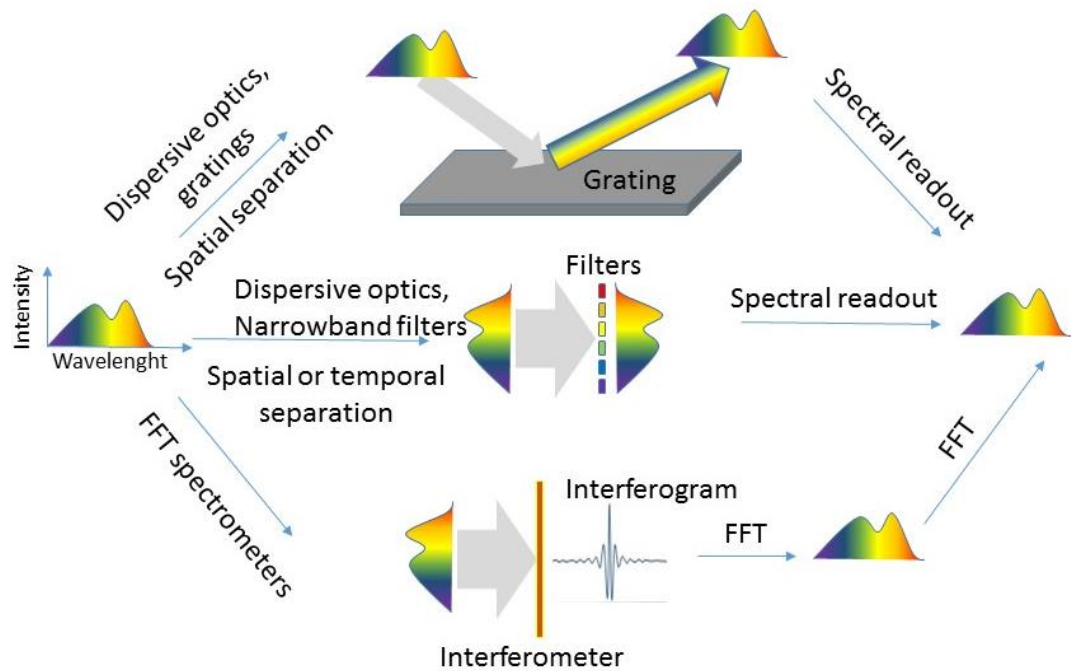


Figure 1. 1 Working principles of three different spectrometers are presented. On top grating based spectrometer is shown. Scheme in the middle presents narrowband filter spectrometer while figure at the bottom shows FFT spectrometers.

In this thesis, Fourier Transform Plasmon Resonance spectrometer is presented. We used a plasmonic interferometer to obtain spectroscopic information of light. Our spectrometer converts spatial interference pattern into spectroscopic information using Fast Fourier Transform Algorithm. We design a slit-groove or slit-ridge plasmon interferometer with varying optical path. Due to the varying optical path, the transmitted light yields a high contrast interference pattern which can be converted into spectroscopic information. In our design, there is no need for a bulky dispersive prism or dispersive optical elements. Our design is based on inherent coherence of the surface plasmons propagating through the subwavelength metal holes.

1.1 Organization of thesis

In this thesis, Fourier Transform Plasmon Resonance spectrometer is presented. The results of measurements are compared with the results of conventional spectrometer. Brief review of surface plasmon interferometers and physics lying behind the surface plasmons are also given in first chapters.

In Chapter 1, an introduction to surface plasmon resonance sensors and different types of spectrometer is made and motivation to Fourier Transform Plasmon Resonance is given.

In Chapter 2, optical properties of metal are theoretically explained. SPP excitation methods are also discussed.

Chapter 3 is a review of surface plasmon polaritons interferometer with experimental calculations

In Chapter 4, Focused ion beam (FIB), Electron induced deposition and application are briefly discussed.

In Chapter 5, we present subwavelength ridge-slit interferometer on gold made by FIB and electron induced deposition.

In Chapter 6, we present characterization of our Fourier Transform Plasmon Resonance spectrometer and compare them with the results of conventional spectrometer. Moreover, in this chapter both FTIR and static FTIR are discussed.

In Chapter 7, we discuss the limitations FTPR spectrometer.

In Chapter 8, brief summary of this thesis is given with some suggestions.

Chapter 2

Surface Plasmon Polaritons

Surface plasmon polaritons (SPP) are collective oscillation of electrons at the interface of dielectric and metal. The coupling of this oscillation with electromagnetic waves is called surface plasmon polaritons. Explaining the optical properties of metal will be a good step to understand SPP behavior.

2.1 Optical properties of noble metals

Optical properties of metals are dependent on frequency of incident light and can be described by complex dielectric function [6]. Electrons in conduction band generally considered as free electrons and they can move in bulk metal almost freely. Moreover, existence of electric field can oscillate these free electrons leading displacement of electron from their equilibrium point. Then individual electric dipoles are created. By adding all individual electric dipoles, polarization per unit volume is obtained. Polarization P is expressed by following equation.

$$\mathbf{P}(\omega) = \varepsilon_0 \chi_e(\omega) \mathbf{E}(\omega) \quad (1)$$

Where ε_0 is vacuum permittivity, $E(\omega)$ electric field dependence of frequency.

Due to the polarization, electric displacement takes place

Electric displacement can be written as:

$$\mathbf{D}(\omega) = \varepsilon_0 \varepsilon(\omega) \mathbf{E}(\omega) = \varepsilon_0 \mathbf{E}(\omega) + \mathbf{P}(\omega) \quad (2)$$

By substituting equation (1) to equation (2) we get following expression.

$$\varepsilon(\omega) = 1 + \chi_e(\omega) \quad (3)$$

From equation (3), it is obvious that dielectric permittivity of metal is strongly dependent to the frequency of external electric field.

2.2 Drude-Sommerfeld theory

Considering only effects of free electron without including interband transition will be a good start to explain SPPs behavior. Drude-Sommerfeld model works well for free electrons in metal.

$$m_e \frac{\partial^2 r}{\partial t^2} + m_e \Gamma \frac{\partial r}{\partial t} = e E_0 e^{-i\omega t} \quad (4)$$

m_e and e represents effective mass and charges of an electron respectively, frequency and amplitude of applied electric field are noted by ω and E_0 . $\Gamma = v_F/l$ where v_F is fermi velocity and l is the mean free path of electron between scattering events, and Γ is proportional to damping term of the equation. Substituting $r(t) = r_0 e^{-i\omega t}$ to equation (4) and using equation (3) we get:

$$\varepsilon_{Drude}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} \quad (5)$$

Where $\omega_p = \sqrt{ne^2/(m_e \varepsilon_0)}$ is plasma frequency. Equation (5) can be written in terms of real and imaginary parts as:

$$\varepsilon_{Drude}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} + i \frac{\Gamma \omega_p^2}{\omega(\omega^2 + \Gamma^2)} \quad (6)$$

By using the constant values of ω_p and Γ one can plot the imaginary and real part of permittivity. Figure 2.1 shows experimentally obtained dielectric constants for silver which fits theoretical dielectric curves well. In this figure, we can see that real part of dielectric constant of silver is always negative, which makes refractive index strongly imaginary. Imaginary refractive index prevents light penetrating to large extend.

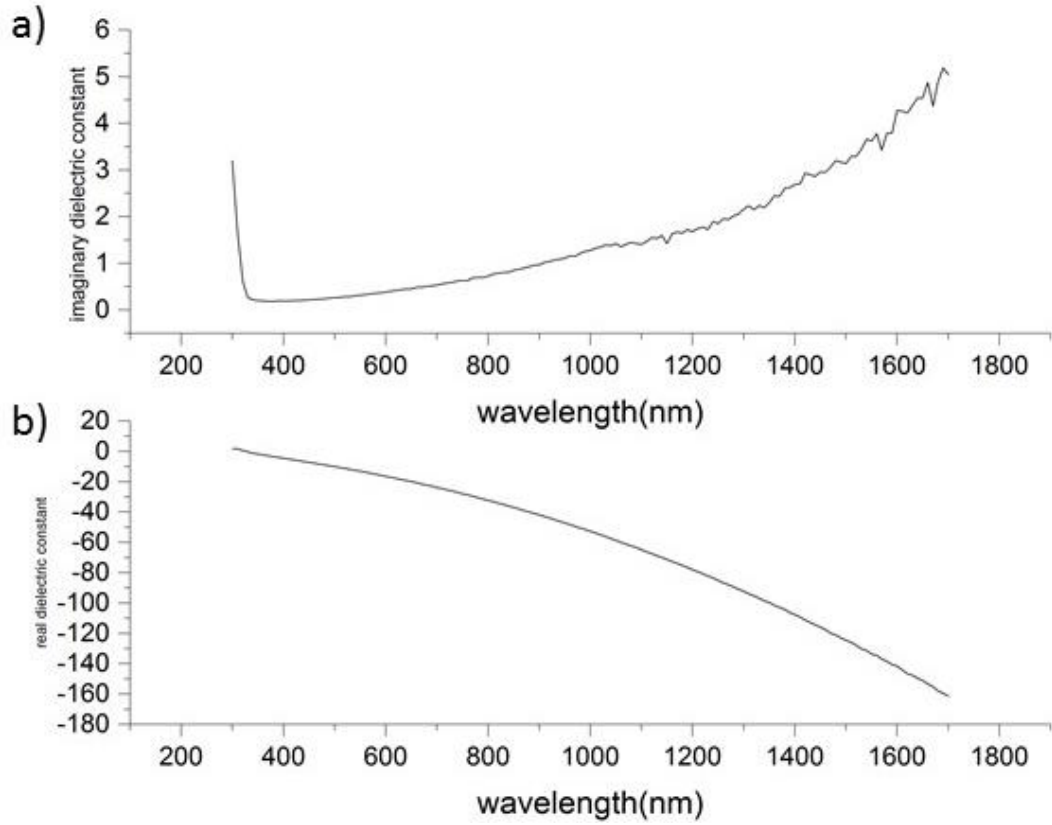


Figure 2.1 Graph of real and imaginary parts of dielectric constants of silver. Graph was calculated from experimental data of silver [7].

2.3 Interband transitions

Drude-Sommerfeld theory can explain the optical properties of metals infrared region. However, this theory is not enough to explain interband transition. Interband transition happens when the higher energy light is applied, typically around 2.5eV (500nm) for gold. Higher energy incident light can excite electrons from lower shells of the atom. These electrons are called bound electrons. Similar equation to Drude-Sommerfeld model with additional terms is used to explain optical behavior of metal including interband transition. Bound electrons excited from lower shells are not free, and they have restoring force.

$$m \frac{\partial^2 r}{\partial t^2} + m\gamma \frac{\partial r}{\partial t} + \alpha r = eE_0 e^{-i\omega t} \quad (7)$$

Where m is effective mass of bound electron. Effective mass of bound electrons and effective mass of free electrons are generally different. γ represents damping constant of radiating bound electrons, while α is standing for spring constant of restoring force to keep electrons around the atom. Using same, $r(t)=r_0 e^{-i\omega t}$ substitution as we did in previous chapter we get:

$$\epsilon_{\text{interband}}(\omega) = 1 + \frac{\omega_p^2}{(\omega_0^2 + \omega^2) - i\gamma\omega} \quad (8)$$

Where $\omega_p = \sqrt{\tilde{n}e^2/m\epsilon_0}$. $\tilde{n}$ is bound electron density, ω_p is plasma frequency and $\omega_0 = \sqrt{\alpha/m}$. As it is done above, equation is divided to real and imaginary parts as:

$$\epsilon_{\text{interband}}(\omega) = 1 + \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 + \omega^2)^2 - \gamma^2\omega^2} + i \frac{\gamma\omega_p^2\omega}{(\omega_0^2 + \omega^2)^2 - \gamma^2\omega^2} \quad (9)$$

When interband transitions of bound electrons are also considered, experimental and theoretical data fit each other well. As mentioned early sections of this chapter,

interband transitions play significant role. Moreover, importance of this transition can be also seen from the equation (9)

2.4 Surface plasmon polaritons at plane interface

Collective oscillation of electrons at the surface or at the interface is called SPP. To understand SPPs we deal with the interface of two medium. One of the medium has complex, frequency dependent dielectric function while other medium has real dielectric function. To describe surface plasmon polaritons at plane interface, homogenous solution of Maxwell's equation is used. Considering $z = 0$ coincides with plane interface, solution for Maxwell's equation will be:

$$\nabla \times \nabla \times E(r, \omega) - \frac{\omega^2}{c^2} \varepsilon(r, \omega) E(r, \omega) = 0 \quad (10)$$

Where $\varepsilon(r, \omega) = \varepsilon_1(\omega)$ when $z < 0$ and $\varepsilon(r, \omega) = \varepsilon_2(\omega)$ when $z > 0$. Electromagnetic field exponentially decreases on both sides of the interface with the increasing distance from interface. In this point, just p-polarization is examined, since s-polarized electromagnetic wave do not excite SPP. P-polarized plane waves are on both upper and lower parts of the interface. In another word, it is on both half spaces. For half spaces j can be taken as $j = 1$ and $j = 2$ and equation can be written as:

$$E_i = \begin{pmatrix} E_{j,x} \\ 0 \\ E_{j,z} \end{pmatrix} e^{ik_x x - i\omega t} e^{ik_{j,z} z}, \quad j = 1, 2. \quad (11)$$

Wavevector component will be held by following relation

$$k_x^2 + k_{j,z}^2 = \varepsilon_j k^2, \quad j = 1, 2. \quad (12)$$

Here $k = 2\pi/\lambda$, λ is wavelength in vacuum. Displacement field is not affected by source $\nabla \cdot D = 0$. This condition is given as:

$$k_x E_{j,x} + k_{j,z} E_{j,z} = 0, \quad j = 1, 2. \quad (13)$$

This helps to write equation (11) as:

$$E_j = \begin{pmatrix} 1 \\ 0 \\ -k_x/k_{j,z} \end{pmatrix} e^{ik_{j,z}z}, \quad j = 1, 2 \quad (14)$$

To simplify, the notation $e^{ik_x x - i\omega t}$ is omitted. Boundary conditions should match and function should be continuous at the boundaries to solve the equation. So, component of electric field which is parallel to the interface and component electric displacement which is perpendicular to the interface should be continuous. Then the next equation can be written as:

$$\begin{aligned} E_{1,x} - E_{2,x} &= 0 \\ \varepsilon_1 E_{1,x} - \varepsilon_2 E_{2,z} &= 0 \end{aligned} \quad (15)$$

Equations (13) and (15) will form four homogenous equations to calculate four unknown components. Possible solutions are obtained when determinant is zero. First solution of equations is when $k_x = 0$ and this does not explain excitation on the interface. Second solution is held when:

$$\varepsilon_1 k_{2,z} - \varepsilon_2 k_{1,z} = 0 \quad (16)$$

From the combination of equation (12) and equation (16) and substituting $k = \omega/c$ we get:

$$k_x^2 = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} k^2 = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \frac{\omega^2}{c^2} \quad (17)$$

One more expression for normal component:

$$k_{j,z}^2 = \frac{\varepsilon_j^2}{\varepsilon_1 + \varepsilon_2} k^2 \quad j = 1,2 \quad (18)$$

From equations (17) and (18) conditions for the existence of interface mode are derived. Imaginary part of dielectric function is taken as small to neglect them so solution for the equation will be easy. Since we are looking propagating wave at the interface, k_x^2 in equation (17) should not be imaginary. To fulfill this condition both product and sum of the dielectric functions should be both negative or positive. Moreover, to obtain solutions at the boundary of the interface, wavevector should be imaginary because of anticipated exponential decay. Wavevector will be imaginary when denominator of equation (18) is negative. Then the final conditions to get wave mode at the interface are:

$$\varepsilon_1(\omega) \cdot \varepsilon_2(\omega) < 0 \quad (19)$$

$$\varepsilon_1(\omega) + \varepsilon_2(\omega) < 0 \quad (20)$$

Here one of the dielectric functions must be negative and greater in magnitude than other. This condition will be held at the interface of noble metals such as gold and silver and some dielectric materials such as glass and air.

2.5 Properties of surface plasmon polaritons

In this part of the chapter properties of surface plasmon polaritons is discussed. Same equations from the previous chapters will be used to explain surface plasmon polaritons. We will consider the imaginary part of dielectric constant of metal due to scatterings and other types of losses. Let's take dielectric constant of metal as:

$$\varepsilon_1 = \varepsilon'_1 + i\varepsilon''_1 \quad (21)$$

Here both ε'_1 and ε''_1 are real. SPPs propagation happens at metal dielectric interface. We assume that our dielectric material has real dielectric constant, ε_2 , to avoid energy losses.

Because of the close relation between dielectric constant and wavenumber, complex wavenumber can be written as $k_x = k'_x + ik''_x$. SPP wavenumber is determined by the real part of wavenumber whereas imaginary part of wavenumber stands for the damping of SPP propagation at the interface. Using equation (17) and assuming $\varepsilon_1 \gg \varepsilon''_1$ real and imaginary parts of k_x are calculated as:

$$k'_x \approx \sqrt{\frac{\varepsilon'_1 \varepsilon_2}{\varepsilon'_1 + \varepsilon_2}} \frac{\omega}{c} \quad (22)$$

$$k''_x \approx \sqrt{\frac{\varepsilon'_1 \varepsilon_2}{\varepsilon'_1 + \varepsilon_2}} \frac{\varepsilon''_1 \varepsilon_2}{2\varepsilon'_1(\varepsilon'_1 + \varepsilon_2)} \frac{\omega}{c} \quad (23)$$

From equation (17) wavelength of SPP is written as:

$$\lambda_{SPP} = \frac{2\pi}{k'_x} \approx \sqrt{\frac{\varepsilon'_1 + \varepsilon_2}{\varepsilon'_1 \varepsilon_2}} \lambda \quad (24)$$

Here λ is the wavelength of light in vacuum.

k''_x defines propagation length of SPP along the interface and at the same time it is responsible for exponential decay of the electric field amplitude. This decay is main source of heat generated in metal. The equation for decay length from the interface is calculated by using equation (18) as:

$$k_{1,x} = \frac{\omega}{c} \sqrt{\frac{\varepsilon'^2_1}{\varepsilon'_1 + \varepsilon_2} \left[1 + i \frac{\varepsilon''_1}{2\varepsilon'_1} \right]} \quad (25)$$

$$k_{1,x} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_2^2}{\varepsilon'_1 + \varepsilon_2} \left[1 - i \frac{\varepsilon''_1}{2(\varepsilon'_1 + \varepsilon_2)} \right]} \quad (26)$$

2.6 Excitation of surface plasmon polaritons

Surface plasmon polaritons are propagating surface plasmons excited by external applied electric field. However, to excite SPPs, energy and momentum conservation should be fulfilled. Just illuminating light on material which has very smooth surface will not excite any plasmon polaritons, because of momentum mismatch. Figure 2.2 shows dispersion curves of light and SPPs. Dispersion curve light is shown in red while dispersion curve of SPPs is in green. From the graph in Figure 2.2 it is obvious that these two curves never meet with each other and SPPs wavevector (k_{spp}) is always bigger than wavevector of light(k). This is the explanation where momentum mismatch comes from. In order to excite SPPs one should overcome momentum mismatch first. There are two ways such as prism coupling and grating coupling to overcome this issue.

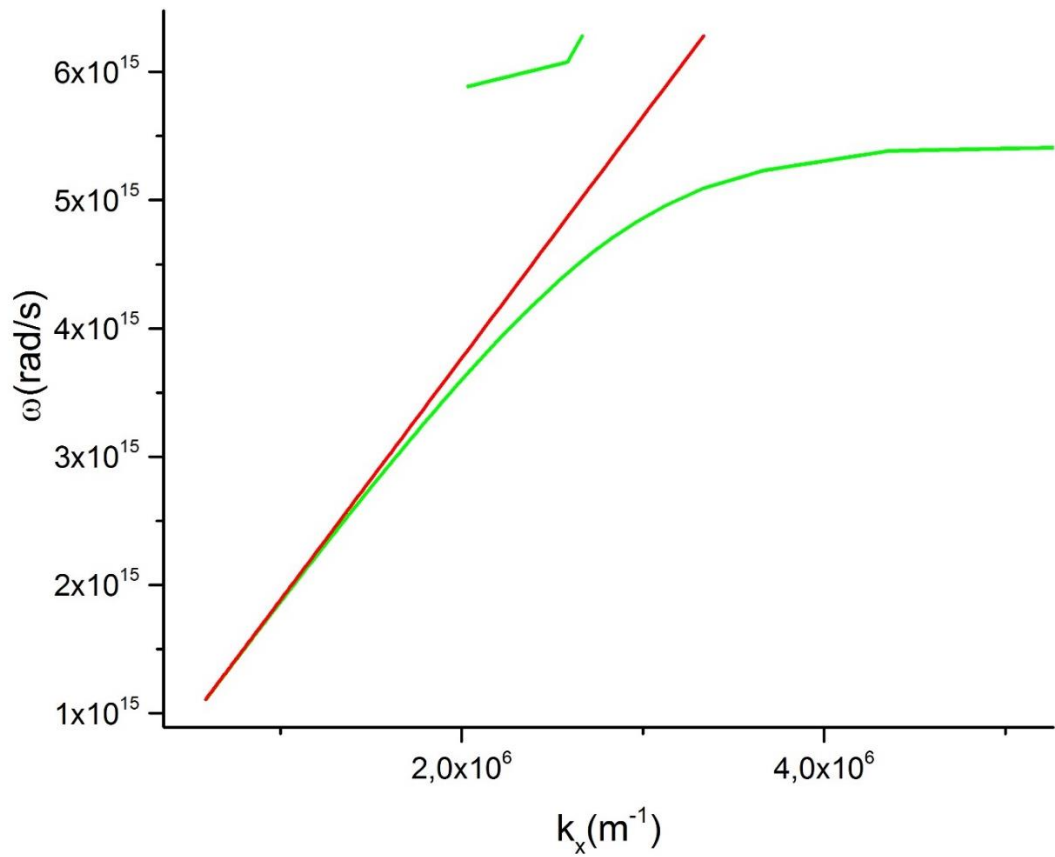


Figure 2.2 Calculated dispersion curve from experimental data for light and SPPs. Red line is standing for light dispersion curve while green is for SPPs. Wavevector (k_{spp}) of SPP is always bigger than wavevector (k) of light, which leads momentum mismatch on very smooth metal surface.

Prism coupling is extensively used method to excite SPP. Although there are two types of prism coupling, their working principles are almost same. First type is Otto configuration[8]. In Otto configuration, there is a gap between metal and prism. See Figure 2.3. Incident light is shown in red. At a critical angle, evanescent wave will be observed on the surface of prism and the tail of evanescent wave will excite the SPP. In figure 2.3 excited SPP is shown in violet. However, the gap between metal and glass should be arranged precisely to excite SPPs.

Kretschmann configuration is an alternative method to Otto configuration[9]. In Kretschmann configuration metal is directly evaporated on prism instead of having a gap between metal and prism as shown in Figure 2.4 [10]. This method solved the gap controlling problem. In this configuration thickness of metal should be controlled precisely, which is easy comparing to gap controlling in Otto configuration. Thickness of metal is important, since when it is too thin SPP will be damped very fast and when metal is too thick SPP cannot be excited due to the absorption.

In both Kretschmann and Otto configurations reflection of light detected to understand whether SPP is excited or not. When SPPs are excited, intensity of reflected light will be minimum. Minimum intensity is due to the destructive interference of surface plasmon and the reflected light. Moreover, when broad band wavelength is used, wavelength which is not reflected, considered to be converted to surface plasmon polaritons [6]. Both of these ways are widely used to observe biomolecular sensing and chemical interactions of specimen between metal.

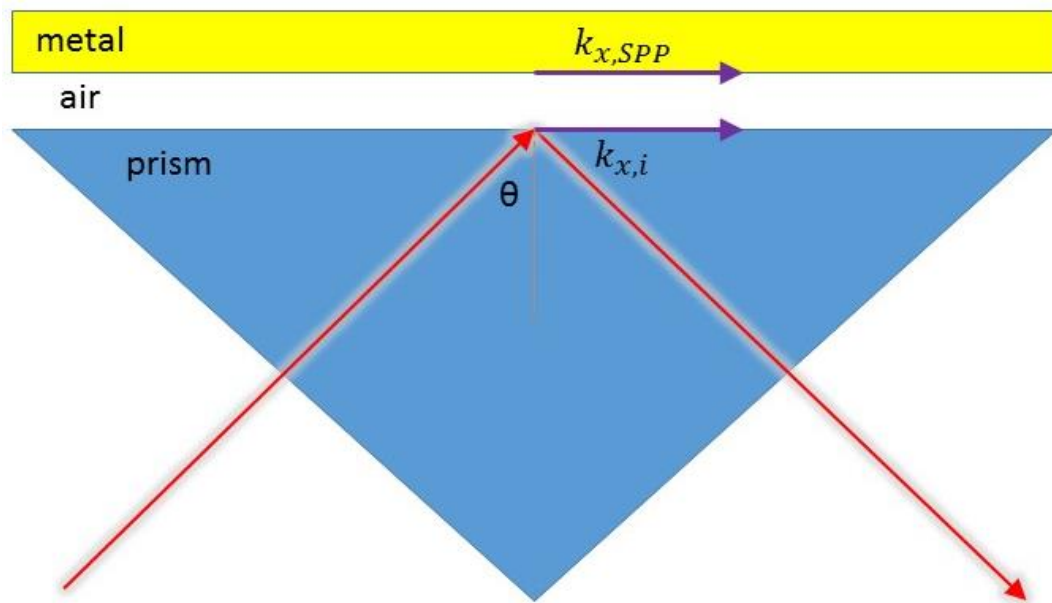


Figure 2.3 Otto configuration. Blue triangle stands for prism while yellow rectangle stands for thin gold metal film. Red line is incident light and violet lines show excited SPP. In Otto configuration, there is a gap between thin metal film and prism

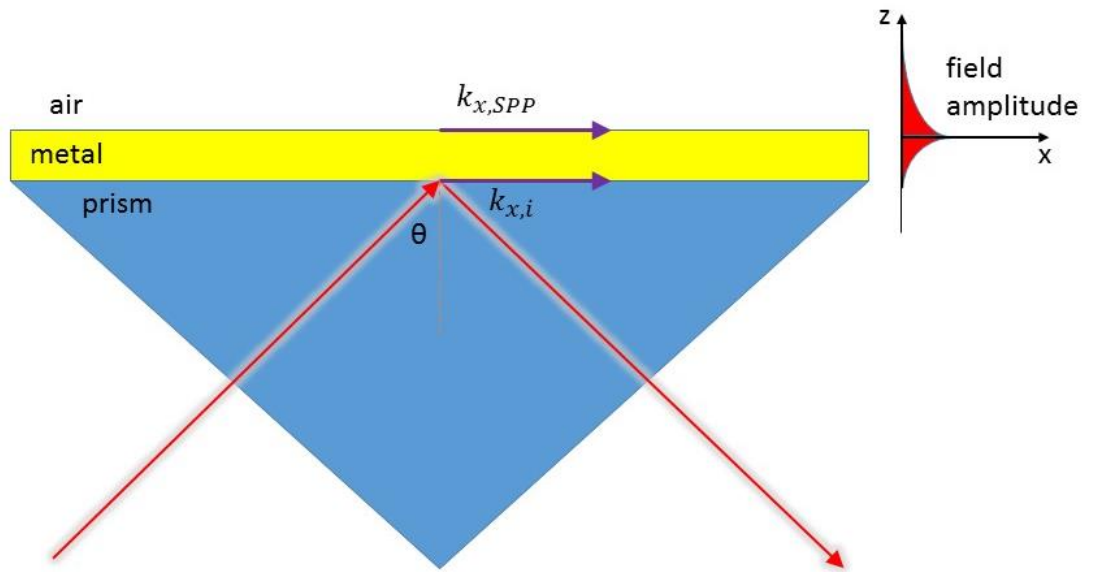


Figure 2.4 Kretschmann configuration. Blue triangle stands for prism while yellow rectangle stands for deposited thin gold metal film. Red line is incident light and violet lines stand for excited SPP.

Patterning the surface of the material is another way to excite the surface plasmons polaritons [10]. Figure 2.5 is schematic drawing of grating coupling. Periodically arranged grating helps to overcome the momentum mismatch.

Let's take SPP propagation constant as β , and periodicity of grating as a . For one dimensional structure SPP will be excited when the following condition is fulfilled:

$$\beta = k \sin \theta \pm n \frac{2\pi}{a} \quad (27)$$

Here n is an integer number ($n = 1, 2, 3, \dots$). Excitation of SPP will be detected by measuring the minimum reflected light, which is same with prism SPP excitation detection

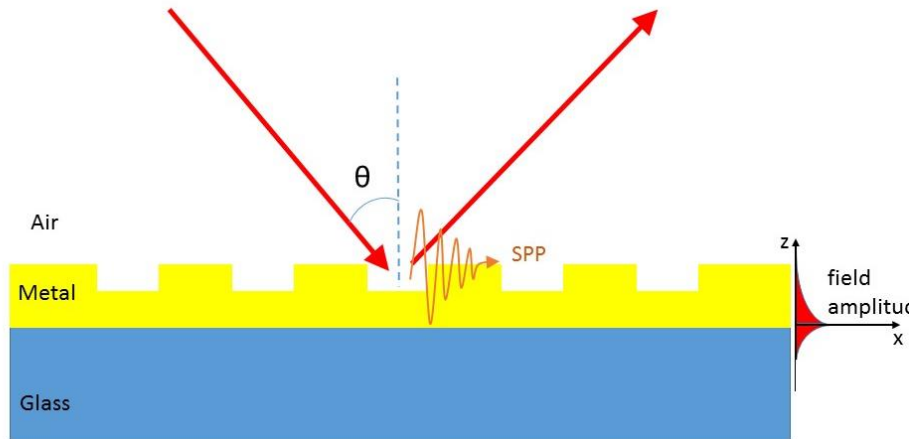


Figure 2.5 Schematic of grating coupling. To overcome momentum mismatch, periodical grooves are etched on the surface of metals. Impinging photons can excite SPP as shown in the figure.

Surface roughness and small defects are another way to excite SPP [11]. There is no need for grating which is an array of grooves or ridges on metal. SPP can be also excited using just ridge or groove instead of arrays, when phase matching condition is fulfilled:

$$\beta = k \sin \theta \pm \Delta k_x \quad (28)$$

Effects of groove and ridge on SPP are theoretically studied by G. Brucoli et. al. [11]. According to their study the depth of groove and height of the ridge are very important for the excitation of SPP.

2.7 Application of surface plasmon resonance

During the last four decades, we have seen development of optical sensors in research on biological interactions and chemical reactions. Some of the common sensors are ellipsometry, spectroscopy, interferometry and SPR sensors. Principle of all these sensors to measure absorbance, fluorescence properties of molecules and refractive index of medium. The main idea of this thesis is based on SPR sensors and following paragraphs mainly focus on applications of SPR sensors.

Potential of SPR sensors was recognized by I. Pockrand et. al in 1978 [12]. In addition, Gordon et. al. also observed process at the interface of the metal by looking attenuated total reflection (ATR) of impinging light [13]. In one of the studies in 1982 gas detection was also achieved using SPR sensors [14]. Since then scientists continuously doing researches on SPR sensors, they come up with different types of SPR sensors. Moreover, some of them even commercialized by several companies [15].

First type of SPR sensor is based on ATR method. In this method Kretschmann configuration is used and incident monochromatic light reflected at the interface of prism and thin metal layer. At critical angle this light evanescently tunnels the thin metal and excited SPR on the outer boundary of the metal[15]. Excitation of SPR will

happen at a critical angle and intensity of reflected light will be minimum at this angle. Since SPR is very sensitive to the medium, changes in the medium will change the angle of minimum intensity reflection.

Using SPR sensors concentration of chemical species can be found in liquid and gas without help of any reagent. Concentration of ethanol in water was calculated by this method[16]. Moreover, ATR based sensors also used to monitor biomolecular interaction on the surface of the metal. This study shows that SPR sensors can detect not only the concentration but also binding specificity and kinetic constants [17].

Kretschmann prism coupling was used and with broad band light for biosensing. Refractive index is determined from the changing resonance wavelength [18].

Although grating coupling sensors are not used as widely as prism coupling sensors, they have some advantages on prism coupling. Grating coupling sensors are easy to produce and low cost fabrication comparing to prism coupling sensors [19, 20]. In 2001 SPR based grating coupling device was presented by Brockman and Fernandez [20] . In their study, they used four hundred array sensing gold channels coated on plastic chip. Reflected light detected by CCD camera. This system further improved by other groups to detect antibody [21].

Chapter 3

Plasmonic Interferometers

In this chapter of thesis plasmon interferometers are presented. There are many studies and applications of surface plasmon interferometers [22-24]. SPPs are electromagnetic waves propagating on the surface of a metal and thus they can interfere constructively and destructively. As in the case of electromagnetic interferometry, high contrast constructive and destructive interferences strongly dependent on relative phase. In plasmonic interferometers, high contrast interference patterns are obtained due to the extraordinary transmission through the subwavelength aperture or slit. This extraordinary phenomenon is first observed by Ebbesen et. al. In their work, they have shown that SPP plays a very important role in transmission through subwavelength holes.

To understand how SPP interferometer works, extraordinary transmission through a subwavelength aperture should be understood first. In the following section, we will explain extraordinary transmission phenomenon.

3.1 Extraordinary transmission through subwavelength apertures

The extraordinary transmission firstly observed by Ebbesen et. al. They used subwavelength aperture arrays to observe extraordinary transmission phenomenon

[3]. This phenomenon has attracted attention of many researchers and they come up with many other geometrical corrugations such as hole arrays [25, 26] and holes surrounded by circular surface corrugations [27]. Moreover, light transmission through subwavelength apertures has been theoretically investigated [28].

Light can be described by a wave and a particle and thus diffraction theory can be used to explain light. However, diffraction of light is really complex even for very simple geometrical shapes of apertures, although transmission through aperture on opaque material is studied more than hundred years. Diffraction theory is explained in many books with different aspects [29]. We will discuss transmission through aperture for two cases. The first case is when the radius of aperture is larger than wavelength ($r \gg \lambda$). This phenomenon can be explained by classical diffraction theory [10]. Huygens-Fresnel principle can be used to study the nature of transition when radius of aperture is larger than the wavelength of light. When the radius of aperture much bigger than wavelength of impinging photons, transmission through aperture will be $T \approx 1$. We are not interested with this case. Extraordinary transmission occurs when $r \ll \lambda$.

There is analytical solution of transmission through subwavelength aperture suggested by Bethe and Bouwkamp for infinitely thin opaque metal [30, 31]. To have infinitely thin and opaque metal, conductivity of metal should be also infinite. However, this transmission is not allowed because real metal has finite thickness and conductivity. Moreover, opaque metal has thickness on the order of several skin depths and when material is thick enough, tunneling of the radiation is not allowed. Therefore, localized surface plasmons significantly influence the transmission phenomenon.

The light transmitted through the subwavelength circular holes was at least 2-3 times larger than classically expected transmission of light. This cannot be explained by just considering diffraction theory. The fact that transmitted light was higher than classically expected transmission suggests that transmission phenomenon is mediated

by SPP through the aperture [3, 32]. Moreover, extraordinary transmission is strongly dependent on shape of aperture, depth of groove and height of ridge [11, 32].

This phenomenon can be also observed using single aperture surrounded by ridges, grooves or any other corrugations with different geometrical shapes. One of the interesting surface corrugation is bull's eye, centric hole surrounded with circular grooves [33]. Grooves excite SPPs and it travels towards the hole and tunnels through the hole exciting far field electromagnetic wave.

In one of the previous studies, instead of holes, arrays of gratings were used to fulfill the phase matching of the SPPs with the incident beam light. In this experiment, they played with groove height in order to tune efficiency of coupling

To increase the transmission, geometrical dimensions of apertures can be optimized. By playing with geometry of nanoaperture, it is possible to determine the spectral position of localized surface plasmon (LSP). Due to the field enhancement at the edge of the aperture, transmission is increased. Moreover, using high index dielectric material and multilayer structures it is also possible to improve transmission through subwavelength aperture.

3.2 Plasmon interferometer

When light illuminated on a slit-groove interferometer, wavefront component on the groove, E_G , partially scatters SPP, which propagates towards the slit. Initial amplitude of scattered SPP is given by groove scattering coefficient, β_G . Reaching the slit after propagating distance d , SPP gains an additional phase [34]

$$\psi(d, \theta) = k_{SPP}d - k_0 \sin(\theta) d + \phi_1 \quad (29)$$

Where k_0 and k_{SPP} are complex wavenumbers for free space and for SPP, respectively. θ represents an angle of incidence, while ϕ_1 is total phase gained during the scattering. SPP interferes with E_S , which is component of wavefront on the slit. Total intensity I_{SG} transmitted through the slit groove interferometer is given by:

$$I_{SG}(d, \omega) = \langle |E_S(\omega) + \beta_G E_G(\omega) e^{i\psi(d, \theta)}|^2 \rangle \quad (30)$$

$$I_{SG}(d, \omega) = I_S(\omega) + \beta_G^2 I_G(\omega) e^{-\alpha d} + 2\beta_G e^{-\alpha d/2} |W_{SG}(\omega)| \cos\{\text{Re}\psi(d, \theta)\} \quad (31)$$

Where $\omega = ck_0$, c is speed of light in vacuum, α is absorption coefficient of SPP, $I_S(\omega) = \langle E_S^*(\omega) E_S(\omega) \rangle$ and $I_G(\omega) = \langle E_G^*(\omega) E_G(\omega) \rangle$ are spectral densities of incident wavefront on slit and groove, $|W_{SG}(\omega)| = \langle E_S^*(\omega) E_G(\omega) \rangle$, is cross spectral density relating the two field with angle brackets indicating averaging. In their study, Drew Morrill et. al. [34] measured quantity of $I_S(\omega)$ using an isolated slit. Assuming $I_S(\omega) = I_G(\omega)$, and normalizing equation 31 to $I_S(\omega)$, normalized transmitted intensity, $I_n(d, \omega)$, is generated:

$$I_n(d, \omega) = 1 + \beta_G^2 e^{-\alpha d} + 2\beta_G e^{-\alpha d/2} |\mu(d, \omega)| \cos\{\text{Re}\psi(d, \theta)\} \quad (32)$$

Here $\mu(d, \omega)$ is spatial degree of coherence. The magnitude of $\mu(d, \omega)$ is obtained from experimental data, determining visibility of the interference fringes:

$$\mu(d, \omega) = v(d, \omega) = \frac{|I_{max} - I_{min}|}{4\beta_G e^{-\alpha d/2}} \quad (33)$$

I_{max} and I_{min} are the maximum and minimum intensities after normalization, respectively

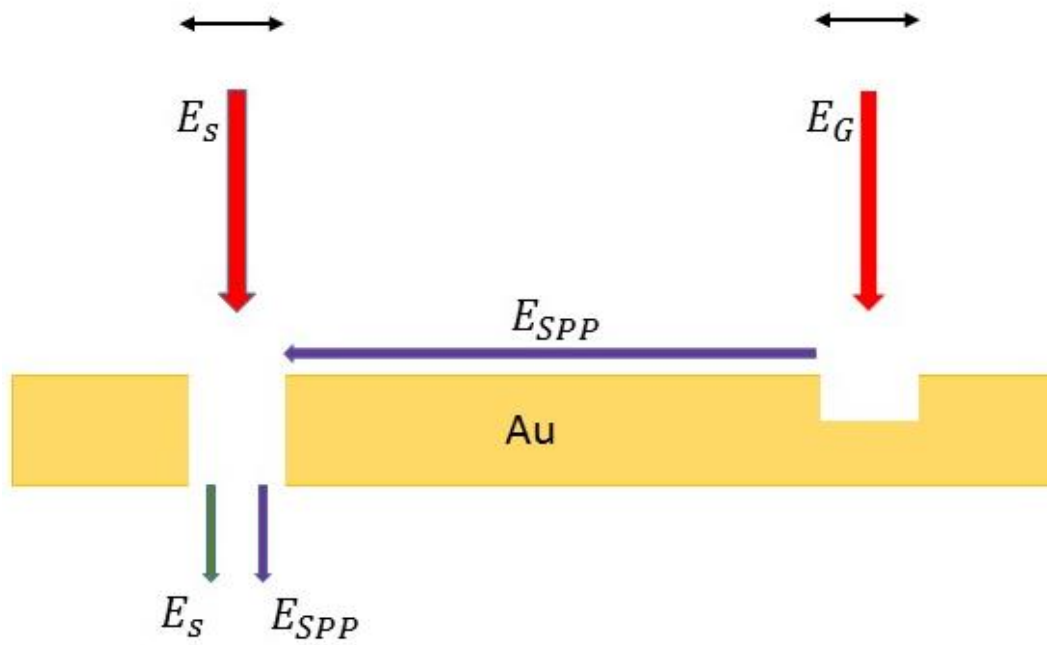


Figure 3.1 Incident beam is shown by red arrows while excited SPP is shown by a violet arrow. Polarization of the incident beam is polarized perpendicular to the groove line.

3.3 Application of extraordinary transmission

In the last part of plasmonic interferometer we will discuss extraordinary transmission and their applications as sensors. Extraordinary transmission is explained in our previous chapter. Many scientist come up with different methods based on nanohole arrays [35-37] and different applications of this transmission phenomenon.

In addition to nanohole arrays, slit-groove pairs also play a very important role in transmission and hence high contrast interferometry can be achieved. This slit-groove interferometers have also many applications [38, 39]. Surface plasmon interferometry, where slit groove pairs etched by focused ion beam, is also used to measure the group velocity of surface plasmon [39].

Plasmon interferometer is one of the very sensitive methods used to understand binding of molecules on surface. In one of the recent works sensing using refractive index has become very popular [40]. By observing the shift of the valleys of the interference high sensitivity is reported.

Feng et al used parallel groove slit groove configuration [5]. Multi-wavelength light is illuminated on the surface of GSG configuration and transmitted light directly observed through the slit. Transmitted light depends on the slit groove distance and wavelength of light. This sensor has very small sensing volume in several tens of femto liters.

One of the interferometry application is to measure the refractive index [1, 41]. Refractive index of ionic liquid is calculated by Yavas and Kocabas [1]. They have used slit-groove pairs on gold with small angle between them. SPPs excited from the groove interfere with SPP on slit and give high contrast interference fringes. From the period of this fringes refractive index of liquid can be calculated.

Chapter 4

Focused Ion Beam (FIB) and Electron Beam Induced Deposition (EBID)

4.1 Focused Ion Beam (FIB)

Focused Ion Beam (FIB) is technique used for ablation and deposition. By using FIB nano 3D shapes can be created. In principle, FIB is very similar to Scanning Electron Microscope (SEM), the only difference between them is the ion source, which is used in FIB, instead of electron source in SEM [42]. FIB instrument contains ion column, detectors, gas inlets, computer, ion sources and vacuum system. It contains three vacuum chamber. One pumping region is for ion source and ion column. Pressure inside the ion column is 10^{-8} torr. High vacuum is required to prevent the ion source from contamination. Second pumping region is for the detector. Last vacuum region is sample chamber where sample is held. To increase the mean free path of ion, high vacuum system is required. Otherwise, ions in the chamber will interact with junk

molecules inside the chamber and thus meaning of free path of the ions will be diminished.

Liquid ion sources are used in FIB. Ga is a very common ion source because of its low melting point. First ion source is melted and very high electric field is applied to ionize the liquid Ga. To accelerate ions, potential difference is applied and energetic ions transferred to the chamber through tungsten needle. Typical applied voltage to accelerate the Ga^+ range from 1keV to 50keV and current can vary from 1pA up to 10-20nA. To control the direction of ions, electromagnetic coils are used. Moreover, FIB has movable stage similar to SEM. Stage can move in x, y, z directions and can also rotate 360° .

Two types of detectors are commonly employed in FIB instrument. One detector is used to detect secondary electrons while other is used to detect secondary ions to image. In either case, applying large current is risky since ions are very massive comparing to the electron and they are destructive. Ion milling and etching starts even in very small applied current.

FIB instruments have dual platform column, where both electron and ion columns are located inside the chamber as shown in Figure 4.1. Electron column is needed to use the equipment as SEM to prevent the sample from being etched while imaging and FIB column is used for milling and etching. Angle between electron and ion column is 52° . Sample can be tilted 52° to make ion gun perpendicular to sample.

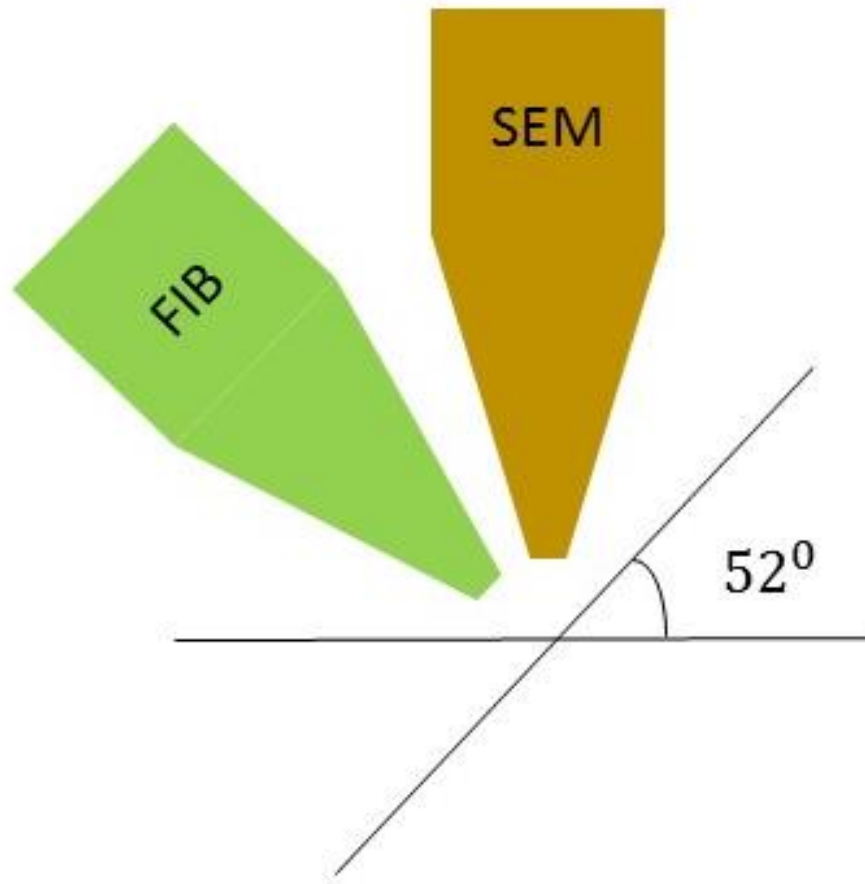


Figure 4.1 Schematic illustration of dual platform FIB. The angle between FIB and SEM is 52° . Sample is tilted 52° to make FIB column perpendicular to the sample

When accelerated ion particles interact with solid sample several processes takes place. Some of the ions will enter the solid and slow down while other ions are backscattered. Moreover, collision of ions may lead to defect formation, electron or photon excitation [43]. In addition, ion collision leads amorphization, crystallization, phase transformation and sputtering.

Energetic incident ion on solid surface transfers its kinetic energy to the atom of the solid. During this process, some of the atoms will be ejected from the surface of the solid. Many of these ejected atoms are generally neutral atoms and some of them are positively and negatively charged ions [43]. Figure 4.2 shows schematic representation of etching process in FIB. Incident accelerated ions are Ga^+ ions shown with blue and ejected gold atoms are shown in yellow. FIB is scanning from left to right.

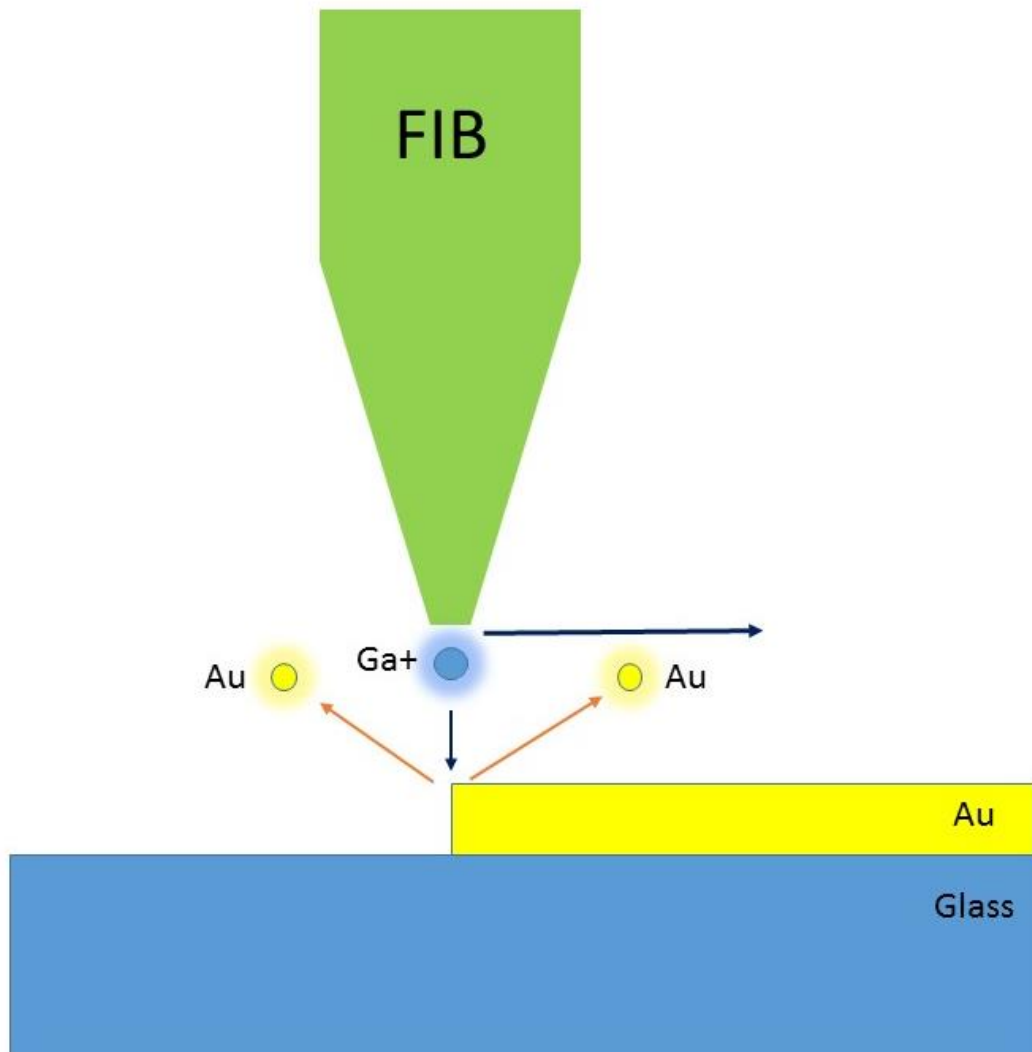


Figure 4.2 Schematic representation of the working principle of a focused ion beam. Highly energetic Ga^+ ions are focused on a gold thin film on a glass surface to generate localized gold etching.

4.2 Electron induced beam deposition

While using SEM for imaging, it is possible to see that the surface of the sample is contaminated. This is because of the deposition of junk atoms inside the chamber. This is unintentional deposition. However, carefully arranging gas injection controlled deposition is possible and it has very useful applications. Decomposition of gaseous molecules by electron beam and deposition of non-volatile fragment is called electron beam induced deposition (EBID). SEM and STEM are both used as accelerated electron provider. SEM has high accuracy and thus very smooth structures can be achieved. Precise nano 3D and complex structures [44] also created using EBID.

As gas injection precursor, liquid, solid and gasified materials are used. These materials are evaporated before they are introduced to the high vacuum chamber. Electron energy can decompose the molecules and deposit, generally secondary electrons are used to decompose. Figure 4.3 shows deposition mechanism of EBID. Gas precursor injects gaseous molecules and hence accelerated electrons decompose molecules. Non-volatile species are deposited on the surface while volatile species are pumped out.

There are wide variety of precursor materials used for FIB induced deposition but in this thesis, we only used Pt source. Although dual platform FIB is very precise and easy to control, a fabrication with FIB is a sequential process and thus large are fabrication is impossible and it is time consuming.

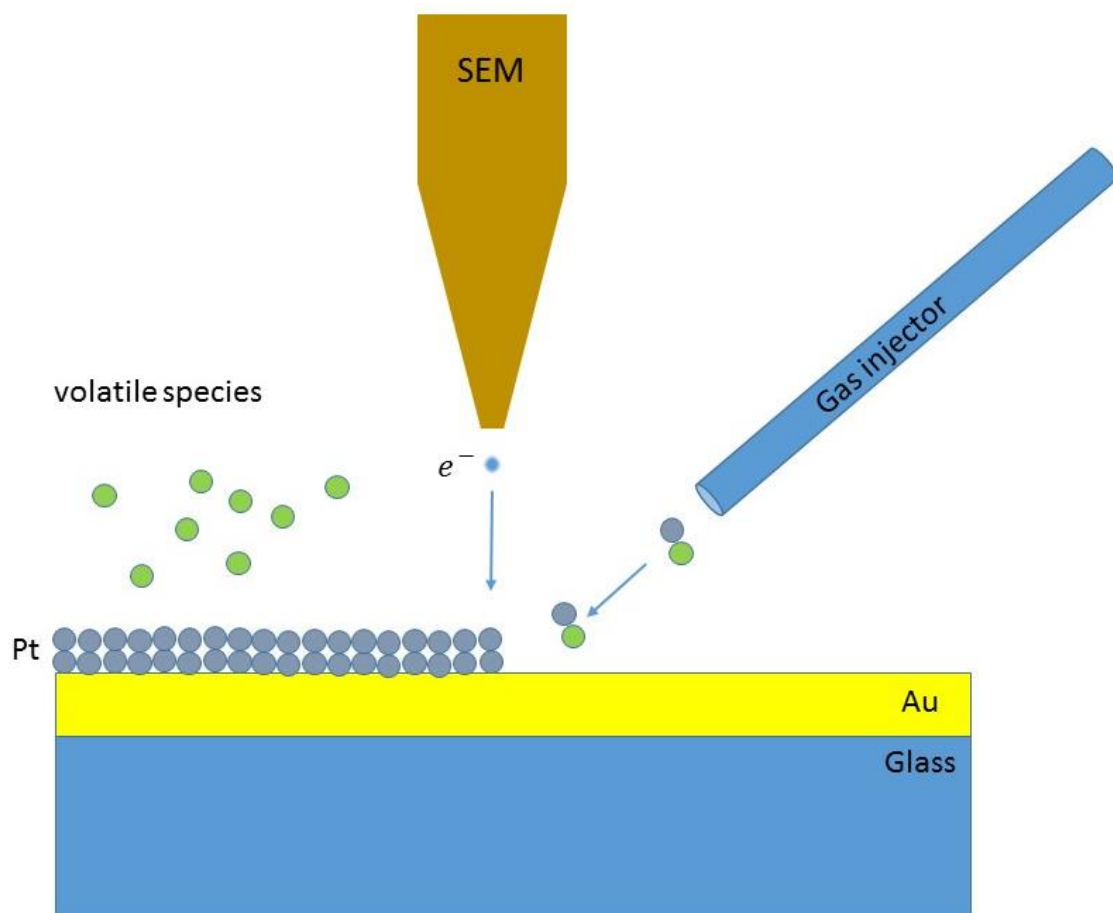


Figure 4.3 Schematic illustration of electron induced deposition of Pt on Au. Electrons decompose gas molecules coming from gas injector and therefore non-volatile species will be deposited while volatile species will be pumped out.

4.3 Focused Ion Beam applications

Nowadays, nanostructure fabrication becomes one of the essential part of nanotechnology and nanoscience since photolithography has limits around its wavelength of exposing beam. Moreover, photolithography needs a mask while FIB does not need any mask [45] to make nanofabrication on solid. FIB can etch sub 5nm structure which makes it very useful in fabricating nanostructures [46].

A. Hemamouche et. al. presented nanoholes and nanomasks on the surface of freestanding Si, SiN and SiO₂ which have few tens of nanometers thickness. They also make nanopores on atomically thin graphene and hexagonal boron nitride. It is claimed that FIB can reproducibly fabricate sub 10nm holes on these materials and this is reproducible.

Creating nanoholes on freestanding graphene can be used for gas permeation [47]. Celebi et. al. presented nanopores on the surface of freestanding graphene and they used for gas sieving.

Nanostructures fabricated by FIB are used to develop nanoimprint masks [48]. By etching Si with FIB and taking the replica of the surface of Si using PDMS they calculated the depth of nanochannels and nanoholes. The fabricated nanostructures on Si can be used many times.

Chapter 5

Fabrication of Plasmon Interferometer using Focused Ion Beam (FIB)

There are many sensor applications of surface plasmon polaritons. One of these sensor applications is plasmonic interferometer. Generally, plasmonic interferometers have slit-groove pairs created on a thin metal surface using FIB [49]. Groove is the main source to excite SPPs while the transmission of light is observed through the slit.

In this part of thesis slit-ridge interferometer on thin gold metal is presented. A slit on a gold thin metal surface is written by using FIB and Pt ridge is deposited by using EBID. Almost all of the plasmonic interferometers have slit-groove pairs, but we replaced groove with platinum ridge. Pt ridge efficiently excites SPPs and high contrast interference patterns are observed.

We used thermal evaporator to evaporate gold on glass and got very smooth 160nm thick gold film on the surface of glass. After thermal evaporation, gold film is etched

with FIB and Pt ridge is deposited using EBID. Figure 4.1 is a schematic representation of slit-ridge interferometer. Yellow thin film is gold on glass, and gap between films shows the etched slit. Blue rectangular line stands for deposited Pt ridge.

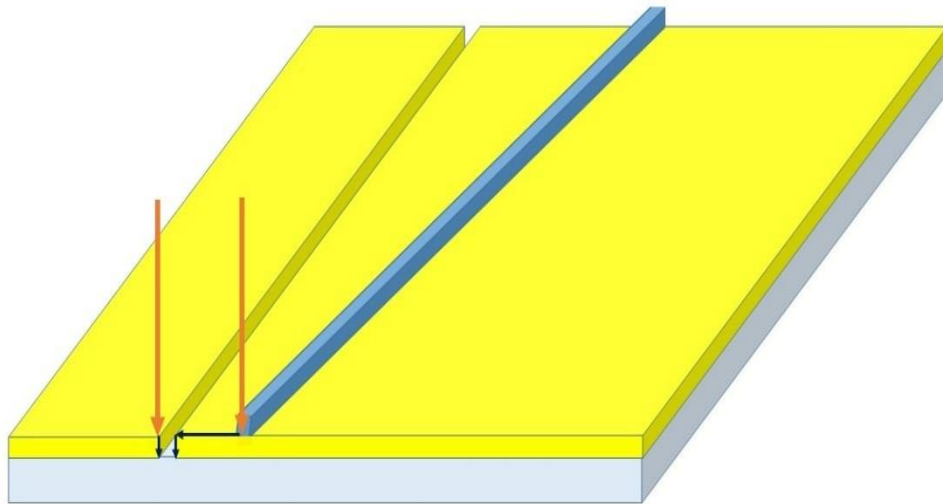


Figure 5.1 Schematic representation of ridge-groove interferometer. Yellow color represents Au on glass and gap between gold films is a slit etched by FIB. Blue long cuboid is deposited ridge and angle between ridge and slit is 5° .

5.1 Fabrication

Many experimental studies showed that the thickness of metal is very important and in order to have high contrast fringes, generally the thickness of metal thin film is around 200nm [38, 50]. In our interferometer device, thickness of gold film was 180 nm which is enough. We used FIB with Ga⁺ source to etch slit. We do not apply high current to Ga⁺ ions in order to avoid destructive etching. To etch efficiently we always keep voltage (30kV) and current (28pA) fixed. We only controlled the dimensions of slit with dwell time without changing the voltage and current. It should be noted here that dwell time is the time spend by incoming beam in the same position point.

We used dual platform FIB instrument in UNAM to deposit platinum ridge. As discussed in the 4th chapter, dual platform FIB instrument has both electron and ion columns. In this FIB instrument, both electron beam induced deposition and ion beam induced deposition can be done. Without taking out the sample from the chamber after the etching process we can immediately deposit Pt on the gold surface. We used electron induced deposition. Applied voltage and current of SEM were 5kV and 1.6nA, respectively. In deposition process, we have controlled the height of Pt ridge is controlled by dwell time as in the etching process.

Another good thing with this machine is that high quality SEM images can be simultaneously obtained. Figure 4.2 is a SEM image of a slit and the Pt ridge. The lengths of both ridge and slit are 150 μ m and scale bar is 20 μ m.

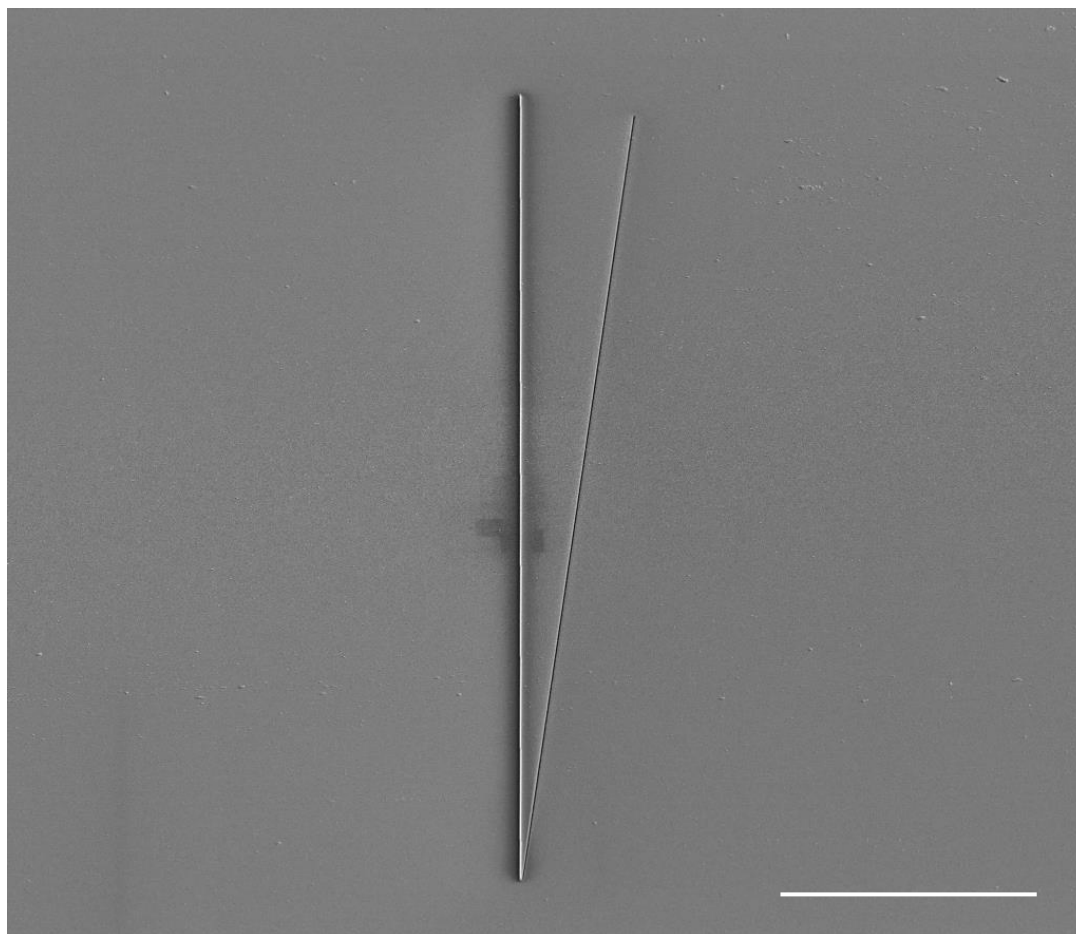


Figure 5.2 A SEM image of a ridge-slit. Lengths of both Pt ridge and slit are 150 μm and scale bare is 20 μm . Left solid line is platinum ridge and groove line is slit etched by FIB.

5.2 Experimental setup

In our experiment, we used laser with a wavelength 635nm and the visible part of the electromagnetic spectrum. Figure 4.1 shows the schematic illustration of our experimental setup. Light is monochromatic and polarized. It is important to notify that the incoming light should be perpendicularly polarized to our ridge to support SPPs. The Pt ridge on gold interferometer, is the main source to excite SPPs and to overcome momentum mismatch. SPPs are excited on Pt ridge and travel towards the subwavelength slit aperture. When SPPs reach to the slit, they tunnel through the subwavelength aperture. Since SPPs can scatter into the far field, they can be observed in the commercial optical microscope. We have collected the light using 20X objective of optical microscope. Before light reaches to CCD camera we have magnified the image 1.5 times.

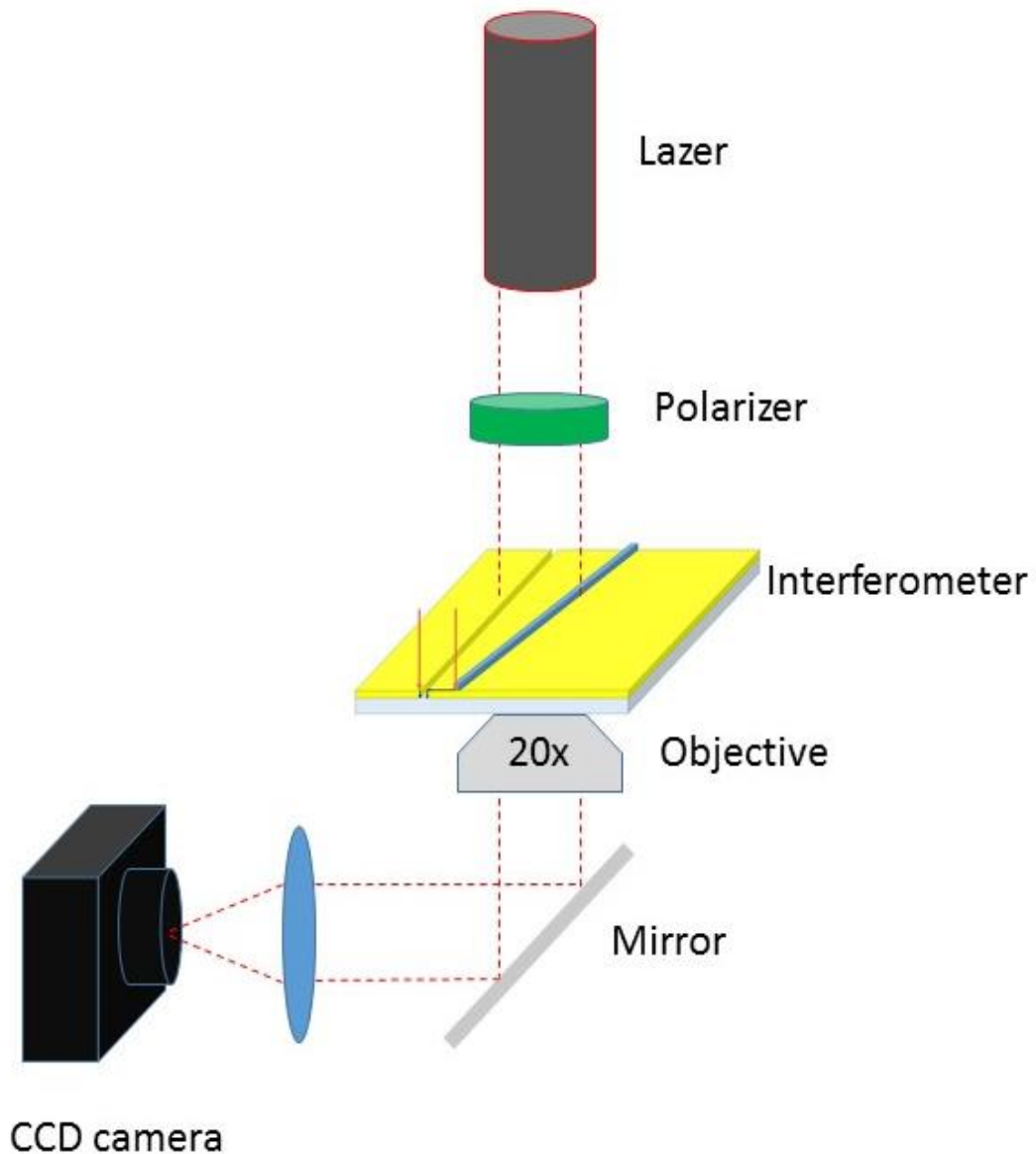


Figure 5.3 Schematic illustration of the experimental setup used to image SPPs on the gold surface. Lazer (635nm) is used as a monochromatic light source. Polarizer is used to polarize the light coming from the laser. Light scattered from the interference fringes is collected by an objective and sent to a CCD camera. CCD camera captures the optical image of the interference pattern.

5.3 Results

In this chapter of Thesis, we demonstrate an interferometer with a subwavelength ridge and groove. There are many examples in the literature about the slit-groove pairs but there is not any study about the slit-ridge interferometers [23]. We show fabrication advantages of slit-ridge interferometers. Controlling the height of deposited ridge is easier than controlling the depth of groove. Moreover, we observed very high contrast interference fringes using slit-ridge pairs.

Basically, we have used the experimental setup discussed above. The length of both slit and ridge is $100\mu\text{m}$ and angle between them is 5° . Monochromatic laser is used to excite SPPs. Excited SPPs on the ridge travel towards the slit and we see constructive and destructive interference patterns. When SPPs reach the slit they tunnel through the slit and excite far field electromagnetic wave which can be observed by an optical microscope. The image is taken by using a CCD camera.

Due to the constructive and destructive interferences of SPPs, we observed high contrast interference fringes. Interference fringe patterns are shown in Figure 4.4 a). We have taken a line profile of the fringe patterns and get an interferogram of image. The interferogram is shown in Figure 4.4 b). By looking at Figure 4.4 a and b, it is easy to conclude that we have very high contrast interference fringes.

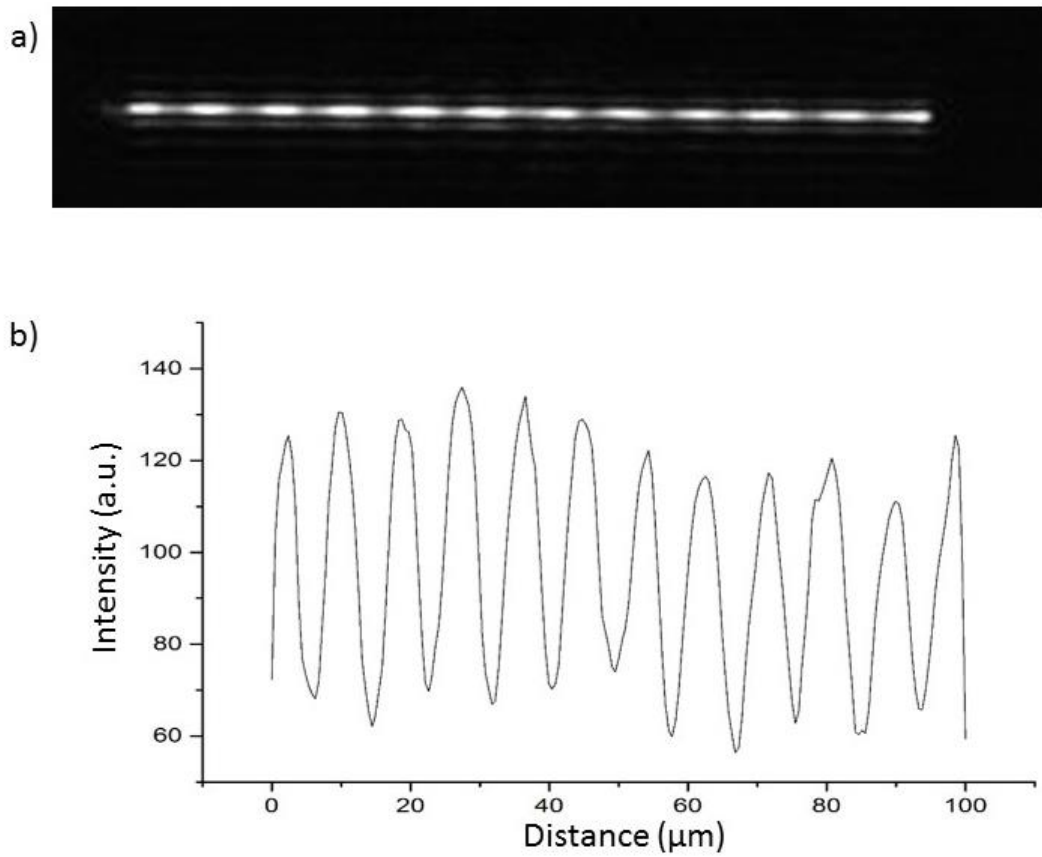


Figure 5.4 a) An image of interference fringes on the interferometry taken by CCD camera. b) The interferogram of the optical image.

5.4 Optimum thickness of platinum ridge for high contrast interference fringes

To find out the optimum height for high contrast fringes, we write array of slit-ridge pairs. We keep the dimensions of slit fixed and change the thickness of ridge. We create six slit-ridge arrays with lengths 100 μ m and thicknesses $t=20$ nm, 35nm, 80nm, 100nm, 135nm and 200nm. Figure 5.5 a) shows the interferogram of six interferometers on the same sample. From left to right, the thickness of the ridge increases. It is obvious that central interferometers have very high contrast interference patterns. As we have done before we took images of interferogram. In order to calculate the contrast of fringes we used Michelson contrast formula [51]:

$$Contrast = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} \quad (34)$$

We took average of maximum and minimum point on the interferogram and by using the formula above we calculate the contrast for each interferometer. Contrast versus height graph is shown in Figure 5.5 b). In the graph, it is clear that the highest contrast is achieved at the ridge thickness of 80-100nm. We keep the width of the Pt ridge same and it was around 130nm. Theoretically expected height to efficiently excite SPPs was 100nm [11]. We have compared our result with the result of our previous work [1]. We showed contrast of slit-ridge interferometer with dashed orange line in Figure 5.5 b), and it is showing that ridge-slit interferometer contrast is very high comparing to slit-groove interferometer. Moreover, after we found optimum height, we used it in all of our following experiments.

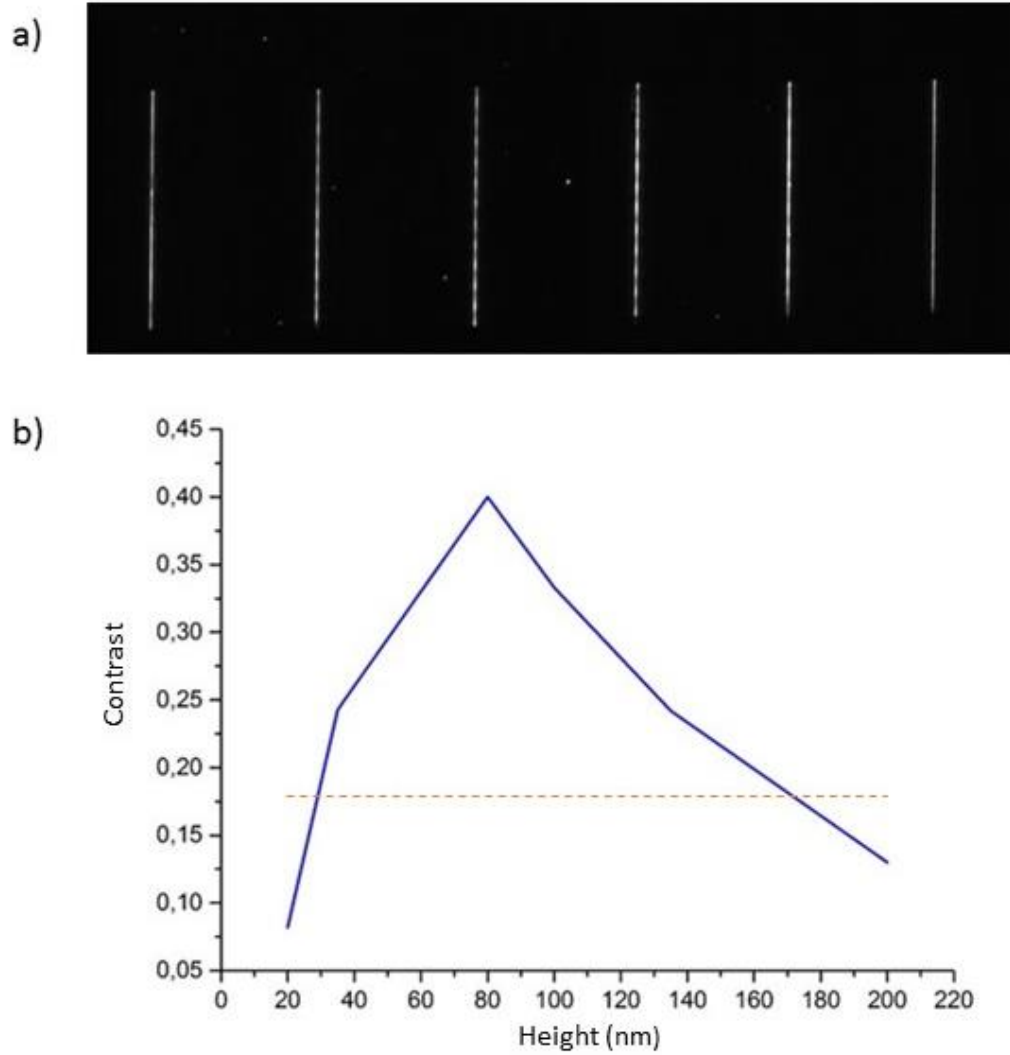


Figure 5.5 a) Optical images of interference patterns on the ridge-slit pairs. Six slit ridge pairs are presented with varying height ($t=20\text{nm}$, 35nm , 80nm , 100nm , 135nm and 200nm). b) Contrast thickness graph, maximum contrast achieved at thickness $t=80\text{-}100\text{nm}$ and orange dashed line shows contrast achieved from slit-groove pairs from our previous work.

5.5 Plasmonic decay

It is well known that SPPs decay exponentially into the dielectric and metal media. To observe decay of SPP, we fabricate slit and ridge of interferometer 200 μm long, which is two times longer than the length of our previous interferometers. The lengths of both slit and ridge have been increased up to 200 μm . Some part of SPPs is converted to heat during the travel at the metal dielectric interface. Increasing the length of the interferometer will be good solution to observe the decay of SPPs, since SPPs decay with increasing distance.

To analyze interferometer, we used the same setup. Optical images of interferometer are shown in Figure 4.6 a. By following the same process, we took a line profile to get an interferogram of the images. In Figure 4.6 b, it is noticeable that intensity of SPPs decreases with the increase in distance. We have observed collective oscillation of SPPs which is due to the oscillation come from diffraction of laser.

In addition, we calculated variation of contrast with the distance between the ridge and slit. As the distance increases, a decrease in the contrast of the image is expected. Length of the interferogram does not give the real distance travelled by SPPs, since SPPs excited on ridge and travel towards the slit. In order to find real distance travelled by SPPs, we multiplied the length of interferogram with a sinus of 5° , which is an angle between the slit and the ridge. After this multiplication, we calculated the contrast using the same Michelson contrast formula and plotted the contrast distance graph in Figure 4.6 c). In this graph, distinct decay in intensity is clearly observed.

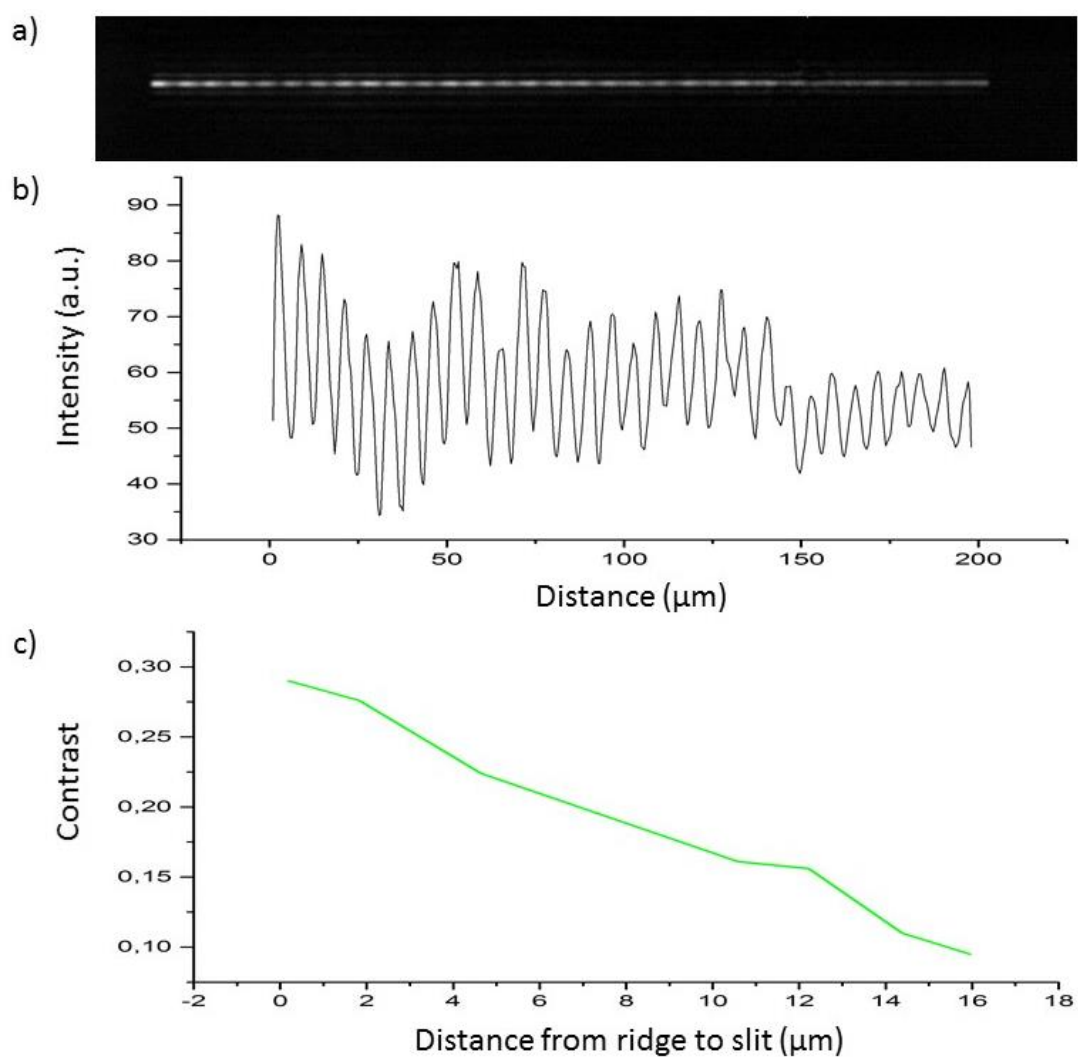


Figure 5.6 a) 200 μm long slit-ridge optical interference image. b) A line profile of the image. c) These is a decrease in the contrast with the increasing distance between the ridge and the slit.

Chapter 6

Fourier Transform Plasmon Resonance (FTPR) spectrometer

6.1 Fourier Transform Infrared spectrometer

The history of Fourier Transform Infrared Spectroscopy goes back to 1880s. In 1880s, Michelson invented an interferometer, which is known as Michelson interferometer. Using his interferometer, he accurately measured wavelengths of light, and he was awarded Noble Prize in physics in 1907. In fact, the discovered interferometer is designed to examine the existence of aether (medium where light waves propagate), and as a result Michelson showed that aether does not exist [52].

Michelson knew the potential of interferometer to obtain the spectrum, but time consuming calculations are needed to convert interferogram to spectrum. The invention of computers made Fourier transform calculations faster. J. W. Cooley J. W. Tukey invented the Fast Fourier Transform algorithm which is a mathematical algorithm. Joining of microcomputers and FFT algorithm leads to the development of FTIR that we know today.

An interferometer measures the interference of light. Incident light is first split by a beam splitter. Reflected lights from the movable and fixed mirrors recombine back. Half of the incident beam travels towards the detector. Beam interference is detected by a detector because of the path difference between the reflected lights from two mirrors.

The most famous interferometer design is Michelson interferometer. Michelson interferometer generally consists of one light source, one fixed and one movable mirror. Right arm of interferometer also includes detector as shown in Figure 6.1. Beam splitter is located at the center of the interferometer[52]. It partially transmits and reflects the beam. Beams reflected from both movable and fixed mirror recombine at the beam splitter and travel together towards the detector. Recombination of beams is a simple process, and it is just interference of light. When amplitudes of light interfere constructively, overall amplitude will become larger and when they interfere destructively, overall amplitude becomes smaller.

To theoretically calculate the optical path difference and interference, we assume that our source sends monochromatic light beam. We will get constructive interference when the optical path difference is $\delta = n\lambda$. At the same time, we will get destructive interference when optical path difference is $\delta = (\frac{1}{2} + n)\lambda$. Here n is an integer number and λ is wavelength of beam light. To achieve constructive path difference, mirror should move with distance $\delta = n\lambda$ and to achieve destructive interference mirror should be moved to distance $\delta = (\frac{1}{2} + n)\lambda$. By moving movable mirror back and forth interferogram is measured. This process is called a scan. Result of one scan is generally very noisy and to get rid of this problem sample is scanned many times. Finally, signal on interferogram is converted to spectrum using Fourier Transform. This is in fact the working principle of FTIR.

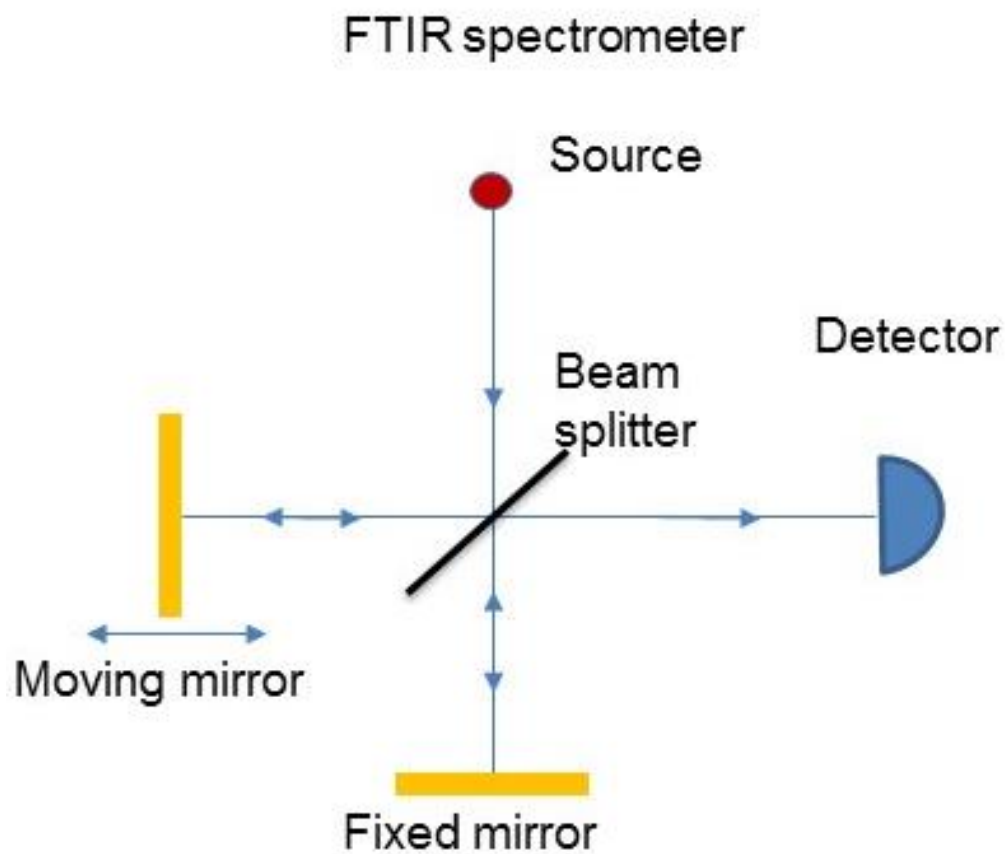


Figure 6.1 Schematic illustration of FTIR spectrometer. Light coming from a source split into two by using a beam splitter. Light recombines and travels towards the detector after it reflects from mirrors. Left mirror moves back and forward to scan the sample while the second mirror is fixed.

Fourier's theorem states that any function can be written in terms of sine and cosine waves. Fourier Transform is numerical calculation of superposition of sine and cosine waves. Interference patterns detected by Michelson interferometer is superposition of long band beam. At zero path difference point, intensity will be very high as shown in Figure 6.2. This interference signal involves all information for both intensity of light and wavenumber. By using Fourier Transform, interferogram (interference signal) is transformed to spectrum back. The right hand side shape in Figure 6.2 shows the spectrum after Fourier transform is taken.

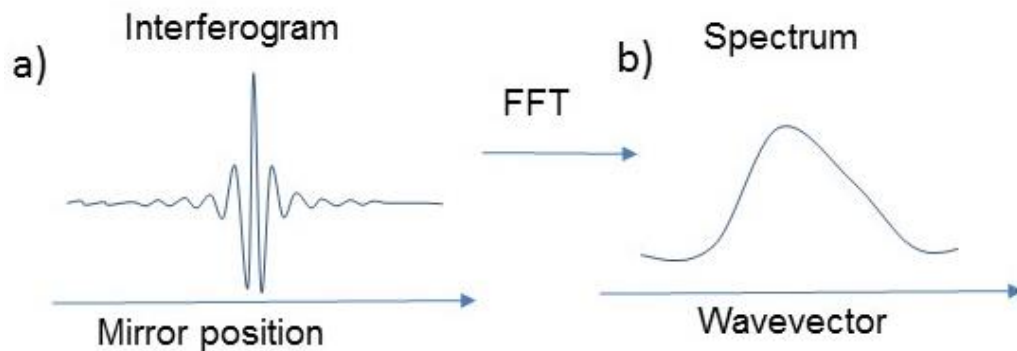


Figure 6.2 Interferogram of broad band beam and Fourier Transform of interferogram.

6.2 Static Fourier Transform Spectroscopy

Stationary interferometers draw the attention of researchers because of no moving parts and no velocity errors. In this type of interferometers, linear array of detector is prepared to read dispersed beam on them [53]. Intensity of signals on each detector is then measured. Taking the Fourier Transform of this signals, spectrum is regenerated.

To design static Fourier Transform spectrometer, birefringent components are used such as Wollaston prism [54]. Figure 6.3 is the schematic illustration of the static Fourier Transform spectrometer. Two similar Wollaston prisms are combined together to form a rectangular block. Wollaston prism is essential part to make path difference between two perpendicularly polarized components of the incident beam. Beam containing orthogonally polarized components passes through the Wollaston prism creating path difference between two components. Interference fringes are obtained at the parallel side of the prism due to the path difference. This interferogram of interference fringes is analogous with Michelson interferometer time domain interferogram.

Initially, lens was used to image the fringes onto detector array [55]. In recent studies, lens was replaced with second Wollaston prism and signals are directly recorded on Wollaston prism with multi-element detector array. Additionally, second prism eliminated distortion of interferogram [56].

After taking the Fourier Transform of signal detected by array of detector, spectrum is reconstructed. Resolving power of Fourier transform is strongly dependent on the maximum path difference, $\Delta\lambda$, of incident beam. Wavenumber resolution is

$$\Delta\sigma_{FWHM} \approx 1/\Delta\lambda. \quad (35)$$

However, maximum path difference is limited by the number of elements on detector. In this case resolution is dependent on the number of elements, N , on array of detector and short- wavelength operating limit, λ_{min} .

Then resolution is written as:

$$\Delta\sigma_{FWHM} \approx 4/\lambda_{min}N \quad (36)$$

In real life, there is little application of static Fourier Transform spectrometer. Every component of the spectrometer should be controlled very carefully. In stationary interferometers, slit is used instead of circular aperture. Slit and interferometer detector should be aligned exactly otherwise serious data loss occurs. Moreover, Static Fourier Transform spectrometer works well just for short wavelength (infrared and visible light).

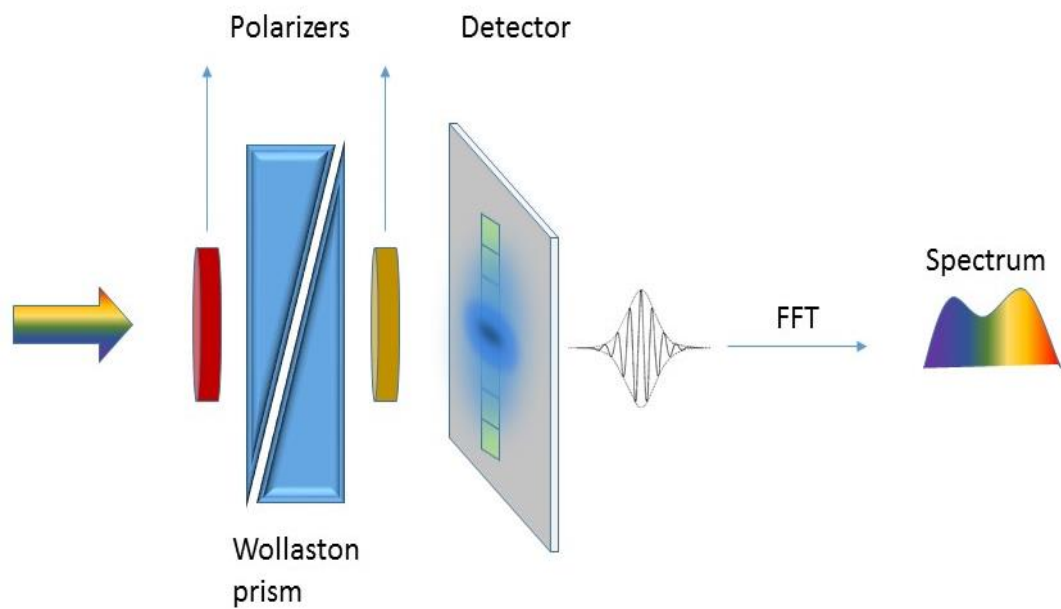


Figure 6.3 Schematic illustration of a static Fourier Transform spectrometer. Wollaston prisms are used to make phase difference between orthogonally polarized light. Signal is detected by array of detectors. FFT of signal is taken to reconstruct the spectrum

6.3 Wavelength of surface plasmon polaritons

Noble metals such as Ag, Au and Cu have almost the same plasma frequencies at around 8eV plasmon energy. However, we see all of these metals in different colors. To explain this, Drude model will not be enough. We should deal with both Drude and Lorentz models. $[\text{Xe}]4f^{14}5d^{10}6s^1$ and $[\text{Kr}]4d^{10}5s^1$ are the electron configurations of Gold and Silver respectively. In silver 5s electron is responsible for its metallic behavior. Since 5s and 4d electron orbitals are close to each other, they are located just below the Fermi level. Using electromagnetic wave, it is possible to excite 4d electron above the Fermi level. This excitation is called interband transition. Interband transition brings resonance which happens around $\omega_0 h/2\pi = 3.9\text{eV}$. Furthermore, interband transition affects real part of the dielectric constant and it becomes zero. Plasma frequency is observed when real part of dielectric constant is zero. Same kind of process happens in gold. However, it has a resonance at $\omega_0 h/2\pi = 2.5\text{eV}$, which corresponds to 500nm, and makes gold emit yellow color. Drude model works well for higher wavelengths but for lower wavelength close to resonance wavelength Drude and Lorentz models should be considered together with experimental data.

In this work, we have used silver instead of gold. In gold, resonance frequency is appeared at $\omega_0 h/2\pi = 2.5\text{eV}$, corresponding wavelength is around 500nm. In case of silver, it appears at $\omega_0 h/2\pi = 3.9\text{eV}$ and corresponding wavelength is around 360nm. For gold, it is difficult to observe SPP below 500nm. Our aim in this study is to use whole visible spectrum, and it is possible by changing our material from gold to silver. Additionally, following equations show that silver is a good candidate in the visible spectrum:

$$\varepsilon_{\text{Drude}}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} + i \frac{\Gamma \omega_p^2}{\omega(\omega^2 + \Gamma^2)} \quad (37)$$

$$\varepsilon_{\text{interband}}(\omega) = 1 + \frac{\dot{\omega}_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 + \omega^2)^2 - \gamma^2\omega^2} + i \frac{\gamma\dot{\omega}_p^2\omega}{(\omega_0^2 + \omega^2)^2 - \gamma^2\omega^2} \quad (38)$$

We have derived these equations earlier in chapter 2. From equation (37), we can see that $\varepsilon_{\text{interband}}(\omega)$ has extra terms. This extra terms affect the dielectric constant very much and effective refractive index is also influenced from this. Dielectric function is in close relation with refractive index and absorption coefficient ($n(\omega) + ik(\omega) = \sqrt{\varepsilon}$) which can be determined experimentally. We have used experimental data from book [57]. Using that data and following equations we can calculate real and imaginary parts of dielectric constant.

$$(n(\omega) + ik(\omega))^2 = \varepsilon = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (39)$$

From this equation, we get:

$$n(\omega)^2 - k(\omega)^2 = \varepsilon_1(\omega) \quad (33)$$

$$n(\omega)k(\omega) = \varepsilon_2(\omega) \quad (40)$$

By replacing n and k with values in experimental data, we calculated dielectric constants. Dielectric constants also change with wavelength or they change with frequency. Here, by using another equation from chapter 2 we calculated wavenumber of surface plasmon polaritons:

$$k_{SPP} = \hat{k}_x \approx \sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \frac{\omega}{c} \quad (41)$$

We know that $k_{SPP} = n_{eff}k_0$. Here n_{eff} is an effective refractive index, while k_0 stands for wavenumber of incident light since $k_0 = \frac{\omega}{c}$. From this equation, we get

$n_{eff} = \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}}$. Using the same experimental data, and taking $\epsilon_2 = 1$ (refractive index of air), we plot n_{eff} versus λ_0 graph in Figure 6.4. It is obvious that for both gold and silver effective refractive index vary with wavelength. However, for gold, refractive index changes dramatically at wavelength around 500nm while for silver refractive index changes at wavelength around 350nm. This used data also shows that silver is a good candidate for full spectrum interferometer.

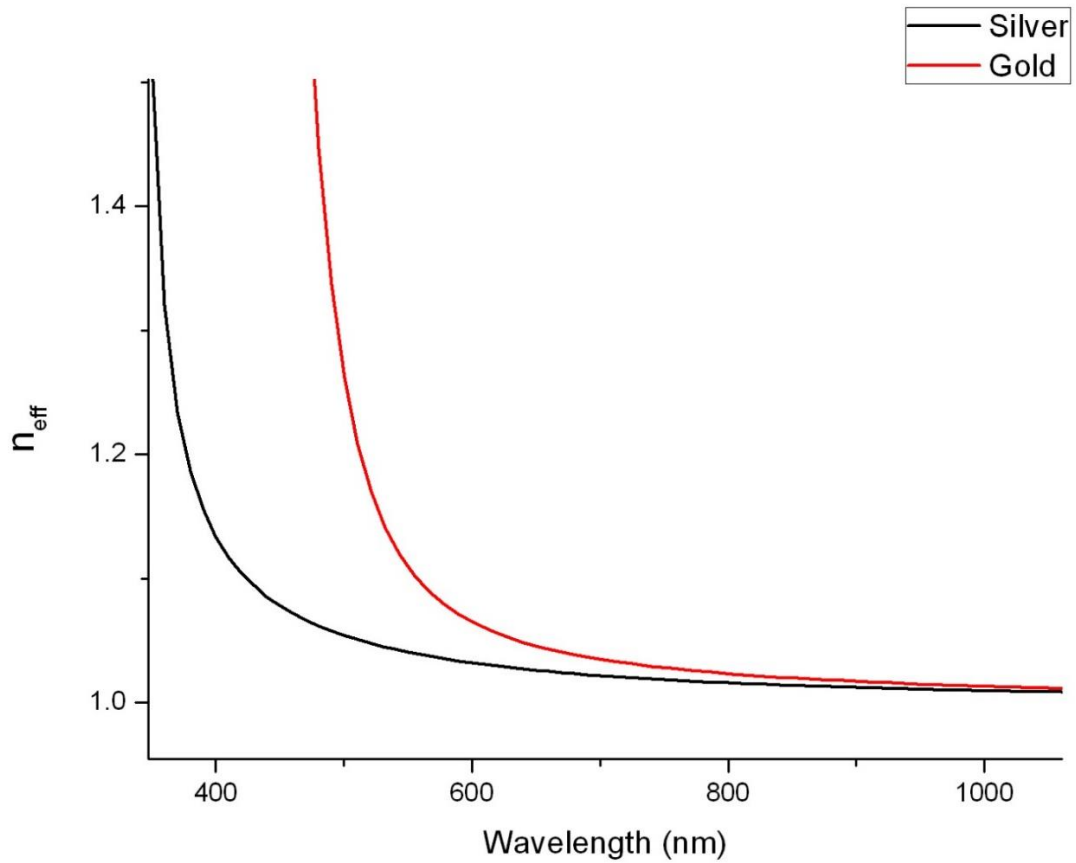


Figure 6.4 n_{eff} versus wavelength graph. Effective refractive index of gold changes dramatically around 500nm, and for silver it is lower (350nm).

From equation 22, we derived following equation:

$$\lambda_{SPP} = \frac{2\pi}{\tilde{k}_x} \approx \sqrt{\frac{\tilde{\epsilon}_1 + \epsilon_2}{\tilde{\epsilon}_1 \epsilon_2}} \lambda \quad (42)$$

Equation 24 can be written as $\lambda = \sqrt{\frac{\tilde{\epsilon}_1 \epsilon_2}{\tilde{\epsilon}_1 + \epsilon_2}} \lambda_{SPP}$. By substituting $n_{eff} = \sqrt{\frac{\tilde{\epsilon}_1 \epsilon_2}{\tilde{\epsilon}_1 + \epsilon_2}}$ we obtain $\lambda = n_{eff} \lambda_{SPP}$. This equation suggests that wavelength of incident light and the wavelength of SPPs are not the same. Incident beam excites SPP with different wavelength. To clarify the wavelength differences and to avoid the wavelength confusion, we present schematic sketch of incident beam and SPPs wavelengths in Figure 6.5 a. We plot SPPs wavelength versus incident beam wavelength graph in Figure 6.5 b for gold and silver using the same experimental data used above. In graph, we notice that wavelengths of SPP and incident light are not same. For our further studies, we used 4th order polynomial fitting to SPP wavelength versus incident light wavelength graph. Polynomial function is given below:

$$f(x) = 302.56927 - 0.43414x + 0.00275x^2 - 2.3779 * 10^{-6}x^3 + 7.72191 * 10^{-10}x^4 \quad (43)$$

Where x is the function of λ . This function is for silver and it will be used in our spectrum results.

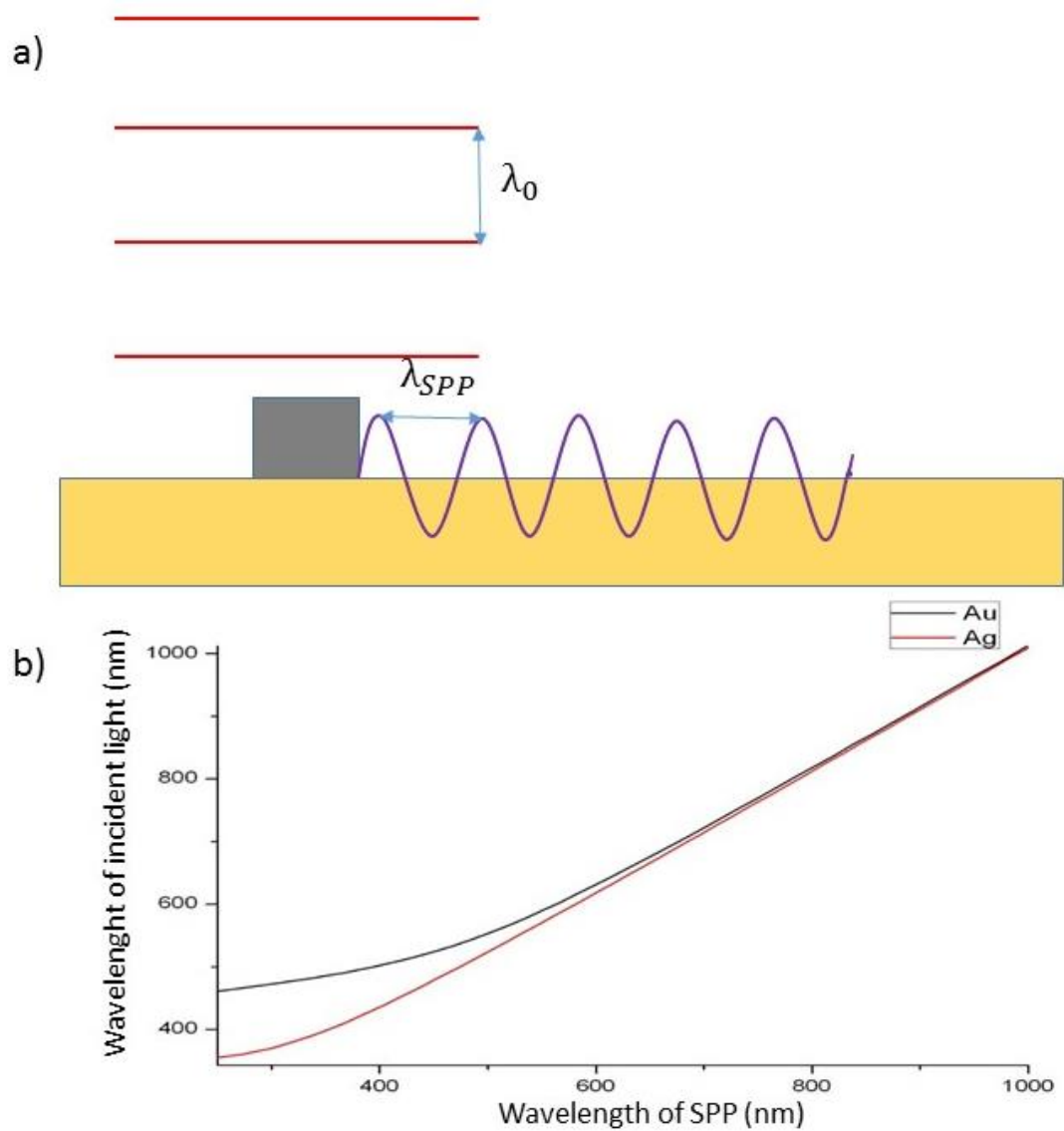


Figure 6.5 a) Excitation of surface plasmon polaritons. b) Incident wavelength versus SPPs wavelength graph calculated from experimental data.

6.4 Fourier Transform Plasmon Resonance spectrometer

In this chapter, we will discuss Fourier Transform Plasmon Resonance (FTPR) spectrometer. SPR sensors have many applications starting from molecular detection to measuring refractive index. Each of these devices can just measure either minimum reflection or transmission. For example, slit groove interferometer can measure refractive index of ionic liquid [1]. There are a lot of other application of SPR. However, to our knowledge, there is not only Fourier Transform Plasmon Resonance (STPR) spectrometer. The idea of FTPR spectrometer is the same with FTIR. In FTIR, interference patterns of light are detected in detector. Taking the Fourier Transform of this signal, spectrum of light is reconstructed. Basically, we will do same operation from different perspective in our FTPR spectrometer.

We here demonstrate Fourier Transform Plasmon Resonance spectrometer. In our device, we used slit-ridge interferometer, which is the same with the slit-groove interferometers. We observed very high contrast interference fringes due to the constructive and destructive interference of SPP. By taking line profile of this interference patterns, we got interferogram of periodical fringes. As it is done in FTIR, we took the Fourier Transform interferogram and rebuilt the spectrum back. We examined both monochromatic and broad band light in our experiment.

We changed our material from gold to silver due to the the limitations of gold listed above. We repeated the same steps on silver as we did on gold. We used the same experimental setup with laser (635nm) and obtained high contrast fringes on silver. Figure 6.6 a and c show interference fringes on silver interferogram. Length of both interferometers are the same (100 μ m), however, angles between slit and ridge are different for two images 5 $^{\circ}$ and 10 $^{\circ}$, respectively. Figure 6.6 b) and d) are the interferograms of images in Figure 6.6 a) and c). From this interferograms, it is also obvious that we have high contrast interference fringes. We discussed gold in our previous chapter, and we showed that SPP on gold decays very fast. From both interferogram images, it is clear that on silver SPP decays slower than on gold. This

was one of the main idea to change the material from gold to silver. Fortunately, interferogram results were promising to use silver in FTPR spectrometer

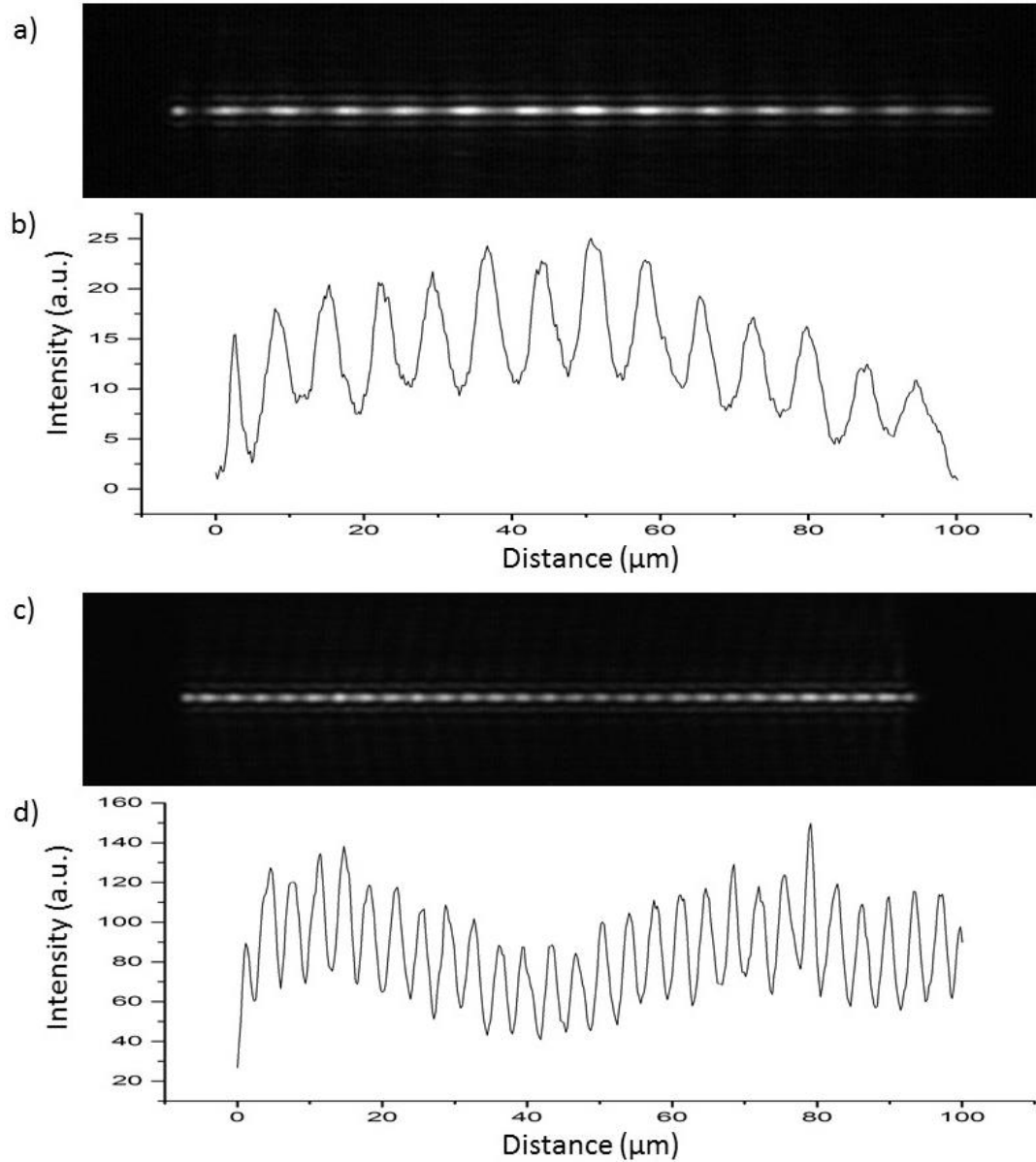


Figure 6.6 Optical images and interferograms. a) and c) optical images of interference fringes on different interferometer with angles 5° and 10° . b) and d) interferograms of optical images in a) and c).

Our next step was to take Fourier transform of interferogram of interference fringes. Before taking Fourier Transform of interferogram, we did one more operation to fringe patterns. Interference fringes on the slit do not give the real distance travelled by SPP. SPPs excited on the ridge and propagated towards the slit. Therefore, before taking Fourier transform of the interference fringes, we converted interferogram to real SPP interferogram by multiplying it with $\sin(\theta)$:

$$d = L * \sin(\theta) \quad (37)$$

Where L is the length of slit, d is the distance travelled by SPPs, and θ is the angle between slit and the ridge.

We took Fourier transform of data to rebuild spectrum. Result of Fourier Transform was very promising but it did not appear at the expected part of the spectrum. It is shown in Figure 6.7 with black color. We used monochromatic laser with a wavelength of 635nm. Although spectrum is sharp stating for monochromatic light we obtained spectrum at around 620nm. This change came from effective refractive index of silver. Using discussed effective refractive index we calculated corresponding SPP wavelengths to each part of illuminating beam wavelength and plotted the graph of SPPs wavelength versus incident beam wavelength. We also used 4th order polynomial function to fit the data, which is in equation 36. Multiplying each point of spectrum with the same polynomial function, we solved spectrum shift problem and spectrum is moved to around 635nm, which is the wavelength of the laser. Red color in the graph in Figure 6.7 is the spectrum after we multiplied with polynomial. On the same graph, blue color shows the spectrum taken from the conventional spectrometer. Comparing FTPR spectrum and spectrum of conventional spectrometer we see that FTPR spectrum is much broader. It is due to the number of data points which affect resolution very much. We will briefly explain these technical limitations in our discussion.

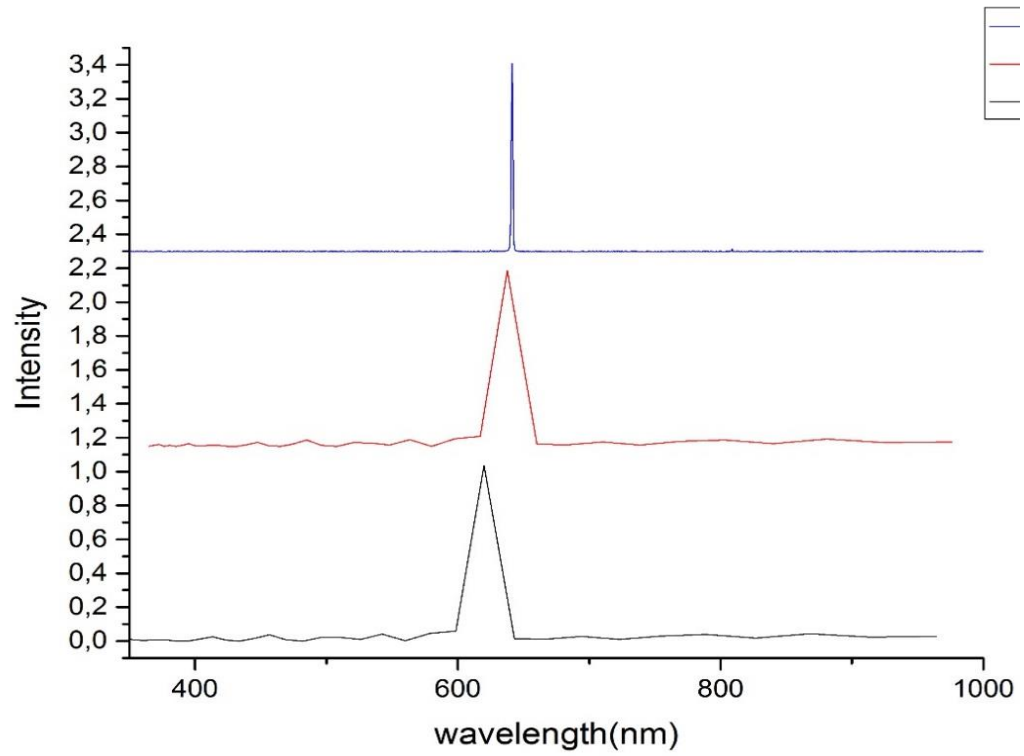


Figure 6.7 FTPR spectrum results. Black line spectrum of SPPs before multiplying effective refractive index, red line represents spectrum after SPPs spectrum is multiplied with effective refractive index. Finally, blue line is spectrum of laser taken by using conventional spectrometer.

We will continue our study with FTPR spectrometer for broad band source. In this part of the study, we made small change in our experimental setup. We have replaced laser with a very broad band source, which can emit light starting from 400nm to 900nm. We used filters to control the spectrum of source. Figure 6.8 is schematic illustration of our experimental setup. Various types of 10nm bandpass filters are followed by polarizer. Since light should be TM polarized to excite SPPs. Light transmitted through the interferometer slit is collected by an objective lens and images are taken by a high sensitive CCD camera.

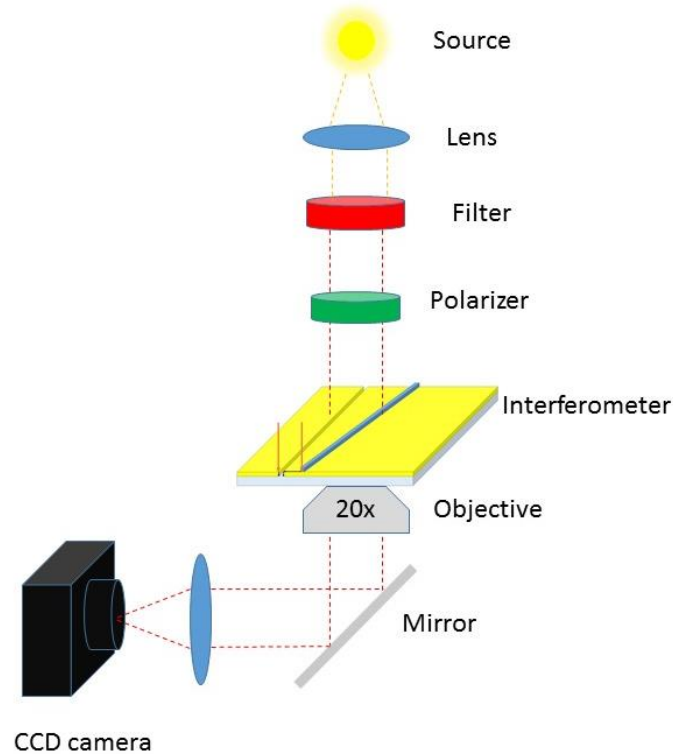


Figure 6.8 Schematic illustration of the experimental setup for broad band source. Broad band source is used instead of laser. Polarizer is used to make light TM polarized. Interference fringes are observed on the interferometry and far field light is collected by 20X objective lens. Then high quality images are taken by a CCD camera

Changing filters one by one, we observed fringes with different periods. In our experiment three different bandpass (10nm) filters with different cut off wavelengths (600nm, 700nm and 800nm) are used. By using 20X objective, we magnify and take images using high sensitive CCD camera. We took 50 images and average them to avoid noise. Figure 6.9 a, b and c are optical images for three different wavelengths given above. Interferograms for these three wavelengths are shown in Figure 6.9 d). On interferogram, we put dashed line to show how the periodicity of the interference fringes are varying with the wavelength of the incident light. Phase shift between wavelengths interfere destructively and hence canceling fringe patterns completely. Moreover, it is clear that contrast is decaying with distance which is due to the broad band source.

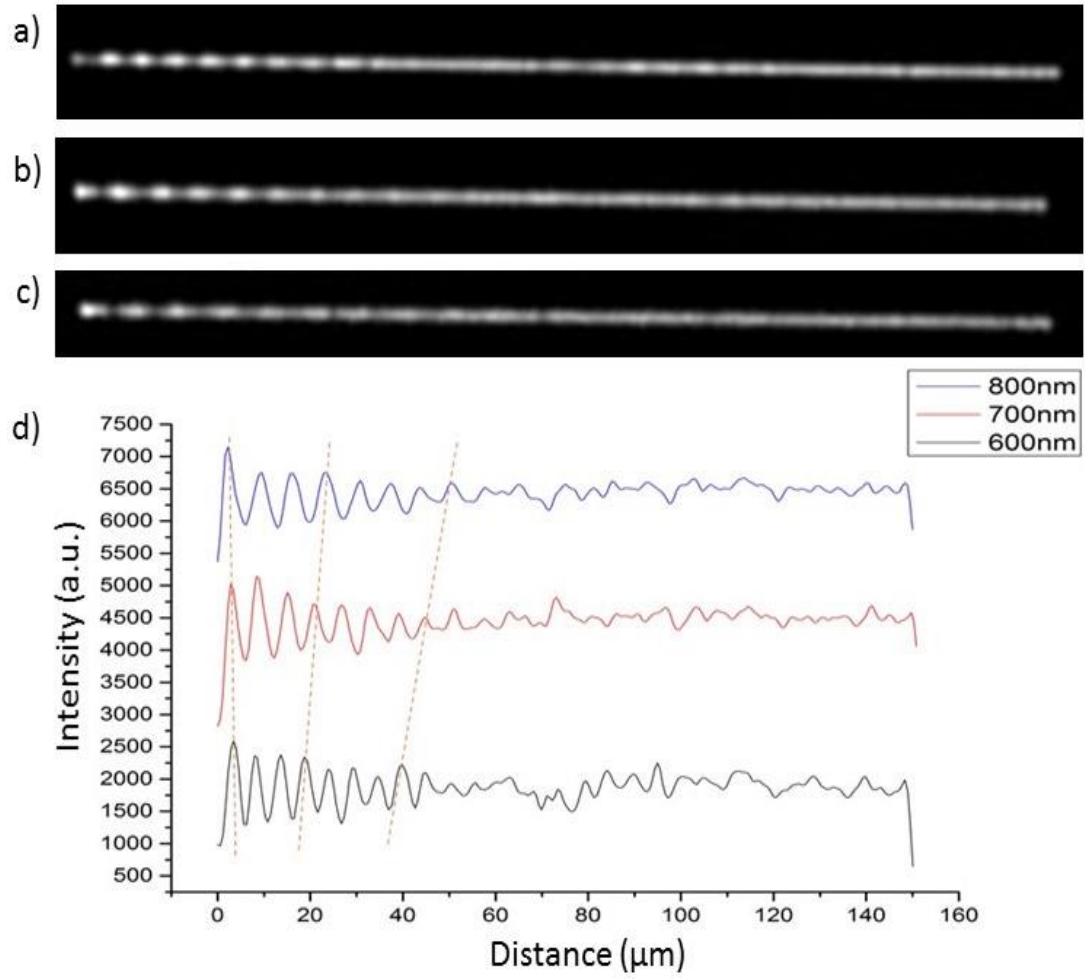


Figure 6.9 Bandpass (10nm) interferometer images. a, b and c are the optical images of interference fringes for different wavelengths 600nm, 700nm, and 800nm, respectively. d) is interferogram of these fringe patterns. Orange dashed line is to shows how the period of fringes are changing.

We took Fast Fourier Transform of interferograms, which are in Figure 6.9 d). For each of them, we got peaks on different parts of the spectrum, in Figure 6.10 a). Three peaks (black, blue and pink) represent spectrum of SPPs, which is spectrum of SPPs. Spectrum is shifted to the left in small amount, because of the effective refractive index. We multiplied all spectrum with a 4th order polynomial function. We did the same procedure in the previous part. After multiplication, all three spectrums are shifted a little bit to the right and spectrum is appeared at the expected part of the spectrum. Red, green and yellow colors in Figure 6.10 a represent spectrum after the colors shifted to the right by polynomial function multiplication.

In order to see the exact spectra of the bandpass filters and compare with our results, we took spectrum of light by using a conventional spectrometer. We compared our FTPR spectrometer results with the results of conventional spectrometer. Figure 6.10 b shows that spectra are matched very well. Spectrum result of FTPR was much broader than expected, which is due to the number of data points. Further explanation on this result will be in the discussion part.

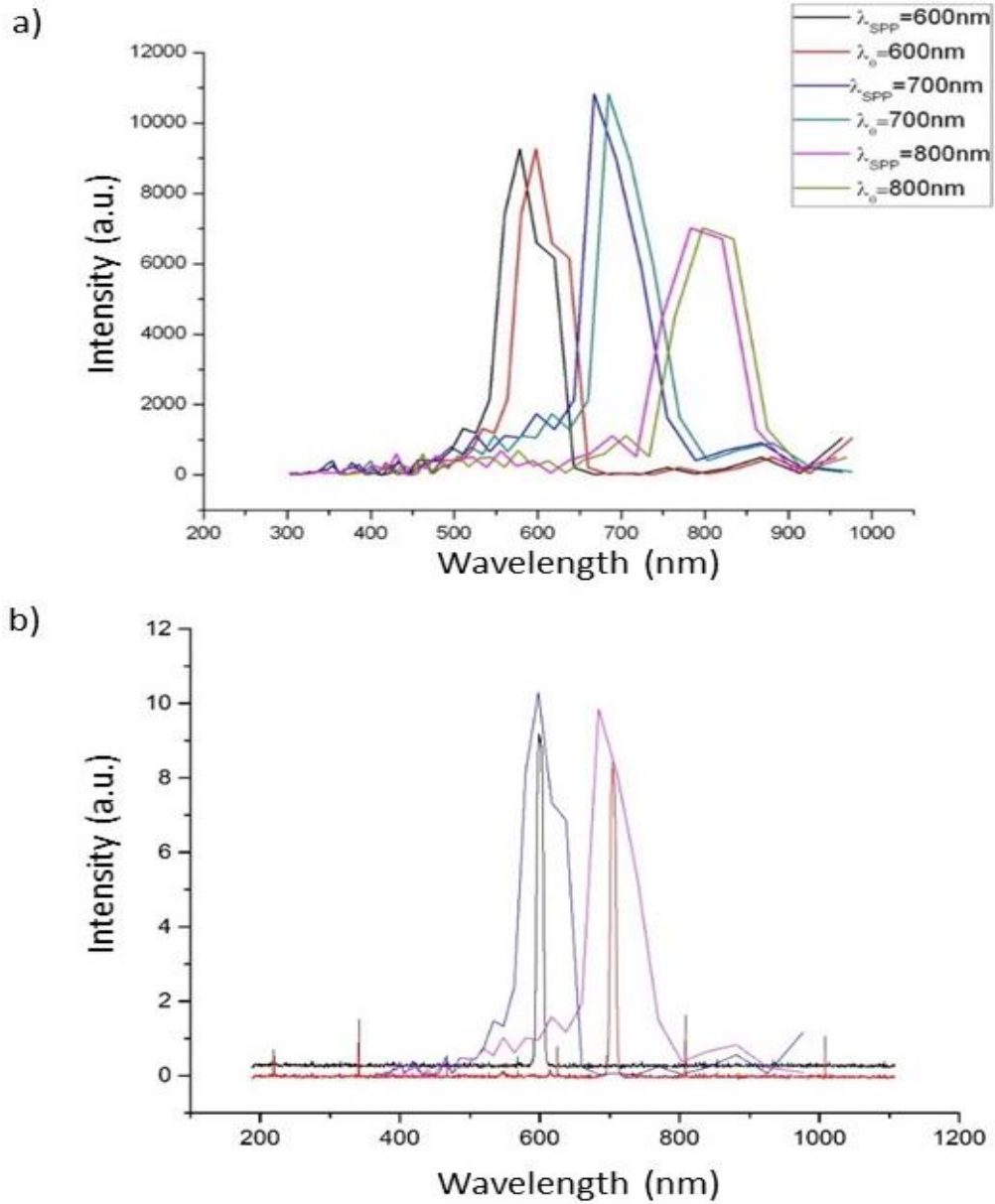


Figure 6.10 a) Black, blue and pink lines represent the spectrum of SPPs, which is not the real spectrum. Other three spectra show spectrum of real spectrum of light after it is multiplied with the effective refractive index. b) Comparison of spectra taken from FTPR and spectra taken from conventional spectrometer. Peak points almost match with each other.

Chapter 7

Discussion and conclusion

In this thesis, using slit-ridge interferometer, Fourier Transform Plasmon Resonance (FTPR) spectrometer is introduced. FTPR spectrometer does not have any moving section and optical dispersive element. Idea of FTPR spectrometer is the same with static Fourier Transform spectroscopy. Now, we will discuss advantages of static Fourier Transform spectroscopy and we will explain how FTPR spectrometer can benefit from this advantages. Moreover, we will review the results and discuss technical and fabrication limits.

7.1 Advantages of Static Fourier Transform spectrometers

First of all, static Fourier Transform spectrometers have two advantages when compared with grating based spectrometers, Fellgett and Jacquinot advantages [53]. Static Fourier Transform spectrometers collect all information simultaneously and do not have any optical dispersive elements. This makes them more advantageous compared to dispersive spectrometers and advantages (Fellgett and Jacquinot) are explained below.

Fellgett advantage (multiplex) is the ability of collecting information from all wavelengths simultaneously. Since the spectrum is not dispersed, high signal to noise ratio is achieved comparing with optical dispersive based spectrometers. Moreover, dispersive spectrum needs to make many scans to increase signal to noise ratio, because intensity of spectrum is decreased with dispersion of spectrum. This takes long time comparing to static Fourier Transform.

Another advantage of static Fourier Transform spectrometer is Jacquinot advantage. Static Fourier Transform spectrometer does not separate broad band spectrum, and spot all spectrum simultaneously so FTS does not lose energy of coming beam [58]. In way signal to noise ratio will be very high comparing to dispersive spectrometers and for some types of instruments the throughput ratio FTS to dispersive spectrometers is around 200 times higher leading FTS to measure spectra from very weak source beam.

FTPR spectrometer, which we designed will benefit from both of this FTS advantages. FTPR do not disperse coming light and collect all information simultaneously. It does not need any moving sections. Using very weak light source, high contrast signal to noise ratio is obtained in FTPR spectrometer.

Another advantage of FTPR spectrometer is its portability. No bulky prism and moving arms are needed to this. It is very small, and just optical microscope is enough to analyze spectrum of light. Moreover, with careful fabrication, optical microscope also might be removed just by integrating device on the CMOS image sensor, Figure 7.1, on the left. By depositing silver on the chip and writing slit-ridge structure on it, portable FTPR spectrometer can be designed as image on the right in Figure 7.1.

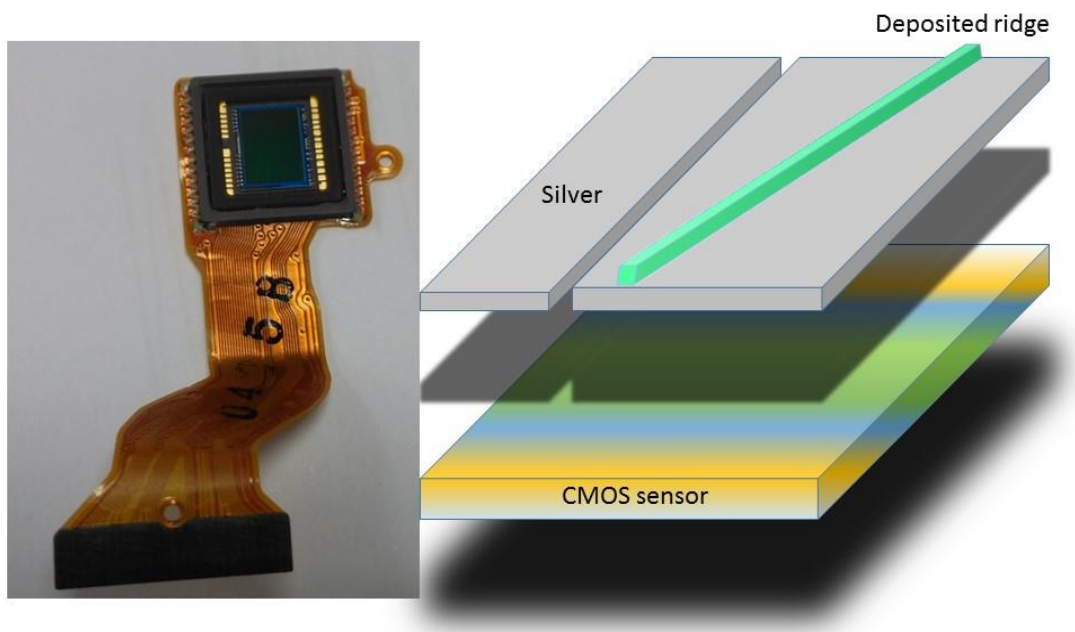


Figure 7.1 CMOS image sensor on the left and portable FTIR sensor integrated on CMOS image sensor to remove camera and optical microscope.

7.2 Limits

We have several fabrication and experimental setup limitations. FIB has writing field limit while images taken by CCD camera contains just about 300 pixels, which is one order of magnitude lower than the data points of conventional spectrometers. In addition, plasmonic decay with increasing distance also prevents having high contrast interferogram. All of these limitations will be explained briefly in following chapters.

7.2.1 Fabrication limits

FIB and EBID are good for creating nanostructures, but when the dimension of structure exceeds several hundreds of micrometers, both FIB and EBID start losing their resolution. Fabrication of 200 μ m slits and ridges with very smooth sides is really challenging. It is difficult to see smoothness and the thickness of the device in SEM, so we used AFM to measure them. Figure 7.2 shows AFM result of slit-ridge interferometer. From Figure 7.2, it is obvious that Pt ridge is not perfectly deposited and thickness is fluctuating with distance. This rocky Pt ridge is one of the main source of noise which affects interferogram. One of the solution for smooth surface can be decreasing the length, but decreasing length will also decrease our number of data points.

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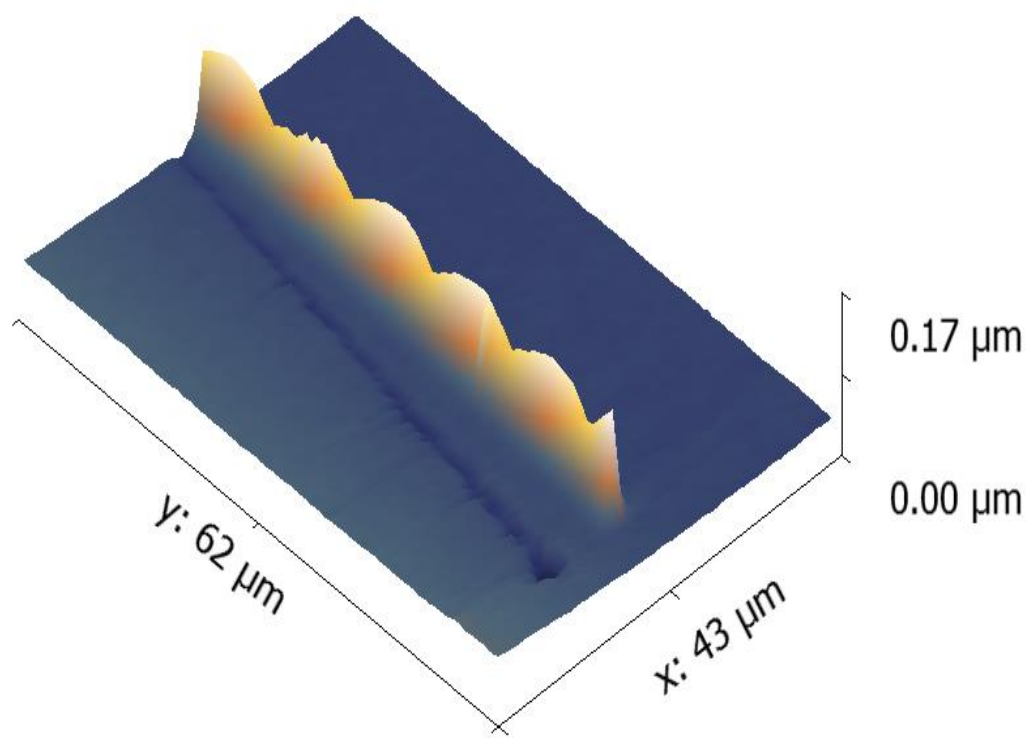


Figure 7.2 AFM images if the slit ridge interferometer. The thickness of ridge varies across the Pt line

7.2.2 Plasmonic decay

SPPs excited from groove or ridge propagate towards the slit. With the distance travelled by SPP, SPP starts to decay exponentially by converting its energy to heat. With the decay of SPPs, signal to noise ratio also decreases leading to decline in contrast. We changed our material from gold to silver in order to prevent plasmonic decay. The decay is reduced but it is not totally eliminated.

One of the possible method to improve contrast and exclude the noise is to take the average of many images. In our experiment, we took average of 50 images and improved interference fringe contrast. However, averaging will just improve the intensity and do not eliminate the plasmonic decay.

7.2.3 CCD camera resolution

There is one more challenge beyond the fabrication and plasmonic decay, which is number of pixels on optical image taken by CCD camera. In our experiment, we used high sensitive CCD camera. Spectrum we obtain from FTPR spectrometer was broader than the predicted spectrum. Largest image taken by CCD camera can only contain around 300 pixels. This number is one order of magnitude smaller than the number of data taken by conventional spectrometer. In chapter 6, we discussed stationary Fourier Transform spectrometer and we showed that the number of data points are important. Equation 31 ($\Delta\sigma_{FWHM} \approx 4/\lambda_{min}N$), where $\Delta\sigma_{FWHM}$ resolution and N is the number of data points, shows that with the increase of number of data point high resolution is achieved. We also believe that by increasing the number of pixels we can improve resolution and spectrum taken by FTPR spectrometer will match.

In this thesis, we have demonstrated Fourier Transform Plasmon Resonance spectrometer. To obtain spectroscopic information of light we used interferogram of plasmonic interferometer. We designed slit-ridge interferometer on the silver film using FIB and EBID. Slit-ridge pairs have an angle between them which leads to varying optical path. Transmitted light through the slit yields high contrast interference pattern due to the varying optical path. We have converted interference pattern into the spectrum using Fast Fourier Transform algorithm. This spectrometer design does not need any bulky prism or dispersive optical elements.

As in many Fourier Transform spectrometers (FTS), FTPR spectrometer also benefit from Fellgett and Jacquinot advantages. In FTPR spectrometer, all wavelengths of light detected without dispersing them. This advantage of FTPR spectrometer decreases time of testing significantly. Since there are not optical dispersive elements used in FTPR spectrometer, incident beam does not lose its energy and high contrast interferogram is achieved from very low light energy.

FTPR spectrometer is very small and compact. Instead of using glass plate, interferometer can be merged with CMOS sensor image and hence can be used as compact and portable spectrometer.

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