

PROBING HOT-ELECTRON EFFECTS IN PLASMONIC SURFACES USING X-RAY PHOTOELECTRON SPECTROSCOPY

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By

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ABSTRACT

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Hot-electron effects in plasmonic structures have been recently investigated as potential alternative mechanisms for solar energy harvesting and photodetection. [1][2][3] Hot-electron effects provide a semiconductor free route for the conversion of photons into electrical power. Here we investigate plasmonic hot electron effects in Metal-Insulator-Metal (MIM) structures using X-ray photoelectron spectroscopy (XPS). XPS has been previously used to investigate optoelectronic effects in semiconductors and nanocomposite surfaces. [4][5][6] Here, a similar approach is used to characterize the plasmonic and hot electron effects in MIM Junctions. Monochromatic Laser excitation with 450, 532 and 650 nm wavelengths are employed to illuminate the plasmonic surfaces fabricated using thermal evaporation, atomic layer deposition and electron beam lithography. The top metal of the MIM structures act as the plasmonic antenna (metal nanodiscs and gratings/stripes) that provide wavelength selective or wide band optical absorption. Plasmonic enhancement at the interface between the top metal and the insulator enhances the absorption of light in the device and leads to excitation of a larger number of hot electrons from the metal. Hot electron effects are characterized through studying the metal-insulator-metal junction and comparing shifts of binding energy belonging to the top metal islands for dark and illuminated conditions. XPS spectrum provides important information regarding the plasmonic and hot electron effects in the interface between top metal and the dielectric. A

systematic study of the dependence of the XPS spectra on excitation wavelength, light intensity, polarization, insulator thickness and nanostructure geometry is presented. Effects of using different metals and insulator materials are also studied in symmetric and asymmetric tunnel junctions.

Keywords: X-ray photoelectron spectroscopy, plasmonics, Metal-Insulator-Metal (MIM), plasmonic antenna, metal nanoparticles, hot-electron effects

ÖZET

PLAZMONİK YAPILARDA SICAK ELEKTRON ETKİLERİNİN X-İŞİNİ SPEKTROSKOPİSİ METODUYLA GÖZLEMLENMESİ

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Sıcak-elektronların plazmonik yapılarda oluşturduğu etkiler bir süredir güneş enerjisi dönüşümü ve fotodetektör teknolojisinde alternatif mekanizmalar olarak araştırılmaktadır. Potansiyel olarak, sıcak elektron etkileri fotonların elektriksel güce çevrilmesi için yarı iletken içermeyen bir yol sağlamaktadır. [1][2][3] Burada, X-ışını fotoelektron spektroskopisi (XPS) kullanarak sıcak elektronun metal-yalıtkan-metal yapılar üzerindeki etkilerini araştırmaktayız. XPS geçmiş yıllarda yarı iletken malzemelerde ve nanokompozit yüzeylerde optoelektronik etkileri araştırmak için kullanılmıştır.[4][5][6] Buna benzer bir yöntem ile, metal-yalıtkan-metal yapılardaki plazmonik ve sıcak elektron etkileri karakterize edilmektedir. Dalga boyu 450 nm, 532 nm ve 650 nm olan lazerler, termal buharlaştırıcı, atomik boyutta katman kaplama ve elektron ışını litografisi kullanılarak elde edilen plazmonik yüzeyleri aydınlatmak için kullanılmıştır. Plazmonik anten (metal nanodiskler ve ızgaralı/şeritli yapılar) olarak davranan metal-yalıtkan-metal yapıların üst tabakasındaki metal, dalgaboyu seçici ya da geniş bant optik soğurma sağlamaktadır. Üst metal tabaka ve yalıtkan ara yüzeydeki plazmonik güçlendirme yapıdaki ışığın soğrulmasını arttırmakta ve metalden daha çok sayıda sıcak elektronun uyarılmasına öncülük etmektedir. Sıcak elektron etkileri üst metal tabakanın bağlanma enerjisindeki kaymaların karanlık ve aydınlık ortamlardaki karşılaştırılması ile karakterize edilmiştir. XPS spektrumu üst metal tabaka ve yalıtkan ara yüzeydeki plazmonik ve sıcak elektron etkileri hakkında önemli

bilgiler sağlamaktadır. XPS spektrumunun, plazmonik uyarılma dalga boyu, ışık yoğunluğu, polarizasyon, yalıtkan kalınlığı ve nanoyapı geometrisi ile olan ilişkisi sistematik bir şekilde sunulmuştur. Simetrik ve asimetrik tünel bariyerlerinde alttaş ve yalıtkan olarak farklı malzemeler kullanılmasının etkileri de ayrıca çalışılmıştır.

Keywords: X-ışını fotoelektron spektroskopisi, plazmonik, metal-yalıtkan-metal yapıları, metal nanoparçacıklar, sıcak elektron etkileri

Dedicated to my family and friends

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Chapter 1

Introduction

Thin films are widely used in optoelectronics. Photodetectors, solar cells, sensors and other devices make use of thin film technology. Hence, the advancement of technology is closely related to the developing and understanding of the thin film technology. Thin films typically contain metal, semiconductor or dielectric layers. A particularly interesting multilayer thin film structure is the metal-insulator-metal configuration, where optical and electronic properties of the surface can be tuned by proper choice of geometry and material properties. It has been widely recognized that such surfaces can exhibit plasmonic effects, where the optical properties of the surface can be tuned by modifying the nanoscale structure of the films. Such plasmonic effects can have wide applications in optoelectronics and sensing and plasmonic enhancement has lately been used in Metal-Insulator-Metal sandwiched thin films to improve performance in solar energy conversion devices and photodetectors. [1]

In this thesis a new technique for probing plasmonic effects in Metal-Insulator-Metal (MIM) structures is introduced. X-ray photoelectron spectroscopy is used to characterize the electric properties of the MIM Junction. Monochromatic Laser light illuminates the samples. The top metal of the MIM structure was reshaped into plasmonic antenna (metal nanoparticles and gratings/stripes) that resonate Surface Plasmon Polaritons. Plasmonic enhancement at the interface

between the top metal and the insulator enhances absorption of light in the device and leads to excitation of a larger number of hot electrons from the metal.

Comparing XPS spectra shifts of the top metal in cases when Laser light is on and off provides important information regarding the plasmonic and hot electron effects in the interface between top metal and the dielectric. Dependence of the energy shift on the following parameters is studied: wavelength of the used Laser light, intensity, thickness of the insulator, size of nanoparticles and band diagram factor.

In all cases Silver is used as the top metal. Layer of TiO_2 , HfO_2 and Al_2O_3 dielectric were used as insulator sandwiched layer. As a bottom layer, we used both Al and Ag in order to investigate junctions having symmetric and asymmetric band diagram.

We characterized and optimized the fabrication process, and in some of the samples nearly perfectly light absorbance was achieved for a wide angle and a broadband range in the visible spectrum, between 300nm and 750 nm. These samples were used as substrates for Raman Scattering, and we show that a simple setup containing a mobile phone can be used to image and count air molecules. Inspiration to use this specific structure came from looking at the band diagram of the device. All the three lights provide transfer to the electron enough energy to pass over the barrier in the Ag- HfO_2 -Ag band diagram. Changing the material would change the band diagram; in turns changing the height of the potential barrier and the shift observed. This is the reason why we use different metal substrate and dielectrics. The Laser light, flood gun voltage

and x-rays affect the band diagram alignment and hence affect the current passing through the insulator. We aim to show that the shifts in the binding energy of the Ag in the surface are due to plasmonic effects.

Chapter 2

Theoretical Background

In this chapter, the theoretical background of Surface Plasmon Resonance, MIM structures and X-ray Photoelectron spectroscopy is given. In the following chapters we will be dealing with these topics, hence it is useful to study these concepts.

2.1 Surface Plasmon

Surface Plasmon waves are coupled oscillation of electrons and photons at the conductor/dielectrics interface. Electrons in the metal can be assumed to be free electrons, and they collectively respond to an excitation caused by an incident light. Surface Plasmon waves are confined to the interface and decay in directions perpendicular to the surface. The dispersion relation of SPPs can be obtained by solving Maxwell equations in metal-dielectrics interface.

2.1.1 The Wave Equation [7]

Maxwell equations in a macroscopic medium has the form:

$$\nabla \cdot \mathbf{D} = 0 \quad (2.1)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (2.2)$$

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \quad (2.3)$$

$$\nabla \times \mathbf{H} = \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} \quad (2.4)$$

Here $\mathbf{B}$ is the magnetic flux density, $\mathbf{D}$ is electric displacement, $\mathbf{E}$ is the electric field and c is the speed of light in vacuum.

If the materials have linear polarization and magnetic response, the following relation can be used to interconnect magnetic and electric components:

$$\mathbf{D} = \epsilon_0 \epsilon \mathbf{E} \quad (2.5)$$

$$\mathbf{B} = \mu_0 \mu \mathbf{H}$$

Here ϵ is the dielectric constant and μ is the magnetic permeability (=1 for nonmagnetic medium). Dielectric susceptibility χ describes the linear relationship between $\mathbf{P}$ and $\mathbf{E}$ as follows:

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E} \quad (2.6)$$

If external current density and charge are both zero, combination of the curl equations (2.3) and (2.4) yields:

$$\nabla \times \nabla \times \mathbf{E} = -\mu_0 \frac{\partial^2 \mathbf{D}}{\partial t^2} \quad (2.7)$$

Using some identities, the previous equations can be rewritten as:

$$\nabla \left(-\frac{1}{\epsilon} \mathbf{E} \cdot \nabla \epsilon \right) - \nabla^2 \mathbf{E} = -\epsilon_0 \mu_0 \epsilon \frac{\partial^2 \mathbf{E}}{\partial t^2} \quad (2.8)$$

If the dielectric profile is taken to be uniform, i.e. $\epsilon(\mathbf{r}) = \epsilon$, equation (2.8) can be further simplified to:

$$\nabla^2 \mathbf{E} - \frac{\epsilon}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = 0 \quad (2.9)$$

Equation (2.9) is the central equation of electromagnetic wave theory. Assuming the electric field has harmonic time dependence, it can be expressed as:

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}) e^{-i\omega t} \quad (2.10)$$

Inserting (2.10) in equation (2.9) yields:

$$\nabla^2 \mathbf{E} + k_0^2 \epsilon \mathbf{E} = 0 \quad (2.11)$$

This relation is known as **Helmholtz equation**.

Inserting equation (2.10) into (2.11) yields the wave equation:

$$\frac{\partial^2 \mathbf{E}(z)}{\partial z^2} + (k_0^2 \varepsilon - \beta^2) \mathbf{E} = 0 \quad (2.12)$$

The curl equations (2.3) and (2.4) are used to find the explicit expressions for the components of $\mathbf{E}$ and $\mathbf{H}$. The following relations are obtained:

$$\frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z} = i\omega\mu_0 H_x \quad (2.13)$$

$$\frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = i\omega\mu_0 H_y \quad (2.14)$$

$$\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = i\omega\mu_0 H_z \quad (2.15)$$

$$\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} = -i\omega\varepsilon_0 \varepsilon E_x \quad (2.16)$$

$$\frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} = -i\omega\varepsilon_0 \varepsilon E_y \quad (2.17)$$

$$\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} = -i\omega\varepsilon_0 \varepsilon E_z \quad (2.18)$$

If x-direction is assumed to be the propagation direction and the material is homogeneous in the Laser direction ($\frac{\partial}{\partial \text{Laser}} = 0$), equations (2.13) – (2.18) can be further simplified to:

$$\frac{\partial E_y}{\partial z} = -i\omega\mu_0 H_x \quad (2.19)$$

$$\frac{\partial E_x}{\partial z} - i\beta E_z = i\omega\mu_0 H_y \quad (2.20)$$

$$i\beta E_y = i\omega\mu_0 H_z \quad (2.21)$$

$$\frac{\partial H_y}{\partial z} = i\omega\varepsilon_0 \varepsilon E_x \quad (2.22)$$

$$\frac{\partial H_x}{\partial z} - i\beta H_z = -i\omega\varepsilon_0 \varepsilon E_y \quad (2.23)$$

$$i\beta H_y = -i\omega\varepsilon_0 \varepsilon H_z \quad (2.24)$$

The wave equation for TM and TE modes can be shown to be [7]:

For TM

modes:

$$\frac{\partial^2 H_y}{\partial z^2} + (k_0^2 \varepsilon - \beta^2) H_y = 0 \quad (2.25)$$

For TE modes:

$$\frac{\partial^2 E_y}{\partial z^2} + (k_0^2 \varepsilon - \beta^2) E_y = 0 \quad (2.26)$$

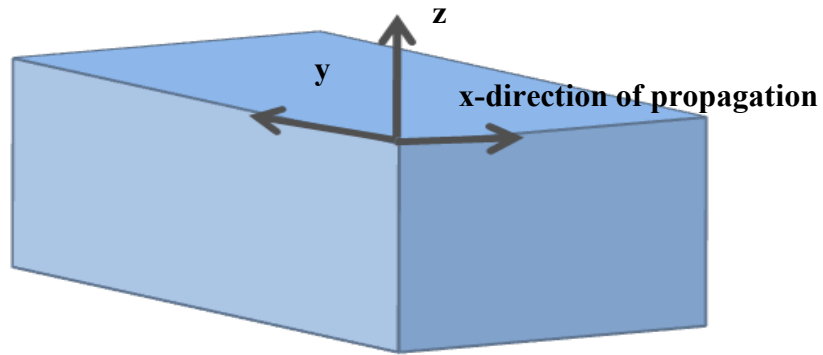


Figure 2.1. Waveguide geometry used. Waves propagate in the x-direction.

2.1.2 Surface Plasmon at a Metal Dielectrics Interface

The interface between a metal and a dielectric is one of the simplest geometries where surface Plasmon Polaritons can be studied. We are looking for solutions of the propagating wave equation at the interface.

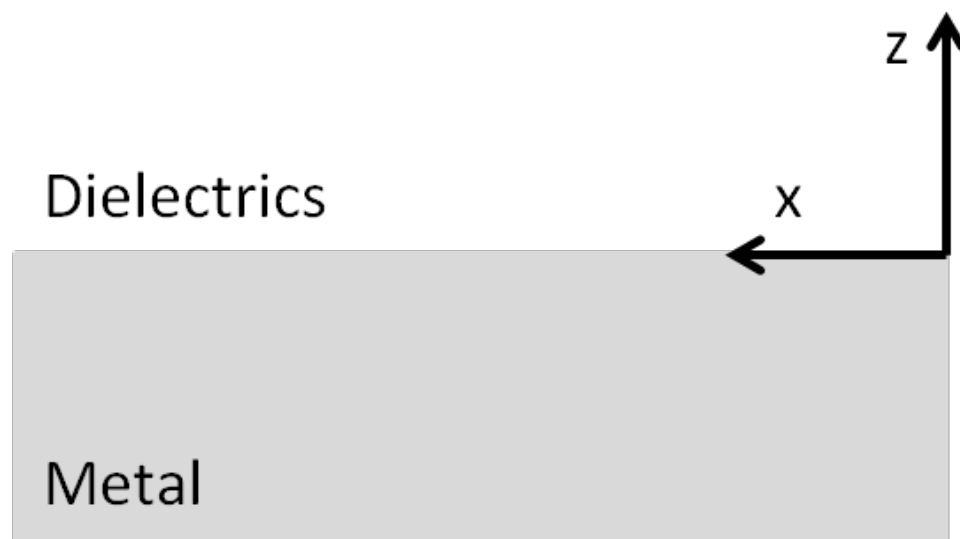


Figure 2. 2. SPP propagate at the metal/insulator interface

For $z < 0$, metal has a dielectric constant $\varepsilon_1(\omega)$. The real part of the dielectric constant of the metal is negative. For $z > 0$, the dielectric half-space has a positive, real dielectric function $\varepsilon_2(\omega)$.

TM solutions for $z > 0$ yield:

$$H_y(z) = A_2 e^{i\beta x} e^{-k_2 z} \quad (2.27)$$

$$E_x(z) = iA_2 \frac{1}{\omega \varepsilon_0 \varepsilon_2} k_2 e^{i\beta x} e^{-k_2 z} \quad (2.28)$$

$$E_z(z) = -A_1 \frac{\beta}{\omega \varepsilon_0 \varepsilon_2} k_2 e^{i\beta x} e^{-k_2 z} \quad (2.29)$$

for $z < 0$, the following result is obtained:

$$H_y(z) = A_1 e^{i\beta x} e^{-k_1 z} \quad (2.30)$$

$$E_x(z) = -iA_1 \frac{1}{\omega \varepsilon_0 \varepsilon_1} k_1 e^{i\beta x} e^{-k_1 z} \quad (2.31)$$

$$E_z(z) = -A_1 \frac{\beta}{\omega \varepsilon_0 \varepsilon_1} e^{i\beta x} e^{-k_1 z} \quad (2.32)$$

As a requirement of continuity of the Laser-component of the magnetic field H_y and $\varepsilon_1 E_z$ at the interface, $A_1 = A_2$ and

$$\frac{k_1}{k_2} = \frac{\varepsilon_2}{\varepsilon_1} \quad (2.33)$$

Expression for Laser has to satisfy equation (2.25). The following equations are a direct consequence of this:

$$k_1^2 = \beta^2 - k_0^2 \varepsilon_1 \quad (2.34)$$

$$k_2^2 = \beta^2 - k_0^2 \varepsilon_2 \quad (2.35)$$

The dispersion relation results if equations (2.33) - (2.35) are combined:

$$\beta = k_0 \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \quad (2.36)$$

Similarly to the TM modes, expressions for the field components of TE modes are found to be:

For $z > 0$:

$$E_y(z) = A_2 e^{i\beta x} e^{-k_2 z} \quad (2.37)$$

$$H_x(z) = -iA_2 \frac{1}{\omega\mu_0} k_2 e^{i\beta x} e^{-k_2 z} \quad (2.38)$$

$$H_z(z) = A_2 \frac{\beta}{\omega\mu_0} k_2 e^{i\beta x} e^{-k_2 z} \quad (2.39)$$

For $z < 0$:

$$E_y(z) = A_1 e^{i\beta x} e^{k_1 z} \quad (2.40)$$

$$H_x(z) = iA_1 \frac{1}{\omega\mu_0} k_1 e^{i\beta x} e^{k_1 z} \quad (2.41)$$

$$H_z(z) = A_1 \frac{\beta}{\omega\mu_0} e^{i\beta x} e^{k_1 z} \quad (2.42)$$

The component of the wave vector perpendicular to the interface, $k_i \equiv k_{z,i}$ ($i=1,2$) has a very important role in quantifying the confinement of the wave. The reciprocal of k_z , $1/|k|_z$, describes the evanescent behavior of the fields perpendicular to the surface. It is equal to the decay length of the field. E_y and H_x have to be continuous at the boundary; hence the following condition should be satisfied:

$$A_1(k_1 + k_2) = 0 \quad (2.43)$$

Condition 2.43 is satisfied only if $A_1 = A_2 = 0$. Therefore surface modes do not exist for TE polarization. Surface Plasmon modes exist only for TM polarization.

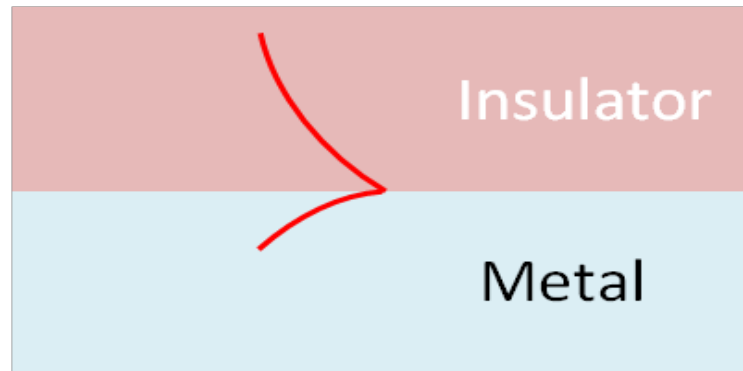


Figure 2. 3 Field decaying at the interface. Decay length depends on the propagation constant in the film. Decay length is longer in the insulator than in the metal film.

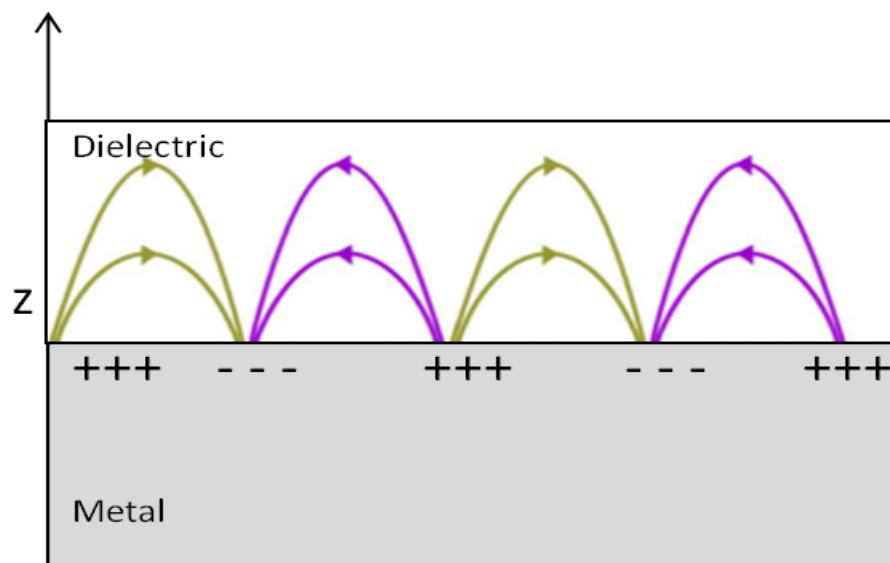


Figure 2. 4. E-field lines of Surface Plasmon Polaritons on a Metal-dielectrics interface.

2.1.3 Prism Coupling Scheme

Direct light cannot excite surface Plasmon polaritons on a metal/dielectric interface. This is due to the difference between the x-component of wave vector of light $k_x = k \sin\theta$, and the SPP propagation constant β (x-direction is assumed to be the propagation direction of SPP-s). For interaction between the photons and plasmons to take place, conservation principles require they have equal energy and momentum. In figure 2.5 dispersion curves are seen to intercept only at the origin. Therefore in normal conditions this cannot be observed. Coupling techniques are needed to excite surface plasmons. Various alternative techniques are utilized to do the phase matching. The prism-coupling scheme is one of them. This is a three-layer system consisting of a metal film inserted between two different dielectrics; one of whose has the form of a prism. Kretschmann configuration is shown in figure 2.6 [Kretschmann and Raether, 1968] [8]. Total internal reflection occurs at the prism-metal interface. Note that surface plasmon excitation occurs only in the metal-air interface.

In the reflected beam intensity the SPP excitation can be recognized as a minimum in the beam intensity.

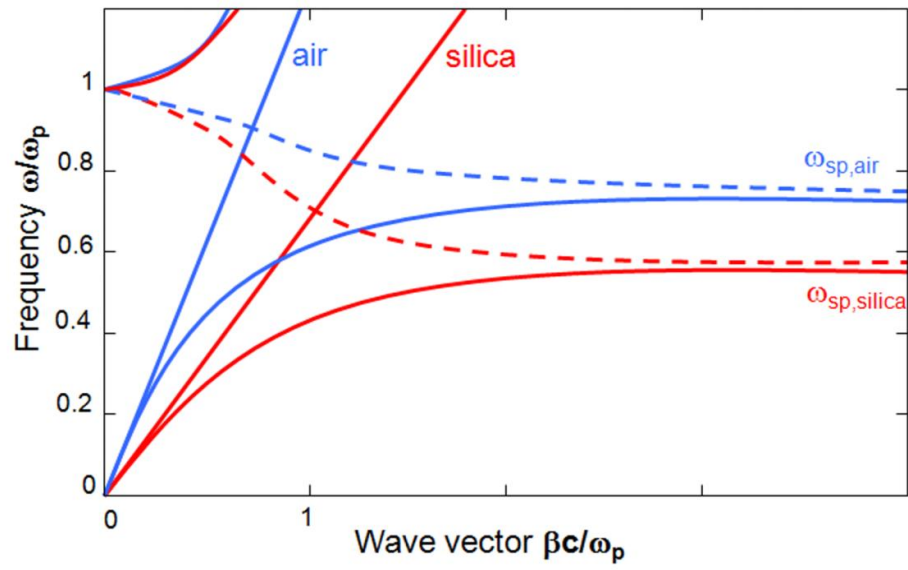


Figure 2. 5. Dispersion curves and photonic lines for air and silica.[17]

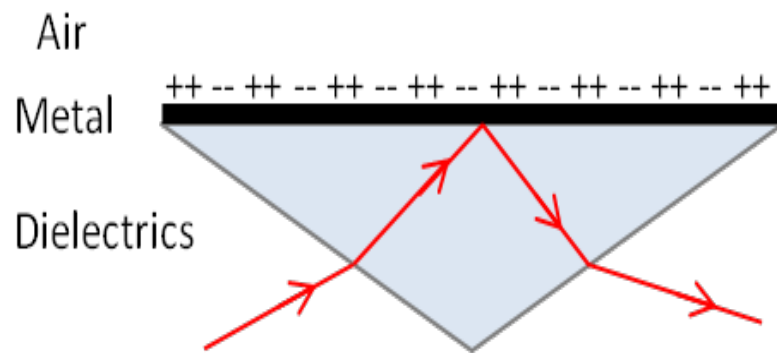


Figure 2. 6. Kretschmann configuration. SPP excitation occurs only at the metal-air interface.

Prism coupling can also be used to excite coupled surface plasmon polaritons(SPP) in MIM junctions. Another widely used phase-matching configuration is Otto geometry [9]. In this configuration the dielectric layer is placed between the prism and the metal. Total internal reflection (TIR) takes place at the prism-dielectric interface. Evanescent field tunneling across the dielectric layer excites surface plasmons on the metal-dielectric interface. Otto configuration is very uncommon because of its very sensitive property of dielectric layer thickness.

2.1.4 Grating Coupling Scheme

Another widely used technique to overcome the mismatch in wave vector between the in-plane momentum of the photons and β is the grating coupling scheme. Here a metal surface having an integrated grating is utilized. When light with wave vector k_i falls on the grating, light gets diffracted. The diffracted light's wave vector $k_{diff,x}$ then becomes:

$$k_{diff,x} = k_{i,x} + mG \quad (2.44)$$

where m is an integer and G is the grating vector along x-direction. The magnitude of the wavevector does not change if the diffracted light does not change medium. Magnitude of the grating vector is:

$$|G| = \frac{2\pi}{\Lambda} \quad (2.45)$$

Here Λ is the period of grating used and G is the grating vector.

As a condition of Plasmon exciting, the wave vector of diffracted light $k_{diff,x}$ should be equal to the wave vector of the surface plasmons, k_{sp} . Therefore the dispersion relation becomes:

$$k_{sp} = k_i + m \frac{2\pi}{\Lambda} \quad (2.46)$$

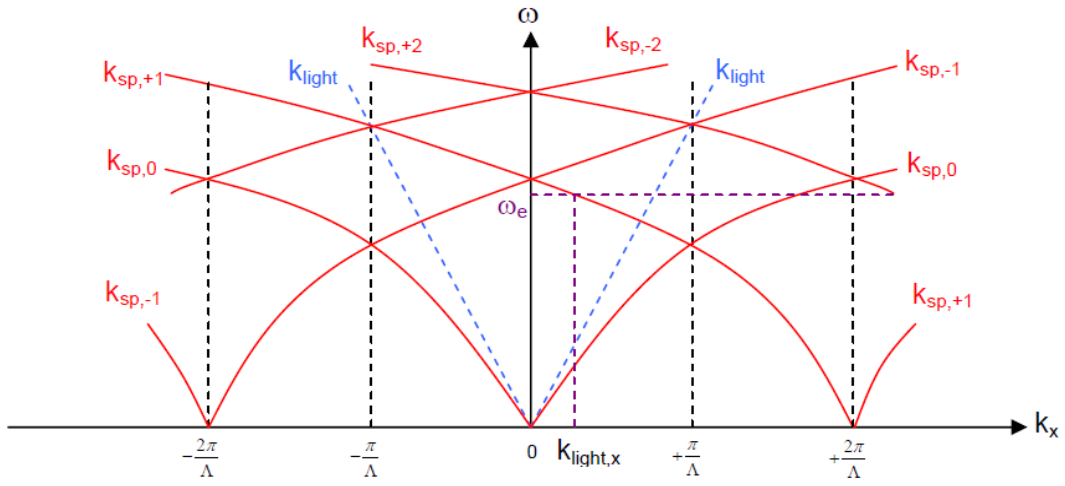


Figure 2. 7. The plasmonic dispersion relation for grating coupling. [17]

2.2 Localized Surface Plasmons

Localized surface plasmons are non-propagating excitations of the conduction electrons of metallic nanostructures coupled to the electromagnetic field.

2.2.1 Localized Surface Plasmon Modes

Localized surface plasmon modes result from the solution of the problem of scattering of a sub-wavelength size conductive nanoparticle in an oscillating EM field. They are a consequence of the curved surface of the nanoparticle, which exerts a restoring force on the driven electrons. Restoring force is the reason of the resonance. Due to the resonance, field amplification is observed inside the particle and in the near zone outside the particle. Localized surface plasmons differ from propagating SPP. Due to the curved surface of the nanoparticles, localized surface plasmons can be excited directly by light illumination. In the propagating SPPs case, an additional prism is needed to excite the plasmon modes.

Now the case of a homogeneous, isotropic sphere in a uniform, static electric field E is considered (Figure 2.8). The sphere has a dielectric response described by the dielectric function $\epsilon(\omega)$. The surrounding has a dielectric constant ϵ_m . Solving Laplace's equation and making use of Legendre's polynomials (derivation details can be found at reference 7) yields a dipole moment $\mathbf{p}$ inside the sphere as follows:

$$\mathbf{p} = 4\pi\epsilon_0\epsilon_m a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \mathbf{E}_0 \quad (2.47)$$

If dipole moment is expressed as:

$$\mathbf{p} = \epsilon_0\epsilon_m \alpha \mathbf{E}_0 \quad (2.48)$$

Polarizability α then becomes:

$$\alpha = 4\pi a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \quad (2.49)$$

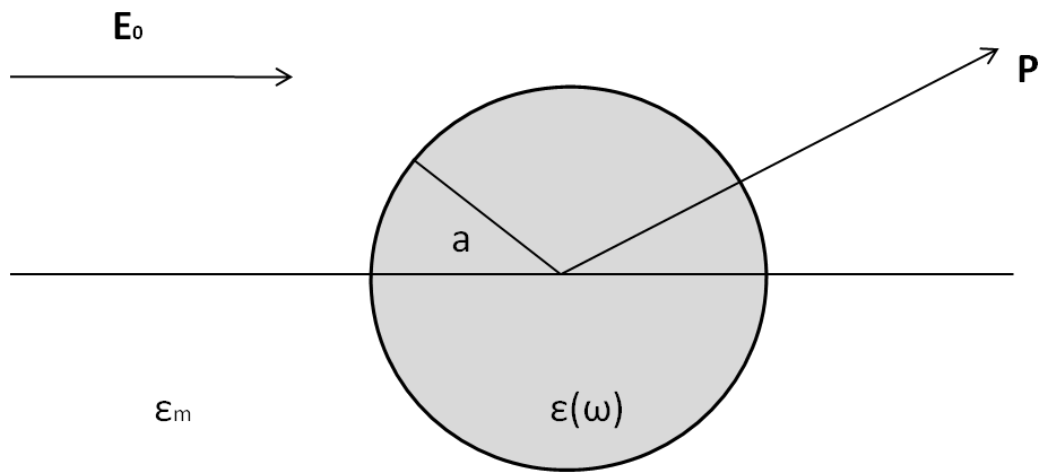


Figure 2. 8. A conducting sphere under the effect of an electric field E . The medium is assumed to be air having an dielectric constant ϵ_m . [Adapted from reference 7]

The condition that $|\varepsilon+2\varepsilon_m|$ is a minimum would resonantly enhance polarizability. The Fröhlich condition is a result of the slowly varying imaginary part of $\varepsilon(\omega)$,:

$$Re[\varepsilon(\omega)] = -2\varepsilon_m \quad (2.50)$$

Modes associated with Fröhlich condition are called dipole surface plasmon of the metal nanoparticle. This relation is an indicator that the resonance frequency on the dielectric strongly depends on environment. This feature makes metal nanoparticles ideal to be used in sensing of changes in refractive index. Any change in environments refractive index changes the resonance.

The electric field distribution is evaluated from the potentials [7]:

$$\mathbf{E}_{in} = \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} \mathbf{E}_0 \quad (2.51)$$

$$\mathbf{E}_{out} = E_0 + \frac{3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}) - \mathbf{p}}{4\pi\varepsilon_0\varepsilon_m} \frac{1}{r^3} \quad (2.52)$$

In this case both the internal and dipolar electric fields are enhanced. The resonant enhancement of the fields is due to the resonance in polarizability. Metal nanoparticles show interesting optical behavior. Light is efficiently absorbed and scattered in metal nanoparticles as a result of the resonantly enhanced polarization α . Pointing vector is used to calculate scattering and absorption cross sections C_{sca} and C_{ab} [18]:

$$C_{sca} = \frac{k^4}{6\pi} |\alpha|^2 \quad (2.53)$$

$$C_{abs} = kIm[\alpha] \quad (2.54)$$

Substituting for α in 2.53 and 2.54 yields:

$$C_{sca} = \frac{8\pi}{3} k^4 a^6 \left| \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right| \quad (2.55)$$

$$C_{abs} = 4\pi k a^3 \text{Im} \left[\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right] \quad (2.56)$$

An important result of equations 2.55 and 2.56 is that for very small particles ($a \ll \lambda$) the absorption efficiency is larger than scattering efficiency. As a result, a very small ($\sim$ tens of nm) object is difficult to be imaged when neighbored by larger scatterers. Special techniques should be employed for imaging in such cases. Equations 2.55 and 2.56 also show that at the particle dipole Plasmon resonance, both absorption and scattering are enhanced.

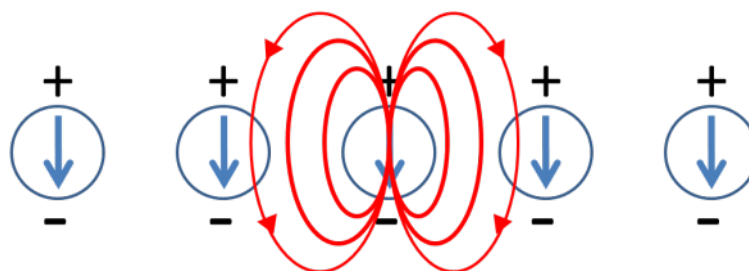
2.2.2 Coupling of Localized Surface Plasmons

Electromagnetic interactions between localized modes of neighboring nanoparticles cause additional shifts in Plasmon resonance. An array of one-dimensional nanoparticles is considered as the easiest case to be modeled and studied. Nanoparticles have size a and inter-particle distance d . They are considered to be close to each other ($d \ll \lambda$). In this case near field interaction is dominant, having a distance dependence of d^{-3} . Kren and his coworkers experimentally studied the case, and in their setup a 1D array of metal nanoparticles was excited using a prism scheme. They observed strong field localization at interstitial sites, obtained by experimental results and supported by simulations. Scattering is suppressed for closely spaced particles.[19] These properties make inter-particle junctions very important in various applications where field enhancement is desired.

A model of interacting point dipoles is used to describe the situation. The particles are modeled as shown in figure 2.9. An incoming in-phase light polarizes the particles. Restoring force acting on the oscillating electrons will be affected by charge distribution of the neighboring nanoparticles. A blue shift is observed when incoming light excites transverse modes (2.9 a). If incoming

radiation excites longitudinal modes, red shift is observed (2.9b). Resonance shift is affected by geometrical parameters of the nanoparticle array: inter-particle distance and nanoparticle length as well as polarization of the exciting light. If the particle separation is large, far-field dipolar coupling with a distance dependence of d^{-1} is dominant. [7]

a)



b)

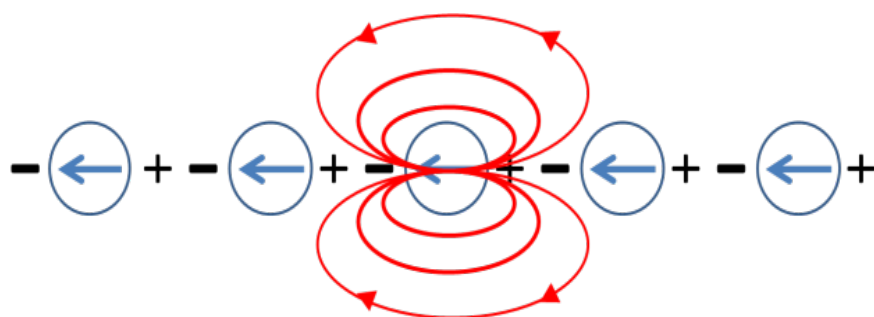


Figure 2. 9. Near field coupling between near neighboring metal nanoparticles. Charge polarization caused by incoming light of two different polarization cases are shown. [Adapted from 7]

2.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is one of the mostly used techniques in surface analysis and characterizing. Its working principle is based on the photoelectric process. An X-ray photon with energy $h\nu$ is employed to eject an electron from the core level. The emitted photoelectron is used to do the analyzing, and the photoelectron spectrum is obtained in the form of a graph of intensity versus electron energy. The electron is identified by the binding energy, and its kinetic energy is employed as a mean to calculate the binding energy as following:

$$E_B = h\nu - E_K - W \quad (2.57)$$

Here E_B is the binding energy of the electron, $h\nu$ is the energy of the incident x-ray photon, E_K is the kinetic energy of the electron and W is the work function. All the quantities except E_B are known, and binding energy can be calculated. XPS provides information about the elements present at the surface, their chemical states, the portion of each chemical state and their spatial distribution. In cases when the material of interest is a thin film, XPS can provide information regarding the film thickness, uniformity of the thickness and uniformity of the chemical composition of the film. [10]

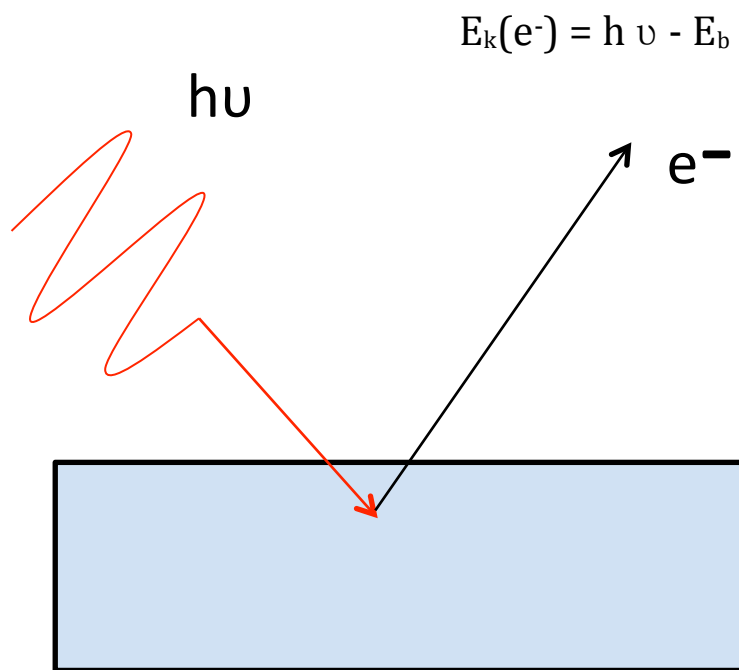


Figure 2. 10. Schematic representation of the photoelectron effect

2.4 Metal-Insulator-Metal Junctions

The samples studied in the following chapters are basically MIM diodes. Here a short description of the working mechanism, electrical properties and plasmonic effects in MIM structures will be given.

2.4.1 Basics of Metal-Insulator-Metal Junctions

In Metal-Insulator-Metal structures two metals are joined by an insulator sandwiched in between.

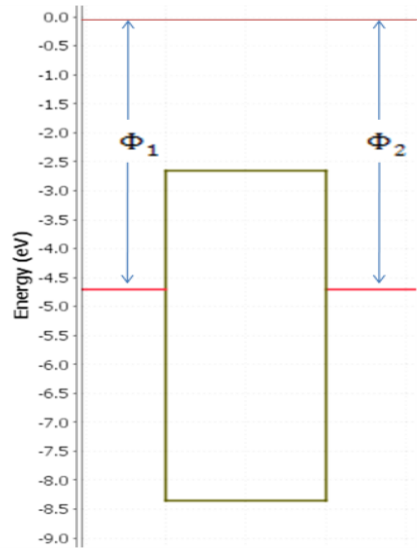
Energy band structure of MIM is determined by the following quantities:

- work functions of each of the metals Φ_1 and Φ_2 ,
- electron affinity of insulator χ
- bandgap of the insulator

With these values known, the band diagram of the MIM structure at equilibrium can be visualized as in figure 2.11. In figure 2.11a, same metal (Ag) is used in both sides of the insulator.

$$\Phi_1 = \Phi_2 \quad (2.58)$$

a)



b)

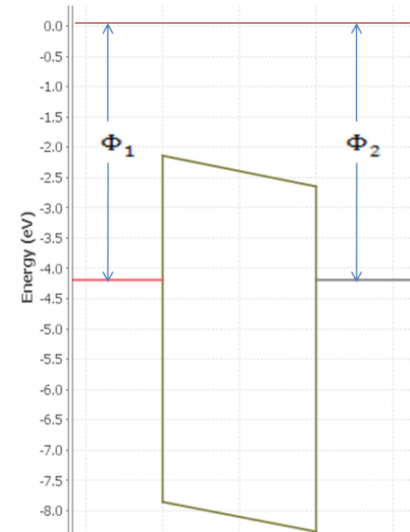


Figure 2. 11. Band diagrams of ideal MIM junctions. At diagram a) same metals are used and at b) different metals are used. Equilibrium is assumed at both cases. Bent of the vacuum energy band due to applied voltage is not shown.

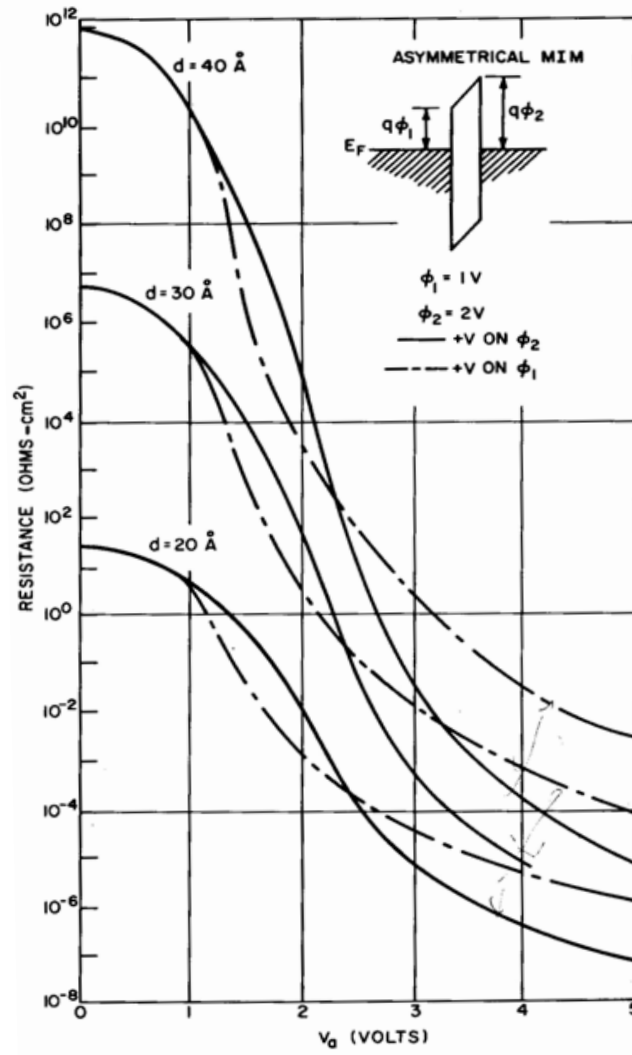


Figure 2.12. Theoretical Tunnel Resistance as a Function of Applied Voltage for an Asymmetrical MIM Structure. [11]

In the diagram shown in 2.11b, different metals (Ag and Al) were used to sandwich the insulator layer. Here a built-in electric field will appear at equilibrium conditions, bending the energy band diagram of the insulator.

At figure 2.12 the tunnel resistance as a function of V for $d = 20, 30$ and $40\text{\AA}$, $\Phi_1 = 1\text{V}$, and $\Phi_2 = 2\text{V}$ is illustrated. [11]

Barrier height and width are determinant factors in the tunneling probability of the electron through the barrier. The transmission probability is given by the Schrödinger Wave equation [12],

$$D = \exp(-2d [2m(V - E)/\hbar^2]^{1/2}) \quad (2.59)$$

Here, V is the barrier height and E is the energy of the particle. D is the transmission probability and d is the thickness of the insulator. As can be inferred from 2.48, electron tunneling becomes less common as thickness of the insulator increases. When different metals are used to sandwich the insulator layer asymmetry is noticed in the behavior of the diode under forward and reverse bias. This is due to the difference in the work functions of the two metals. If current flows only due to tunneling of electrons across the diode, i.e. we are dealing with a tunneling diode, in the forward bias case the road an electron has to travel through the potential barrier is shorter than in the reverse bias case. Therefore more electrons will pass the barrier and contribute to the current in the forward bias than there will be in the reverse bias. The performance of a diode is strongly limited by the difference in the work functions of the two metals. Using metals with different work functions improves the performance of a diode. [13]

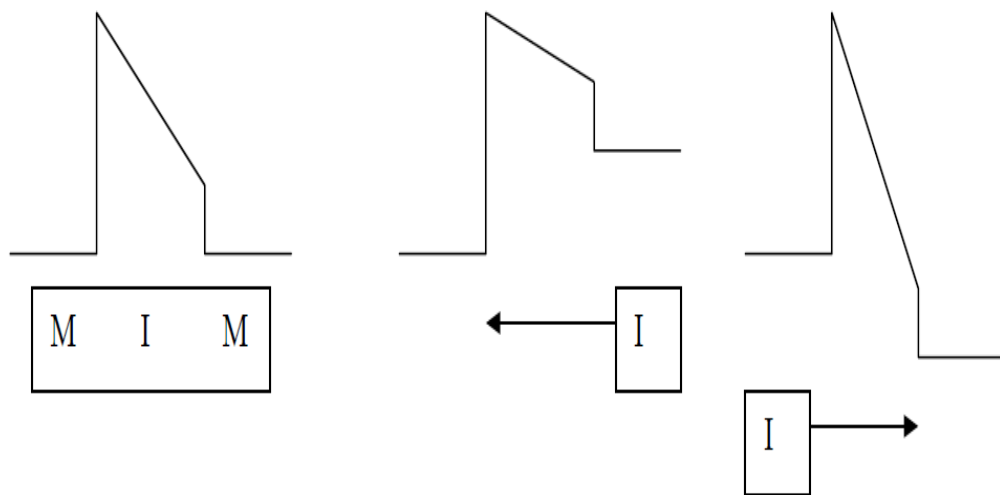


Figure 2. 13. Energy band diagram of MIM junctions under different bias conditions. From left to right: No bias, Reverse Bias, Forward Bias. [13]

2.4.2 Plasmonic Effects in MIM Structures.

MIM structures are multilayers consisting of an insulator layer sandwiched between two metal layers. The structure hosts two metal-insulator interfaces in the middle (the metal layers are considered to be semi-infinite).

Both interfaces host SPPs that decay perpendicularly to the surface with a decay length depending on the material properties of the metals and the insulator. When the thickness of the insulator layer is smaller than or comparable to the decay length of the interface mode, interactions between SPPs of the two interfaces gives rise to coupled modes.

The field components for non-oscillatory TM modes in the z -direction (schematically shown in figure 2.14) are described as follows:

For $z >$

$$H_y = A e^{i\beta x} e^{-k_3 z} \quad (2.60)$$

a :

$$E_x = iA_2 \frac{1}{\omega \epsilon_0 \epsilon_3} k_3 e^{i\beta x} e^{-k_3 z} \quad (2.61)$$

$$E_z = -A_1 \frac{\beta}{\omega \epsilon_0 \epsilon_3} e^{i\beta x} e^{-k_3 z} \quad (2.62)$$

For $z <$

$$H_y = B e^{i\beta x} e^{k_2 z} \quad (2.63)$$

−a

$$E_x = -iB \frac{1}{\omega \epsilon_0 \epsilon_2} k_2 e^{i\beta x} e^{k_2 z} \quad (2.64)$$

$$E_z = -B \frac{\beta}{\omega \epsilon_0 \epsilon_2} e^{i\beta x} e^{k_2 z} \quad (2.65)$$

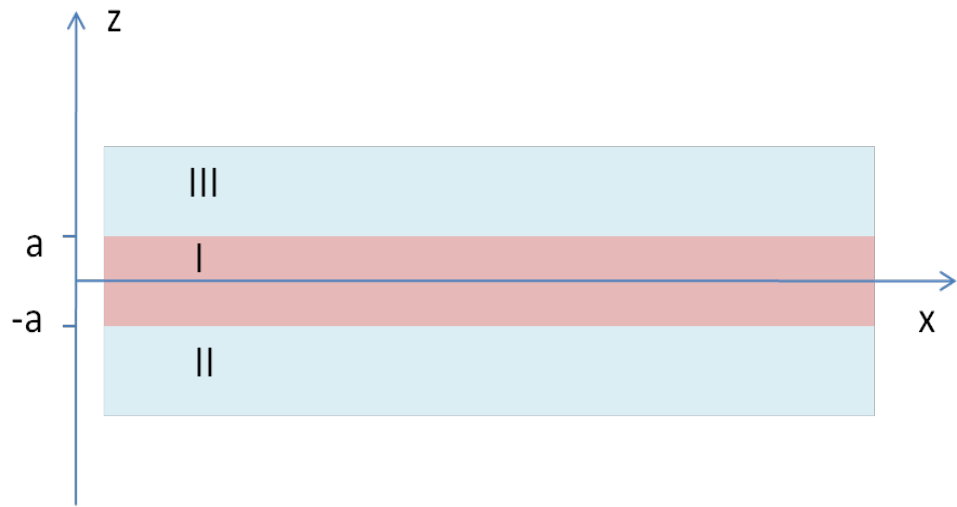


Figure 2.15. MIM structure geometry. The coordinative system shown is used in derivations.

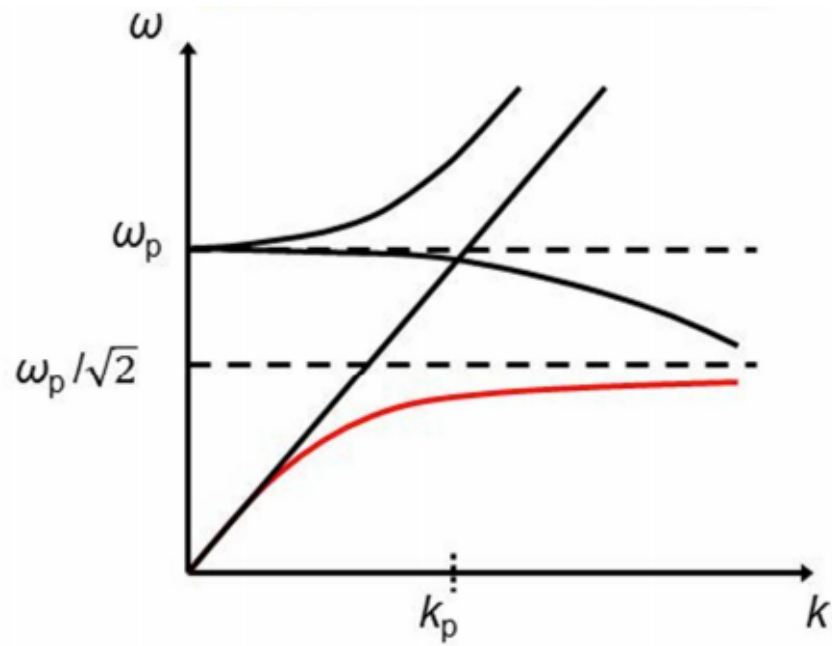


Figure 2.14. Dispersion plot for MIM structure [20]

Fields in regions II and III are expected to decay exponentially. Modes localized at both the interfaces couple at the insulator. The vector component of each field can be added to yield:

$$H_y = C e^{i\beta x} e^{k_1 z} + D e^{i\beta x} e^{-k_1 z} \quad (2.66)$$

$$E_x = -iC \frac{1}{\omega \varepsilon_0 \varepsilon_1} k_1 e^{i\beta x} e^{k_1 z} + iD \frac{1}{\omega \varepsilon_0 \varepsilon_1} k_1 e^{i\beta x} e^{-k_1 z} \quad (2.67)$$

$$E_z = C \frac{\beta}{\omega \varepsilon_0 \varepsilon_1} e^{i\beta x} e^{k_1 z} + D \frac{\beta}{\omega \varepsilon_0 \varepsilon_1} e^{i\beta x} e^{-k_1 z} \quad (2.68)$$

Using of the continuity of H_y and E_x at the interfaces $z=a$ and $z=-a$, the dispersion relation is obtained after solving the set of linear equations.

If the top and bottom metals are of same material, the dispersion relation can be expressed as:

$$\tanh k_1 a = -\frac{k_2 \varepsilon_1}{k_1 \varepsilon_2} \quad (2.69)$$

$$\tanh k_1 a = -\frac{k_1 \varepsilon_2}{k_2 \varepsilon_1} \quad (2.71)$$

$$e^{-4k_1 a} = \frac{k_1/\varepsilon_1 + k_2/\varepsilon_2}{k_1/\varepsilon_1 - k_2/\varepsilon_2} \frac{k_1/\varepsilon_1 + k_3/\varepsilon_3}{k_1/\varepsilon_1 - k_3/\varepsilon_3} \quad (2.70)$$

Equation 2.70 and 2.71 show the odd and even vector parities respectively. In the odd vector parity case $E_x(z)$ is odd, $H_y(z)$ and $E_z(z)$ are even functions. In the even vector parity $E_x(z)$ is even function $H_y(z)$ and $E_z(z)$ are odd functions. The equations derived so far were general for multilayer structures. For the MIM case, $\varepsilon_2 = \varepsilon_2(\omega)$ is the dielectric constant of the metal, considering same metal is used in the top and bottom contacts, and ε_1 is the dielectric constant of the insulator. If top and bottom metals are not made of same material, the coupling between SPP modes at the two interfaces changes a lot

because of the metals different dielectric constants. The difference in dielectric constant will prevent the phase matching [21]. Coupling in both cases is a strong function of the insulator thickness, and with the insulator becoming thicker the coupling will fade after a certain point.

2.4.3 QM Tunneling Mechanisms in MIM Structures.

Quantum mechanical tunneling describes the transition of carriers through energy state classically forbidden. In the case of the MIM structures the forbidden energy state is insulator bandgap. According to classical mechanics, the probability that the particle passes through the energy barrier is zero. However, due to the wavelike behavior of particles on the quantum scale, quantum mechanics predicts a probability value, even though small, for the particle to be on the other side of the barrier. Direct tunneling, Fowler-Nordheim tunneling and trap-assisted tunneling (TAT) are the tunneling mechanisms mostly affecting tunneling current. In direct tunneling electrons propagate through the barrier without using the conduction band of the dielectric. Direct tunneling is temperature dependent and it increases exponentially with decreasing oxide thickness. The most important characteristic of direct tunneling is that it does not create oxide defects after repeated cycle operations, leaving the oxide structure unaffected [15]. Fowler-Nordheim Tunneling is a special case of direct tunneling (Figure 2.16b). Here electrons tunnel from one side of the insulator to the other side by passing the conduction band of the oxide. Trap-assisted tunneling becomes significant after a large number of carriers have passed through the dielectrics creating defects in its structure. Only one defect would not create a large leaking current, but many defects would deter the performance of the MIM device. [16]

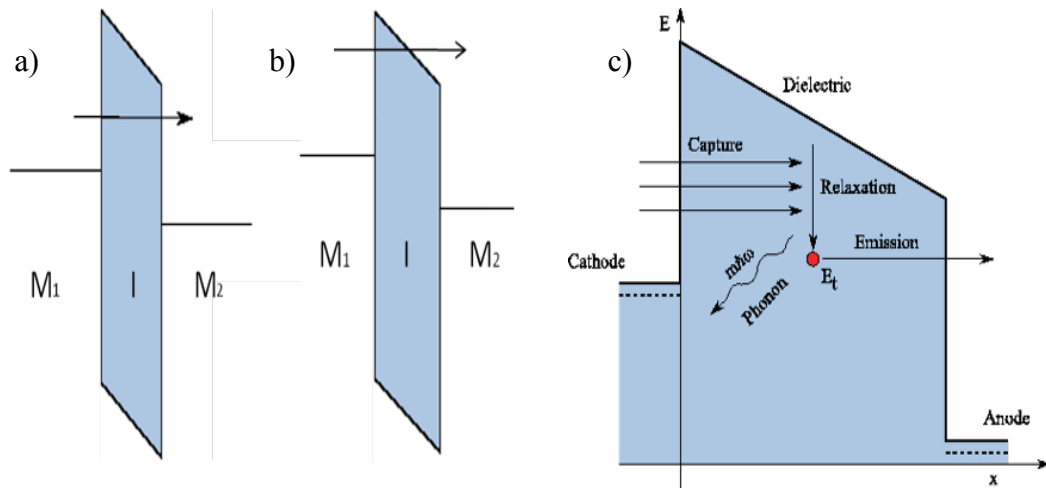


Figure 2. 16. Schematic view of tunneling mechanisms. a)Direct tunneling, b)Fowler-Nordheim Tunneling, c)Trap-assisted Tunneling [14]

Chapter 3

Hot-electron and Plasmonic effects in Metal-Insulator-Metal structures.

In the previous chapters a theoretical review of Surface Plasmon, X-ray photoelectron Spectroscopy and metal-insulator-metal junction were given. In this chapter a detailed review of recent studies of plasmonic and hot electron effects in MIM structures is provided. MIM junctions are used in applications such a photodetectors and energy harvesting devices. MIM junctions are fabricated by well known, simple and controllable thin film deposition techniques. This feature is desirable for engineers and it makes MIM more attractive for applications. Understanding and modeling the effect of surface plasmons and hot electrons in MIM structures is hence very important. Lately a number of papers on this topic have been published, and many groups are trying to fully understand the theory laying behind. When photons hit an MIM junction each photon excites an electron at the metal, giving it energy and depending on the energy the electron may or may not excite over the Fermi level. If kinetic energy of the excited hot electron exceeds insulator barrier, there is a probability for the electron to travel through the insulator and contribute to the current. Different models have been proposed to model the hot electron behavior at MIM sandwiched structures. Recently Chalabi et al [3] used a 5-step model to describe the photoemission of electrons across a barrier. Their approach was based on the earlier method used by Spicer [22]. In their work, Chalabi and her coworkers reshaped one of the metallic contacts in the MIM structure, so that it supported plasmonic resonances. Hence they enhanced the efficiency by using one of the contacts as antenna that resonate Surface Plasmon Polaritons. The device they used consisted of an Au metallic substrate coated by a layer of Al_2O_3 . Top Au layer was shaped by means of lithography. The 5-step model is shown in figure 3.1.

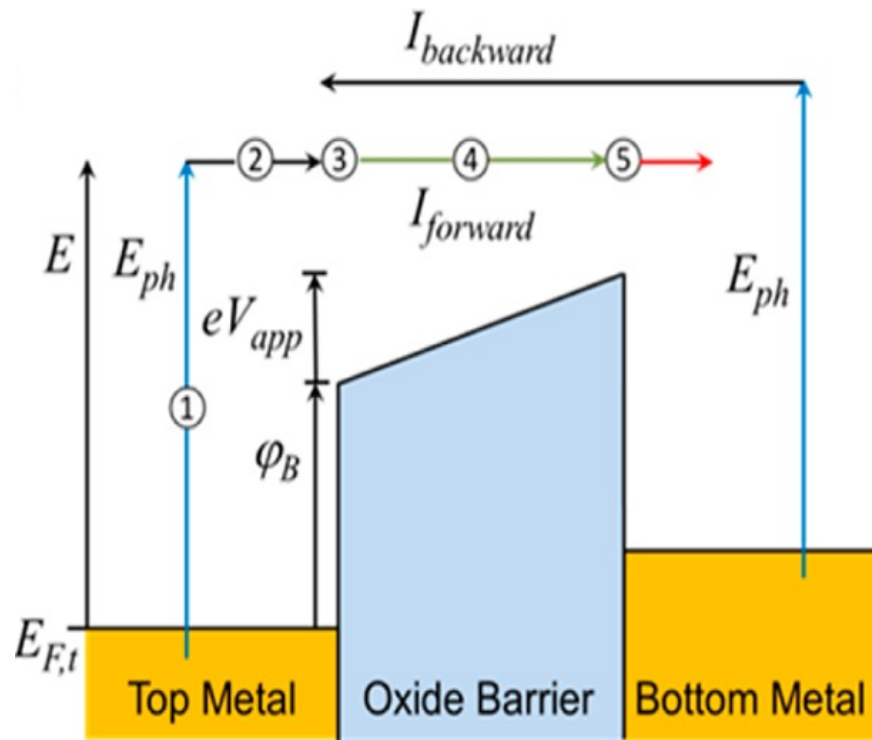


Figure 3.1. Photocurrent caused by electrons passing through the barrier. Photoelectrons are excited at the top and bottom metals as well, so backward current will be produced even if less than the forward current. Here a voltage has been applied.[3]

In the first step hot electrons are generated in the top metal and excited to an energy level equal to the incoming photon. Here an important assumption is made. The electrons in the metal are assumed to behave as free electrons, and the energy gained by interaction with the photon goes totally to kinetic energy used to “lift” the electron in the band diagram. Also the electrons momentum is assumed to be equally distributed in all directions; isotropic. At step 2, statistically half of the electrons will move towards the metal-insulator interface. Only a small fraction of those make it to the interface. Many will lose their energies in inelastic interactions. The fraction of electrons arriving to the interface can be found by making use of the mean free path of energetic electrons in solids. Step 3 is at the interface. If the electron has kinetic energy smaller than the barrier, there is a small probability that it will tunnel according to quantum mechanics. Even if the electrons kinetic energy is larger than the barrier and enough to pass it, the probability for the electron to inject into the oxide will still be small due to the contrast in wave vector between the injected electrons and the oxide electrons. While passing through the oxide there is a certain probability that the electron will pass without inelastically colliding and make it to the next interface and this is step 4. In step 5, at the junction between the insulator and the bottom metal reflection is possible due to the mismatch in wave vectors.

Further, *Chalabi et al* and her coworkers have experimentally studied the voltage-dependence, spectral-dependence, stripe-width dependence and polarization-dependence of the photocurrent in the device.[2] The materials used are Au-Al₂O₃-Au. This makes device’s potential band diagram to be symmetrical under equilibrium conditions. According to optical simulations, light of the light is absorbed at the top stripe that at the bottom metal (at least 1 order of magnitude difference). Due to the asymmetric absorbance of light in the two metals, even at 0V bias forward current is larger than the backward current and a net photocurrent has been observed. To show the effect of plasmonic enhancement in the photocurrent, they have fabricated samples with different stripe width and compared their electrical properties. Also a polarizer has been

employed to provide TM and TE polarized light. It has been observed that the photocurrent for the TM polarized light was much larger than for the TE polarized light falling on the strips. The explanation provided is related to excitation of SPP-s in the grating- oxide interface by the TE polarized light. [2]

Wang and Melosh et al also demonstrated theoretically and experimentally that hot electrons excited in the metal electrode could be collected and converted into solar energy by using a MIM structure. They described the hot electron-Plasmon effect, and proposed that the detrimental nature of surface Plasmon decay in fact can be used to boost energy conversion. The metal film is utilized to absorb light and emit electron at the same time, and the electron energy is harvested before converting to heat.

They have studied the effect of the thickness of the upper metal on the current. An optimal thickness exists. If the metal is too thick, more photons would be absorbed but there is a longer way for the electrons to reach the metal-insulator interface. The probability that electron would scatter is therefore larger. On the other hand, absorbance in thin metal layers is poor.

Even though most of the electrons would make it to the interface, poor absorbance leads to many reflected photons, and not enough photons are absorbed to excite the electrons. Kretschmann geometry has been used to excite SPs and it is compared to the case when direct illumination was used.[2]

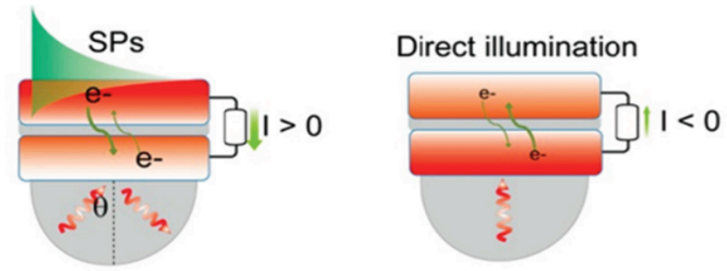


Figure 3.3. Mechanism of hot electron transmission in MIM devices in cases when excitation of SPs and direct illumination. [2]

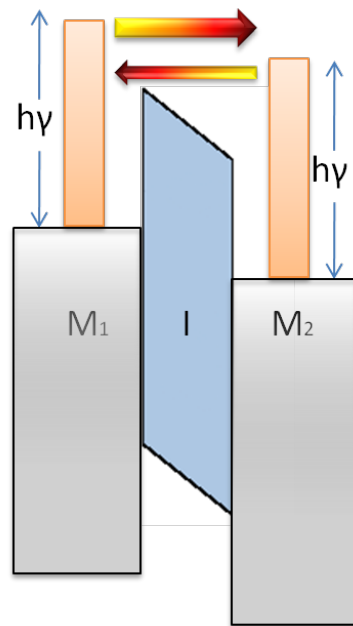


Figure 3. 2 Energy diagram of the MIM device. Electrons are excited to higher energy states (hot electrons) incoming photons with energy $h\nu$. Hot carriers are excited in the top and bottom metal as well. [2]

The probability that an hot electron reaches the interface is proportional to: $\exp[-d/(\lambda_e \cos\theta)]$. Here d is the metal thickness; λ_e is the mean free path of the electron in the metal. For Silver the mean free path of an electron having a kinetic energy of 1.96eV is 56 nm. [2],[23]

MIM device can be adjusted to absorb light at any wavelength. The system can be set that only the hot electrons above the barrier generate power. Both the open circuit voltage and short circuit current can be tuned by changing the thicknesses of top and bottom metal layers. [24]

Melosh et al has also used MIM devices to determine the wavelength of monochromatic light in a power-independent fashion. The main promising feature of this device is that the ballistic electron transport is very fast, in the range of picoseconds; hence the device is thought to work good even at high frequencies. The open circuit current of the device is independent of the device area, therefore the device can be scalable to nanometers sizes. The open circuit voltage, V_{oc} can be calculated as follows [2]:

$$V_{oc} = \frac{(E_{ph} - \Phi_e)}{e} \left(1 - \frac{I_{sc}^{btm}}{I_{sc}^{top}} \right) \quad (2.1)$$

Here E_{ph} is the energy of the photon, Φ_e is the barrier for the electron and I_{sc}^{btm} and I_{sc}^{top} are the short circuit currents for the top and bottom metals. If $I_{sc}^{btm} \ll I_{sc}^{top}$, the second bracket of equation 3.1 can be approximated to be 1, and equation 3.1 takes the following form:

$$V_{oc} = \frac{(E_{ph} - \Phi_e)}{e} \quad (2.2)$$

Chapter 4

Fabrication and Characterization of Plasmonic Surfaces

In this chapter the design, fabrication and characterization techniques used will be described. The devices fabricated and used here can be divided in two categories. In the first category, Silver nanoparticles were deposited on an insulator layer, that itself was deposited at different thicknesses on a metal substrate. Different materials were used for both the bottom metal layer and the insulator. We worked towards optimizing the optical properties of the substrates. We aimed to achieve high light absorption. Indeed, at a defined combination of the insulator thickness, Ag nanoparticles size and distribution, almost perfect absorption of light was achieved at visible spectra (350-750nm).

The second category is similar to the first but differs in the fabrication methods used and the form of the top metal layer. Here, instead of the nanoparticles with random distribution and size used in the first case, metal gratings with well defined geometry were patterned and deposited on the insulator layer.

Atomic layer deposition (ALD) and thermal evaporation were used to deposit the insulator layer and the metal layers respectively. All fabrication processes are conducted in Class100 clean room facility at UNAM.

Atomic Layer Deposition

Atomic Layer Deposition is a Chemical Vapor Deposition technique. In ALD the precursors are pulsed into the reactor alternately, one at a time. During one pulse, firstly the first precursor is exposure. After that, purge or evacuation of the reaction chamber occurs. A purging or evacuation periods is needed between each precursor pulse to clean the sample from the first precursor and prepare it for the other precursors. Exactly the same process is repeated for the second precursor.

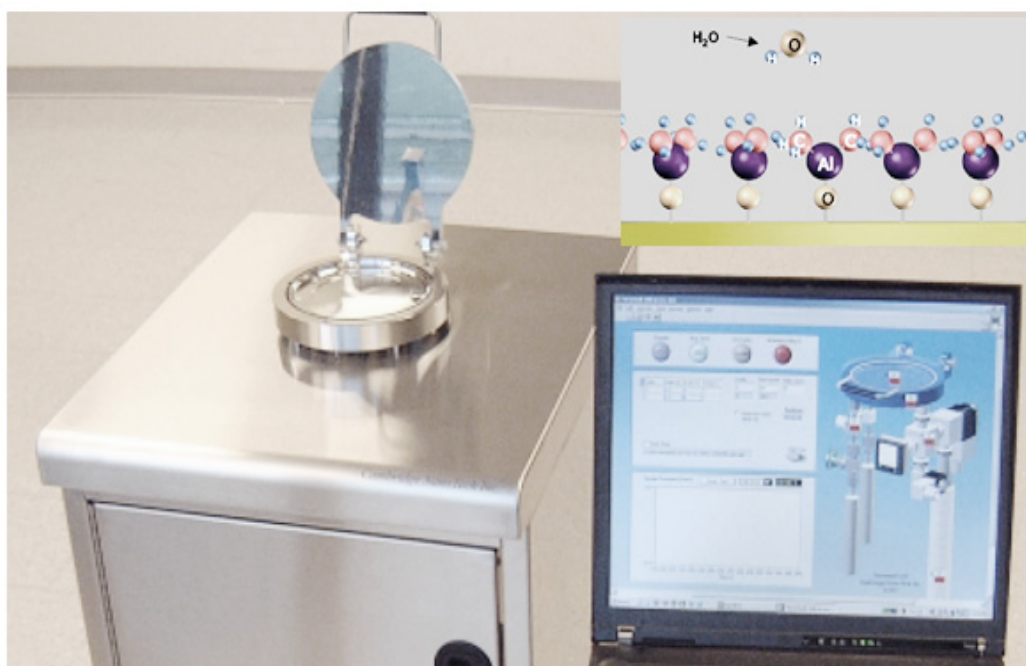


Figure 4. 1. Savannah Atomic Layer Deposition system at UNAM [25]

In this manner, this process is repeated as many times as needed to obtain the thickness aimed. The number of pulses needed to obtain a film of a certain thickness can be precisely determined. This is due to self-limiting property of ALD. Each cycle grows exactly one monolayer. The greatest advantage of ALD is the uniformity of the deposited film. This is due to the self-limiting growth mechanism of ALD. This feature of the ALD grown insulator films gives confidence about the electrical insulating of the oxide layer, and the probabilities that there will be some leakage of current through the insulator becomes minimal. Insulating layers of HfO_2 and Al_2O_3 were deposited by ALD.

Thermal Evaporation

Making use of the VAKSIS PVD Vapor-3S Thermal Evaporation System bottom metal layer is formed. At the process, metal is heated to several hundreds of degrees in a vacuum environment. When evaporation temperature is reached, vapor particles from the source move towards the sample and condense to a solid state on the surface. The chamber is at vacuum so the probability that the vapor particles collide on the way towards the substrate is minimal. The main parameters of thermal evaporation systems are:

- Chamber pressure
- Substrate temperature
- power applied to source material
- the distance between the source and the substrate.

Thermal evaporator is widely used in microfabrication for making metal contacts. An advantage of thermal evaporation system is that different layers can be deposited without breaking the vacuum. This allows for clean process and reliability of the sample. A wetting layer of 3 nm Germanium is deposited first on the silicon wafer. The silicon substrates are chosen to be undoped so that they provide an insulating environment and do not affect the electrical properties of the MIM structure on them. Without opening the chamber, on the wetting layer

70 nm thick Ag metal is deposited. During the processes the chamber pressure is held at around 10^{-6} Torr. Material coating rate is kept constant at $0.5 \text{ \AA/sec}$.

To deposit the top metal layer, different Ag thicknesses were deposited. We tried depositing 1nm, 3nm, 5nm, 7nm and 9nm silver on top of silicon to check the nature of the formed film. It is a matter of fact that the distribution and size of the formed nanoparticles on top of silicon will be different from the ones on top of the oxides that we will use. Anyway, this was the first step towards improving our samples.

The Deposition rate was held constant at $0.7\text{-}1 \text{ \AA/sec}$ in this step. To characterize the samples, we made use of the Scanning Electron Microscope (SEM) facilities at UNAM.

The SEM images for different thicknesses of Ag metal on Si wafers are shown in the following pages.

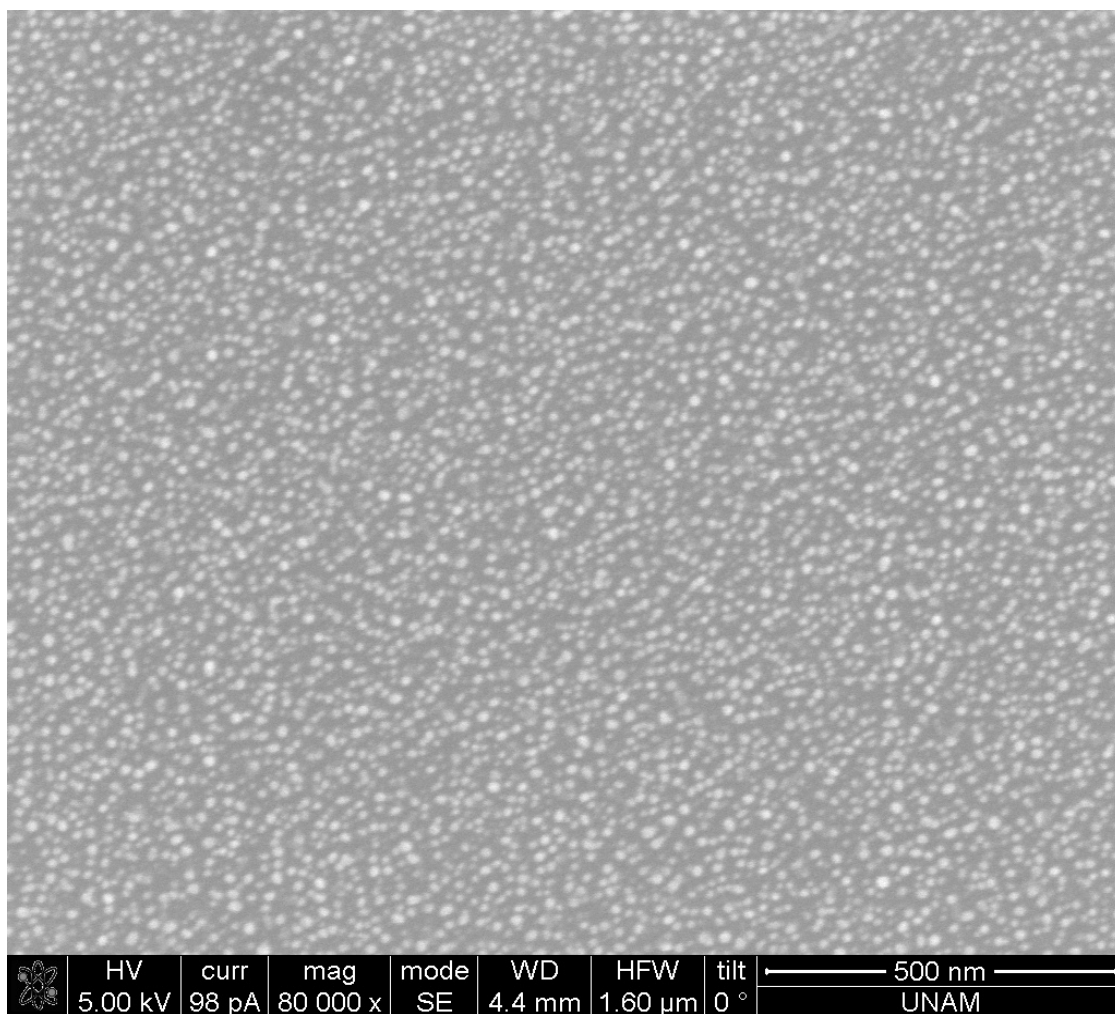


Figure 4. 2. SEM image, 1 nm Ag is deposited on Silicon. Random silver nanoislands of diameter 7-10 nm are formed. Nearly all the particles are independent and not connected to each other.

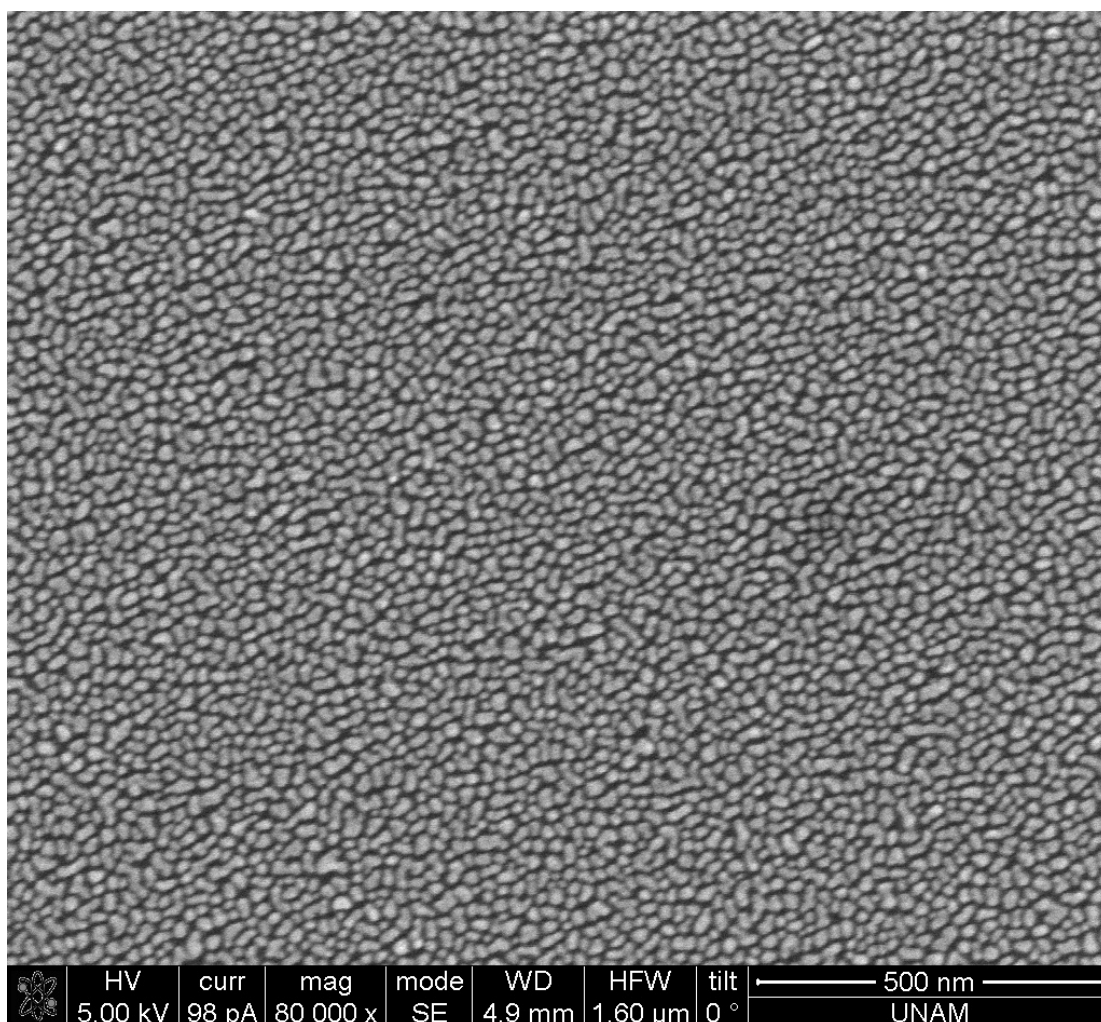


Figure 4. 3. SEM image, 3 nm Ag is deposited on Silicon. Diameter of the randomly formed silver nanoislands is larger than that in the previous case. Here the nanoparticles have a diameter of average 20-30nm. Also the distance between neighboring islands decreases.

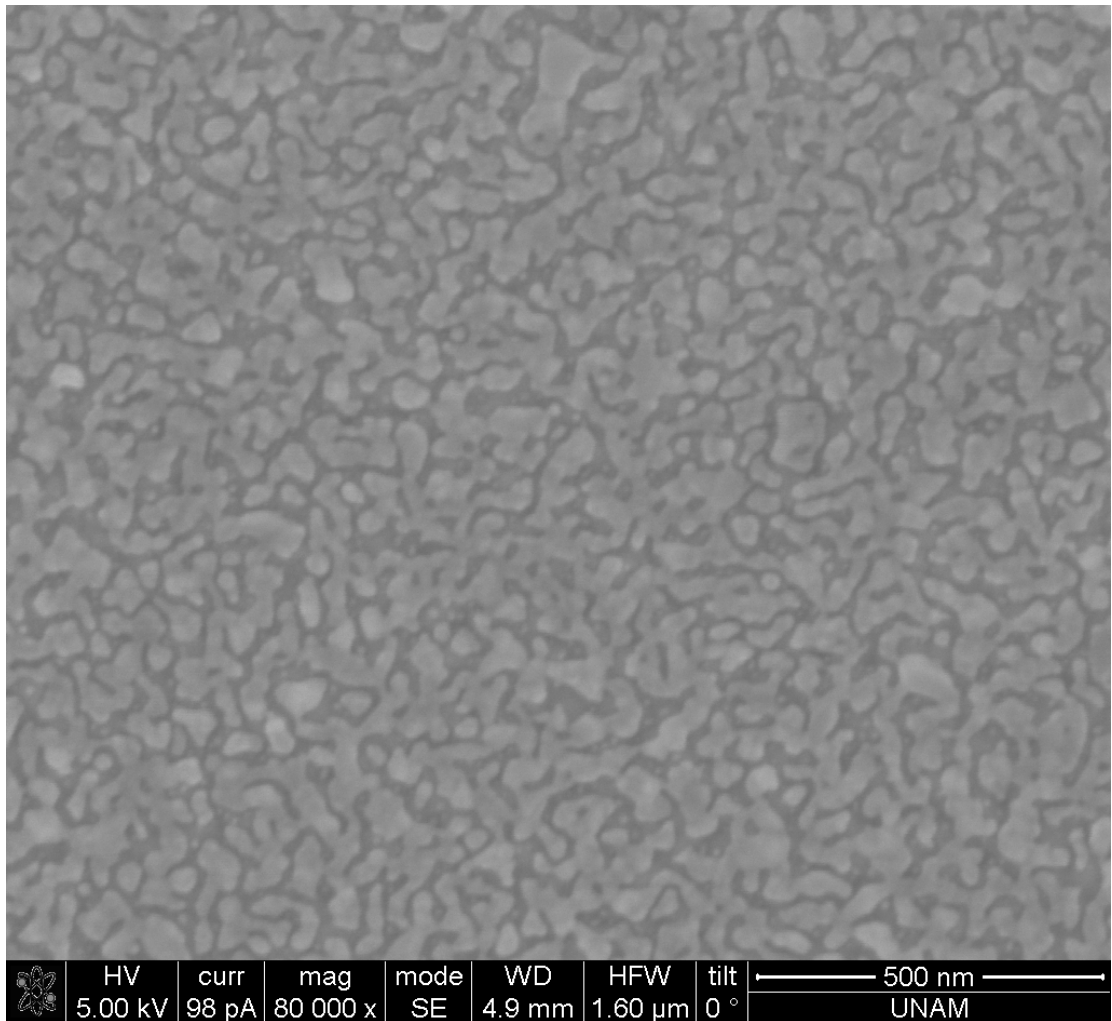


Figure 4. 4. SEM image, 5 nm Ag is deposited on Silicon. Here the nanoislands shown in the previous cases are connected to each other. Still it cannot be claimed to be a continuous half-film. Empty space between is still comparable in area to the to the area of the Ag structure.

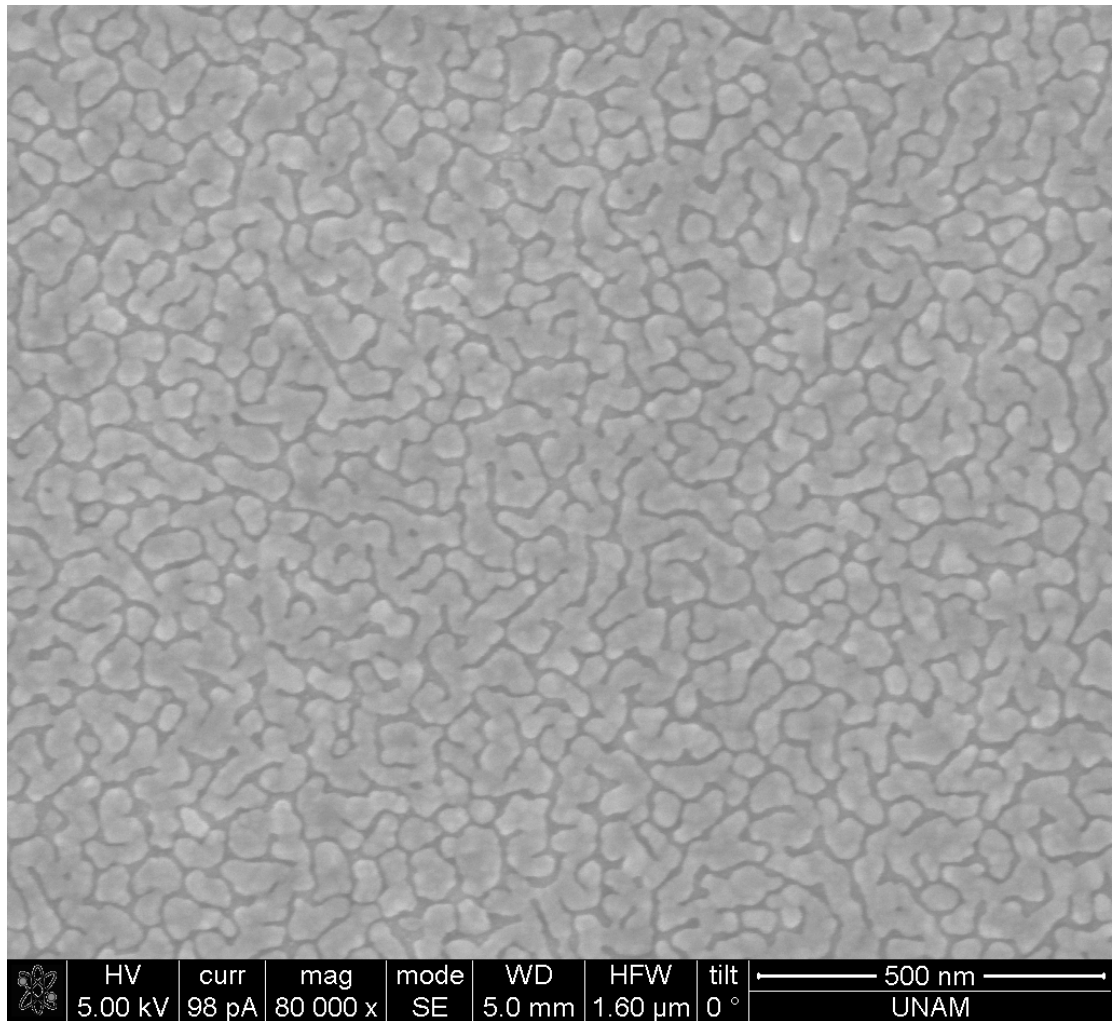


Figure 4. 5. SEM image, 7 nm Ag is deposited on Silicon. Here a quasi-continuous film is formed. Empty space between Ag is obviously less than the following case. It seems that most of the Ag layer is interconnected. Also the structure has larger dimensions than the previous case where 5 nm Ag is deposited.

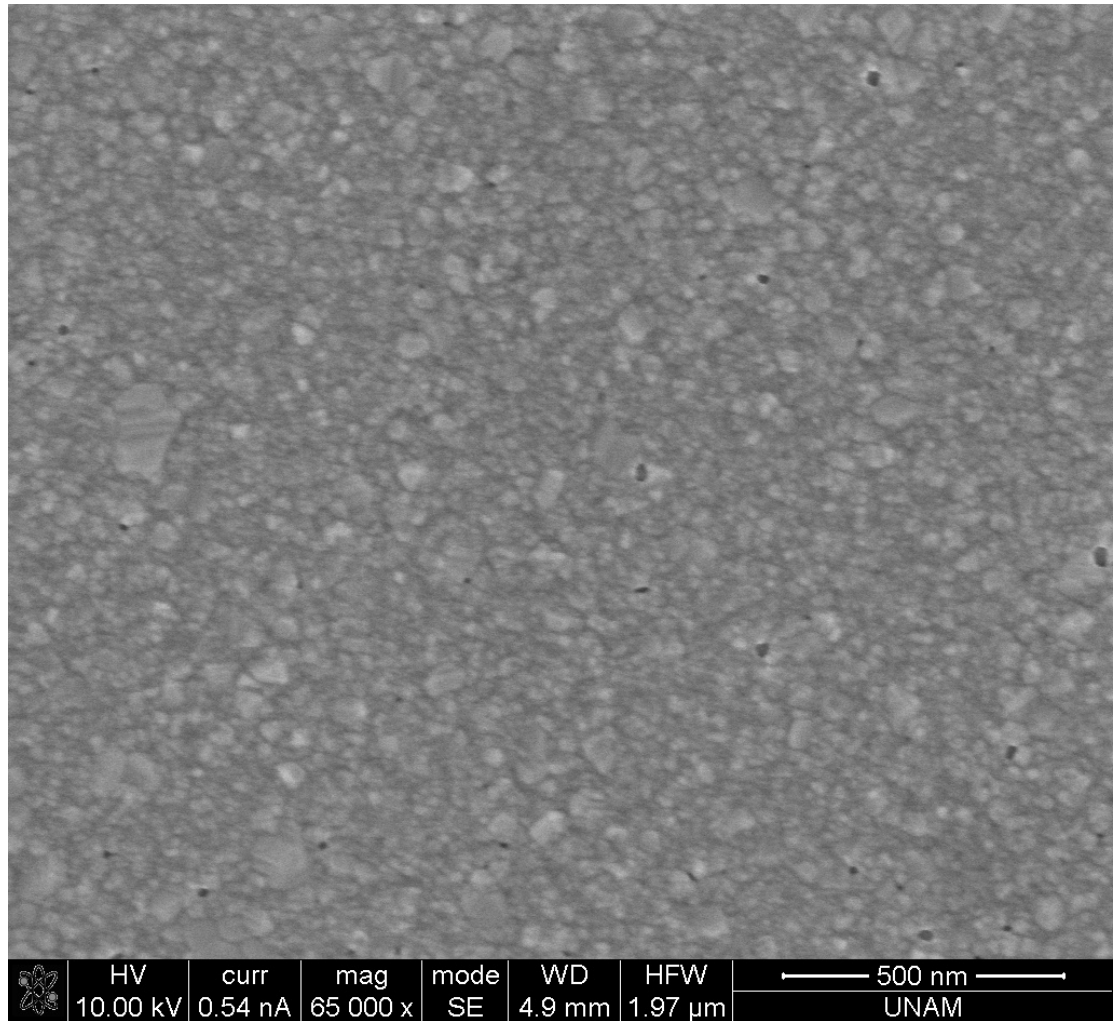


Figure 4. 6. SEM image, 9 nm Ag is deposited on Silicon. Here a continuous film is formed.

Up to now, fabrication and characterization of Ag layers of different thickness on top of silicon wafers was performed. It was shown that the properties of the formed Silver layer depend on how much metal is evaporated. Other thermal evaporator parameters such as chamber pressure and deposition rate also affect the formed structure. Here, these parameters are held constant and the same recipe was followed in all the deposition processes.

Next, after optimizing the fabrication process, the MIM devices are fabricated and their optical properties are characterized. Spectroscopic ellipsometer is utilized to characterize the optical properties of the fabricated samples.

A set of devices was fabricated (Figure 4.7), all having equal bottom metal thickness of 70 nm. Various thicknesses of HfO_2 (5 nm, 10 nm, 20 nm, 30 nm) and top metal (1 nm, 3 nm, 5 nm) are deposited on the Ag layer. Also during our work we used samples having Al as the bottom metal and also some others having Al_2O_3 as spacer.

Finally the reflection spectra are taken for all the devices. Following the reflection spectra for various angles is shown for each of the components of the set. Firstly, the set having 1 nm Silver deposited on different thickness of HfO_2 layer is studied. Ellipsometer results and SEM images are shown.

Firstly, the SEM image of the deposited top nanoparticles is shown. As it was claimed earlier in this section, distribution and dimension of the self ordered nanoparticles might be different in the case they are deposited on oxide than in the case they were deposited on silicon. This happens because adhesion forces are different in these cases. Crystal orientation also plays a crucial role. The SEM image of the as deposited 1 nm Ag on top of HfO_2 layer is shown below.

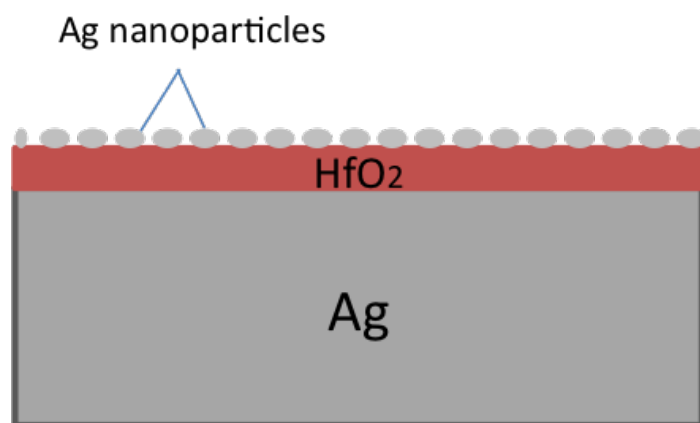


Figure 4. 7. Schematic representation of the fabricated device. Different samples were used having HfO₂ thicknesses of 5, 10, 20 and 30 nm. Also the top Ag metal was deposited at different quantity in order to obtain nano-islands of different dimensions.

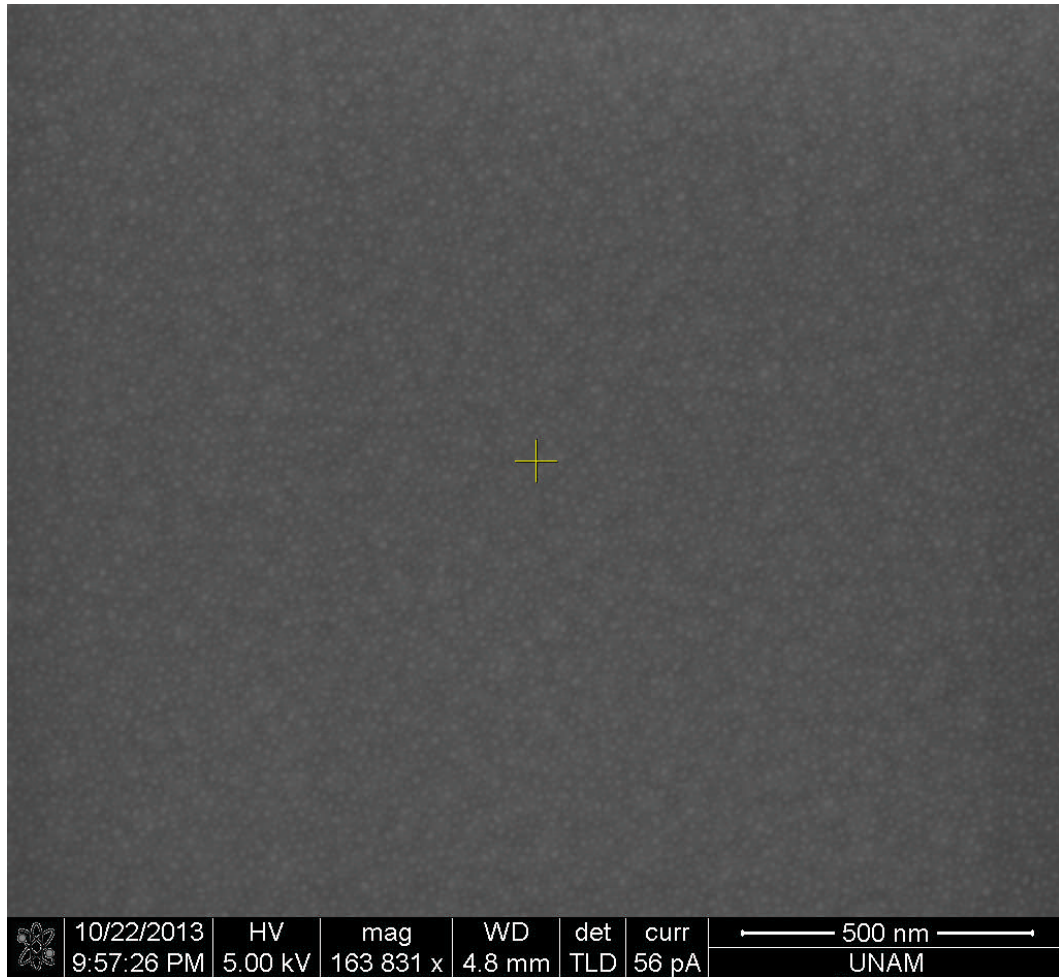


Figure 4. 8. SEM image of the as deposited Ag (1nm) on top of HfO₂ layer. The SEM image is not of great quality due to the charging effects caused by the presence of the insulator. Also the bottom metal structure is visible in the background.

Diameter of the nano-islands is in the range of 8-15 nm, similar to the case when nanoparticles were deposited directly on silicon wafers. Below the reflection spectra for samples having 1 nm Ag deposited on different HfO₂ thicknesses is shown.

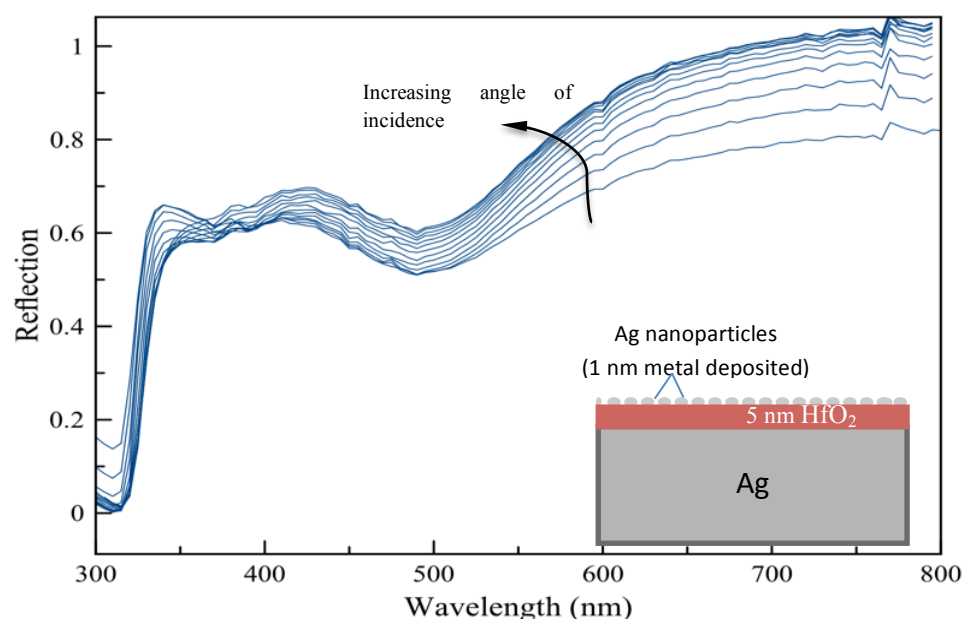


Figure 4. 9. Reflection spectra (p-polarization) for sample having 5 nm oxide layer in between the bottom Ag layer and the 1 nm deposited Ag top metal. Spectra is shown for angles of incidence between 15°- 75°, with 10 ° intervals.

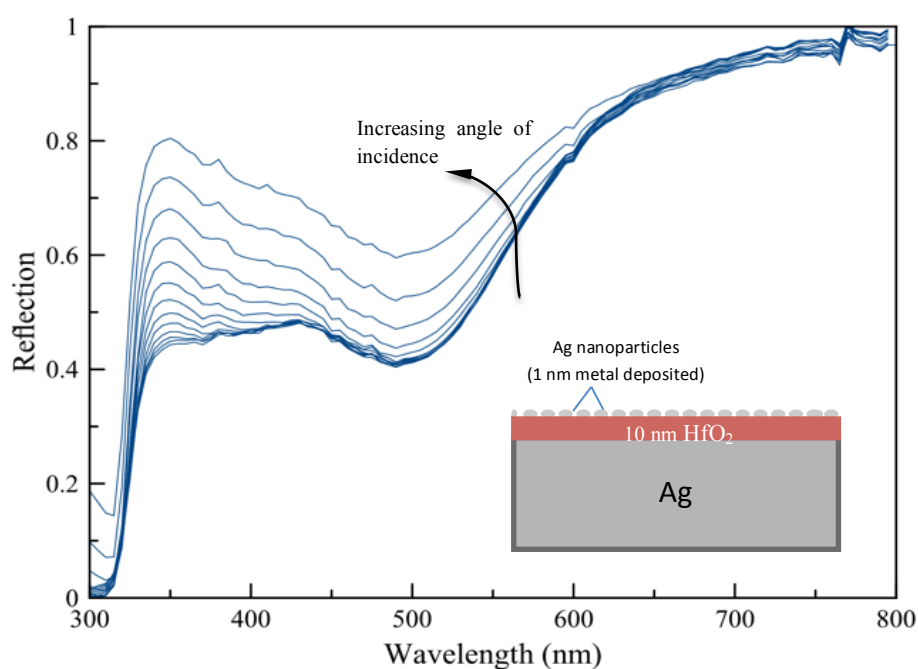


Figure 4. 10 Figure 4.10. Reflection spectra (p-polarization) for sample having **10 nm oxide layer** in between the bottom Ag layer and the **1 nm deposited Ag top metal**. The spectra is shown for angles of incidence between 15°- 75°, taken with 10 ° intervals.

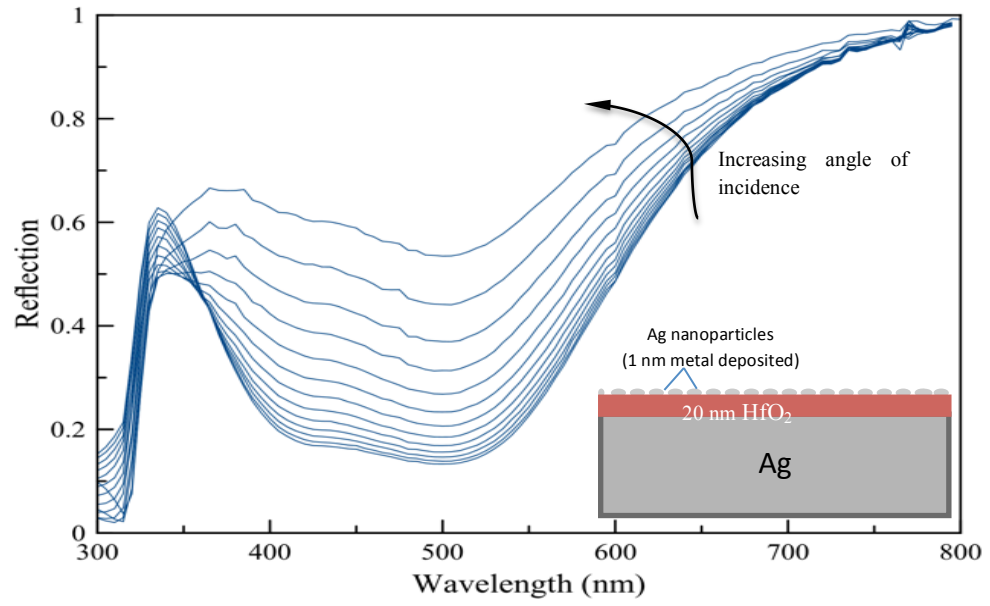


Figure 4. 11. Reflection spectra (p-polarization) for sample having **20 nm oxide** layer in between the bottom Ag layer and the **1 nm deposited Ag top metal**. The spectra is shown for angles of incidence between 15°- 75°, taken with 10 ° intervals.

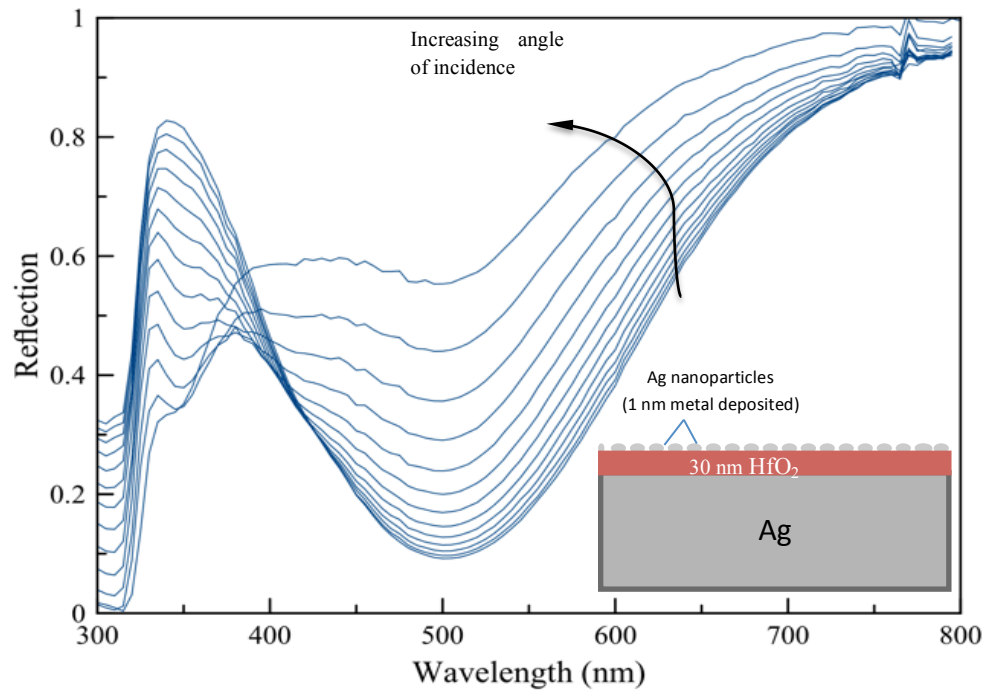


Figure 4.12 Reflection spectra (p-polarization) for sample having **30 nm oxide** layer in between the bottom Ag layer and the **1 nm deposited Ag top metal**. The spectra is shown for angles of incidence between 15°- 75°, taken with 10 ° intervals.

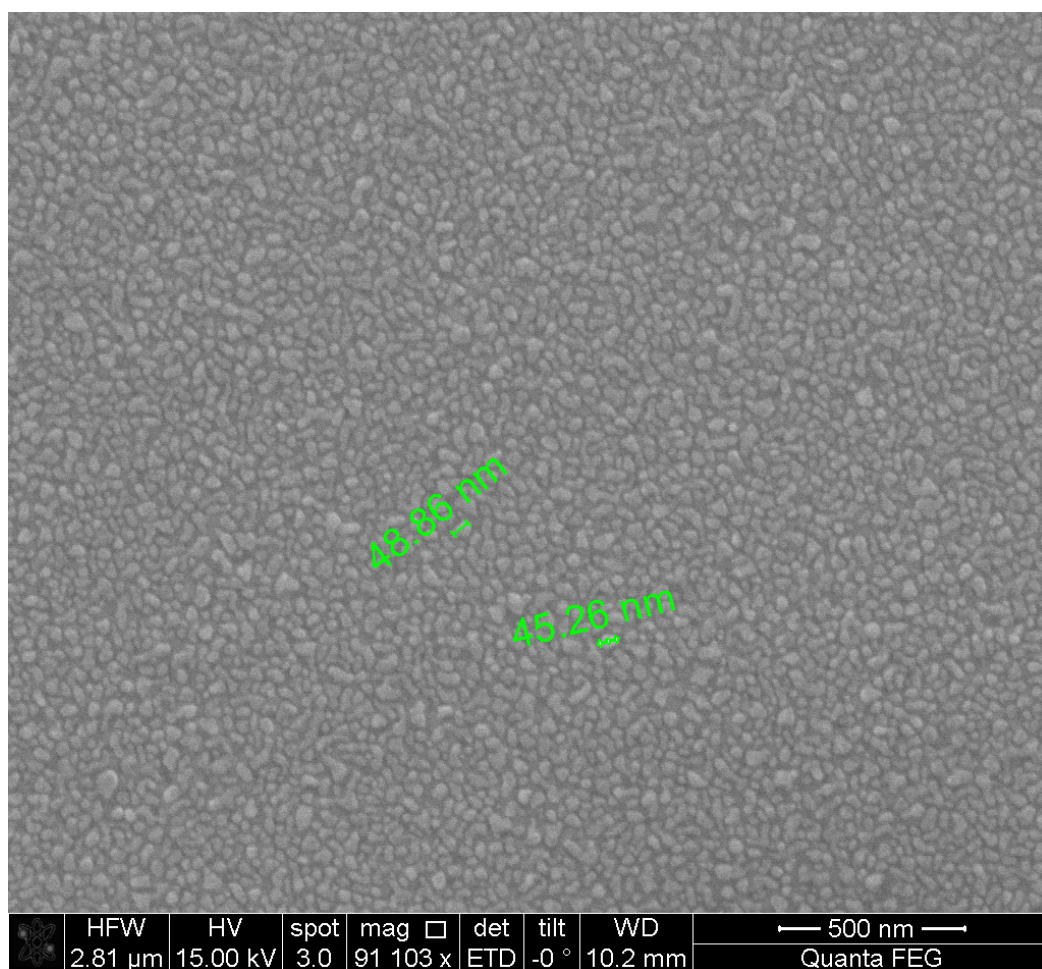


Figure 4. 13. SEM image of the as deposited Ag (3nm) on top of HfO₂ layer. Dimension of the formed nanoparticles is different than the case when the same Ag quantity was deposited directly on silicon.

It is seen that light absorption (can be approximated as unity minus reflection) increases as the insulator layer becomes thicker. However there should be an optimal value for the thickness, and since at 30 nm the surface absorbs light almost perfectly (at 75° , reflected light $< 10\%$), 30 nm can be considered to be near the optimal thickness value. Next, we continue with characterization of the plasmonic surfaces for the samples having 3nm Ag and 5nm Ag deposited.

SEM image and ellipsometer results are shown for 3 nm Ag deposited on different insulator thicknesses. The SEM image is given to compare it to the one where same silver quantity was deposited directly to Si wafer. In figure 4.13, SEM image of the as deposited 3 nm silver on the HfO_2 layer. As it can be seen by the measurement of the nanoparticle size taken by the SEM, size of the nanoparticles is larger than in the case when the same Ag quantity was deposited directly on silicon. Here, nanoparticles having diameter in the range of 30nm – 60 nm are seen. Despite the change in size, still the formed layer is not a continuous film and each particle is not connected to the neighboring particles. Next, the ellipsometer results for these surfaces are shown.

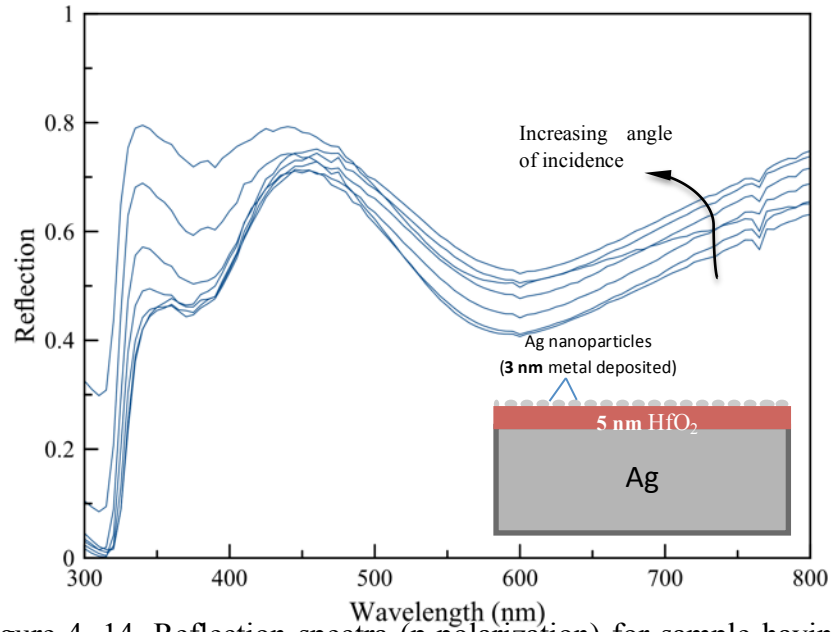


Figure 4. 14. Reflection spectra (p-polarization) for sample having **5 nm oxide layer** in between the bottom Ag layer and the **3 nm deposited Ag top metal**. The spectra is shown for angles of incidence between 15°- 75°, taken with 10 ° intervals.

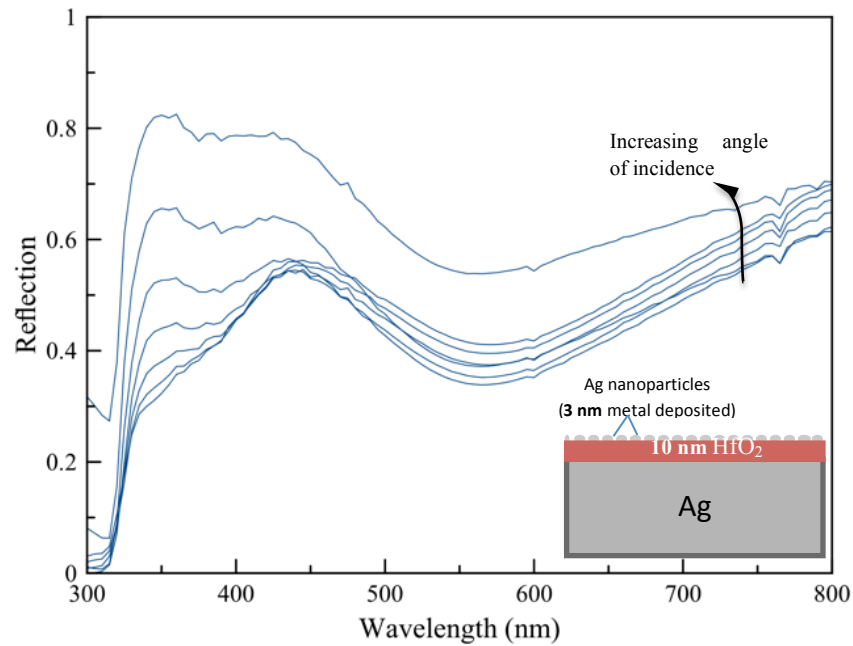


Figure 4. 15. Reflection spectra (p-polarization) for sample having **10 nm oxide layer** in between the bottom Ag layer and the **3 nm deposited Ag top metal**. The spectra is shown for angles of incidence between 15°- 75°, taken with 10 ° intervals.

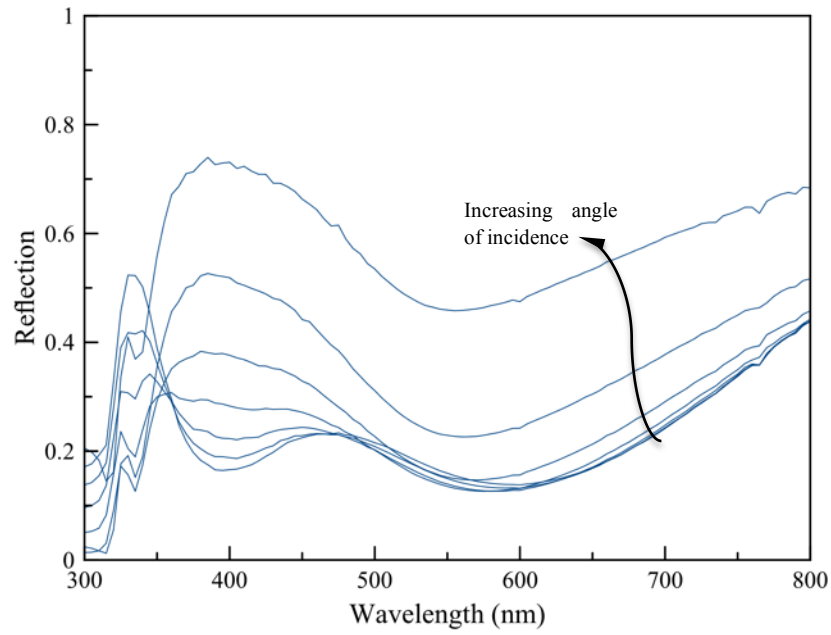


Figure 4. 16. Reflection spectra for sample having **20 nm oxide layer** in between the bottom Ag layer and the **3 nm deposited Ag top metal**. The spectra is shown for angles of incidence between 15° - 75° , taken with 10° intervals.

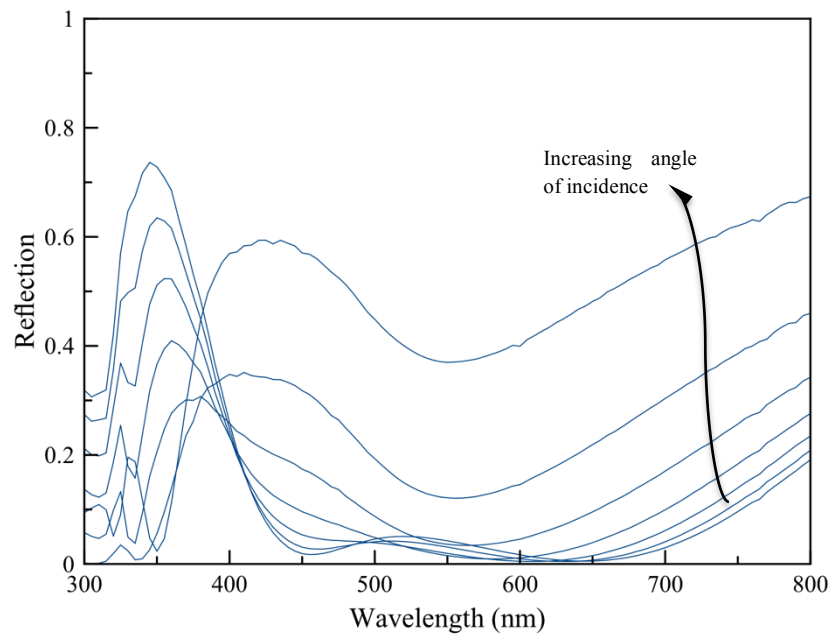


Figure 4. 17 Reflection spectra (p-polarization) for sample having **30 nm oxide layer** in between the bottom Ag layer and the **3 nm deposited Ag top metal**. The spectra is shown for angles of incidence between 15° - 75° , taken with 10° intervals.

The last set studied consists of samples having 5 nm Ag dewetted on the insulator layer. In this case, the world nanoparticles cannot be anymore associated with the structure formed by the evaporated Ag. A semi-continuous film is formed. The SEM image is shown in figure 4.18. The best absorption enhancement is observed in the sample having 30 nm oxide spacer and 3 nm Ag deposited on that. A broadband perfect absorber is obtained for the wavelength range 400nm -750nm.

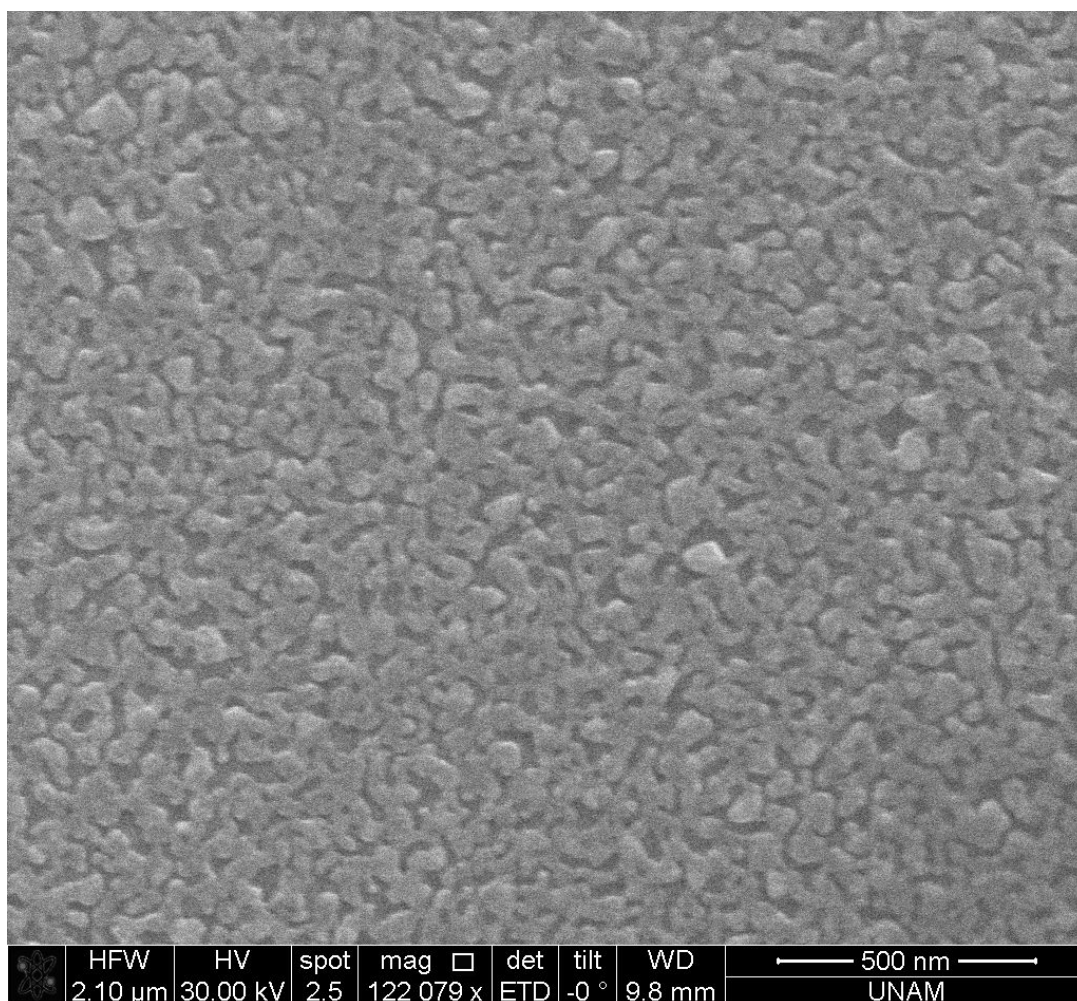


Figure 4. 18. SEM image of the as deposited Ag (5nm) on top of 20 nm HfO₂ layer.

A quasi-continuous film has been formed in this case.

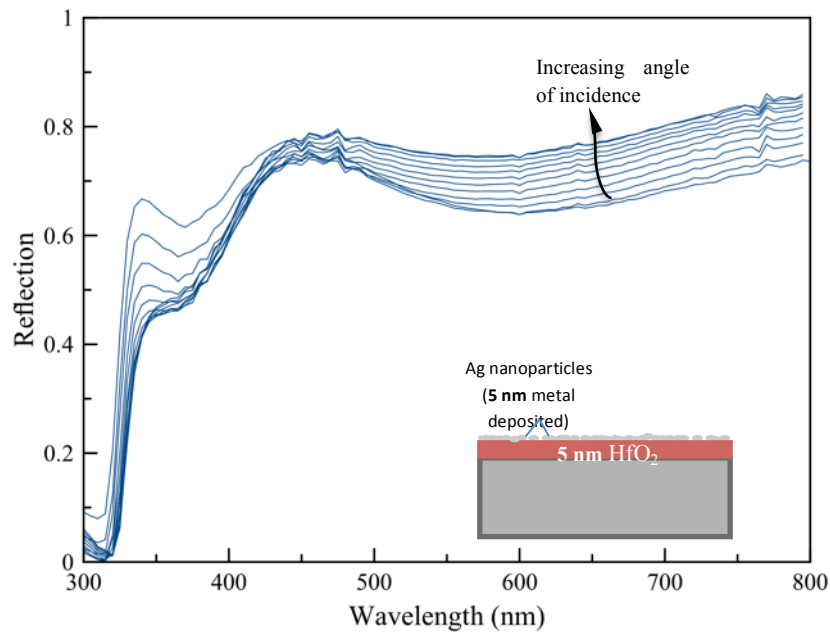


Figure 4. 19. Reflection spectra (p-polarization) for sample having **5 nm oxide layer** in between the bottom Ag layer and the **5 nm deposited Ag top metal**. The spectra is shown for angles of incidence between 15°- 75°. Most of light is reflected (~80% reflection).

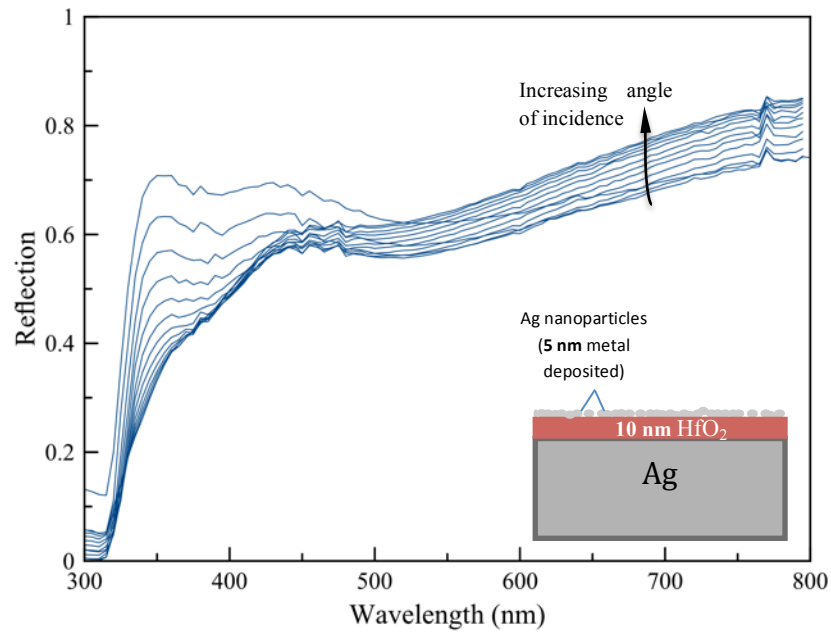


Figure 4. 20. Reflection spectra (p-polarization) for sample having **10 nm oxide layer** in between the bottom Ag layer and the **5 nm deposited Ag top metal**. The spectra is shown for angles of incidence between 15°- 75°, taken with 10° intervals.

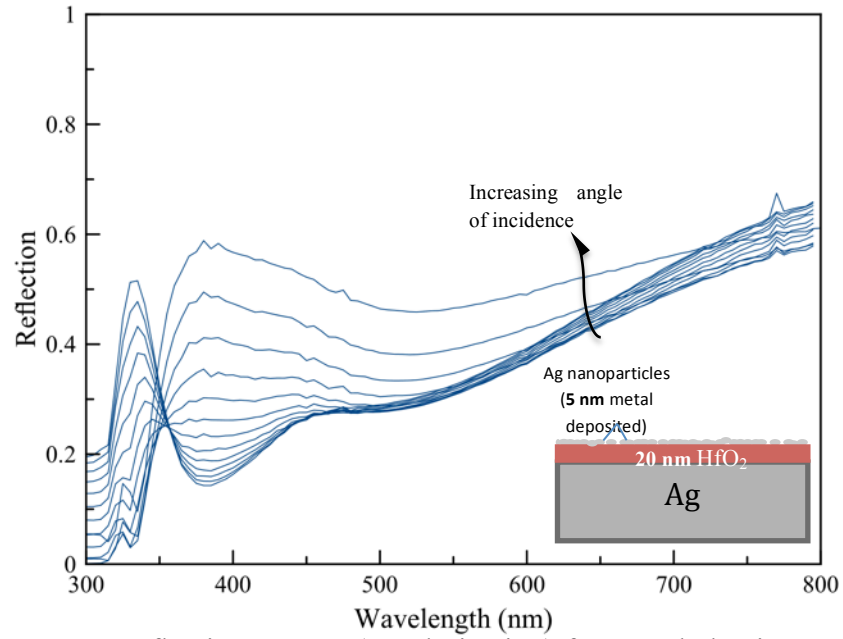


Figure 4. 21 Reflection spectra (p-polarization) for sample having **20 nm oxide layer** in between the bottom Ag layer and the **5 nm deposited Ag top metal**. The spectra is shown for angles of incidence between 15°-75°, taken with 10° intervals.

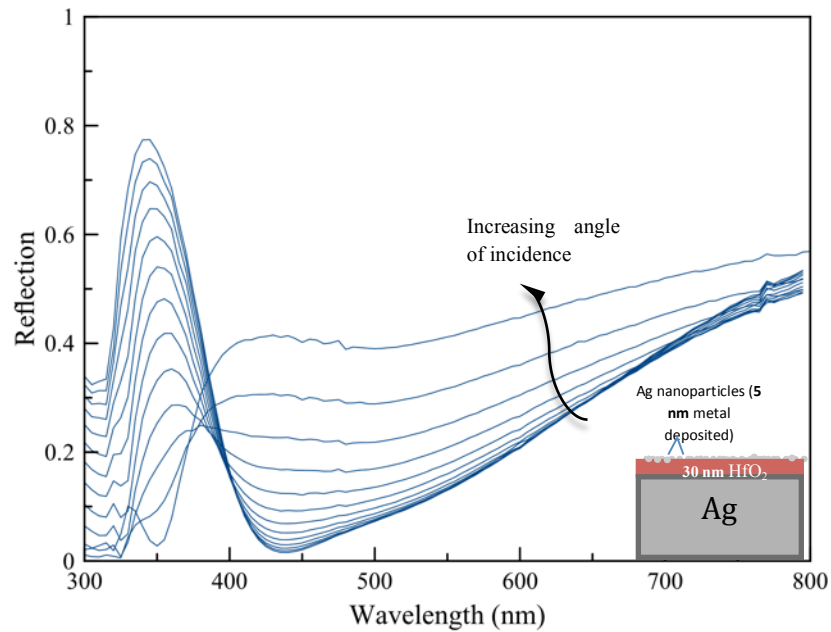


Figure 4. 22. Reflection spectra (p-polarization) for sample having **30 nm oxide layer** in between the bottom Ag layer and the **5 nm deposited Ag top metal**. The spectra is shown for angles of incidence between 15°-75°, taken with 10° intervals.

Fabrication of metal gratings

Firstly 3 nm Germanium was evaporated on the Silicon wafer as a wetting layer. Without opening the chamber, 70 nm Ag is evaporated on the Ge layer. Then 5 nm HfO_2 is deposited by means of ALD. Metal stripes are patterned by E-beam lithography. To prepare the sample for the e-beam lithography process, 100nm PMMA is spin coated and annealed at 180°C for 90 seconds. Then, patterns are formed using e-beam lithography system. After that, 50nm of Ag is deposited using thermal deposition. Final patterns are obtained by final lift-off process.

Two sets of gratings were fabricated perpendicular to each other. Width of the gratings is 150 nm and period is 250 nm. Length of each strip is 50 μm . The dimensions of each set are 250 μm X 250 μm , and each set contains an array of 5X5 groups of gratings. There are 200 strips in each grating. 250 μm X 250 μm gratings are fabricated to enhance signal level of photoelectrons originating from Ag, during the XPS measurements where Ag signal comes only from e-beam lithography patterned regions. Gratings of each set are parallel to the gratings of the same set but are perpendicular to the gratings in the other set. Each set is labeled with a number, and when discussing the results of the XPS experiments in the next chapter the same convention will be employed.

The SEM view of the formed metal strips is shown in figure 4.24.

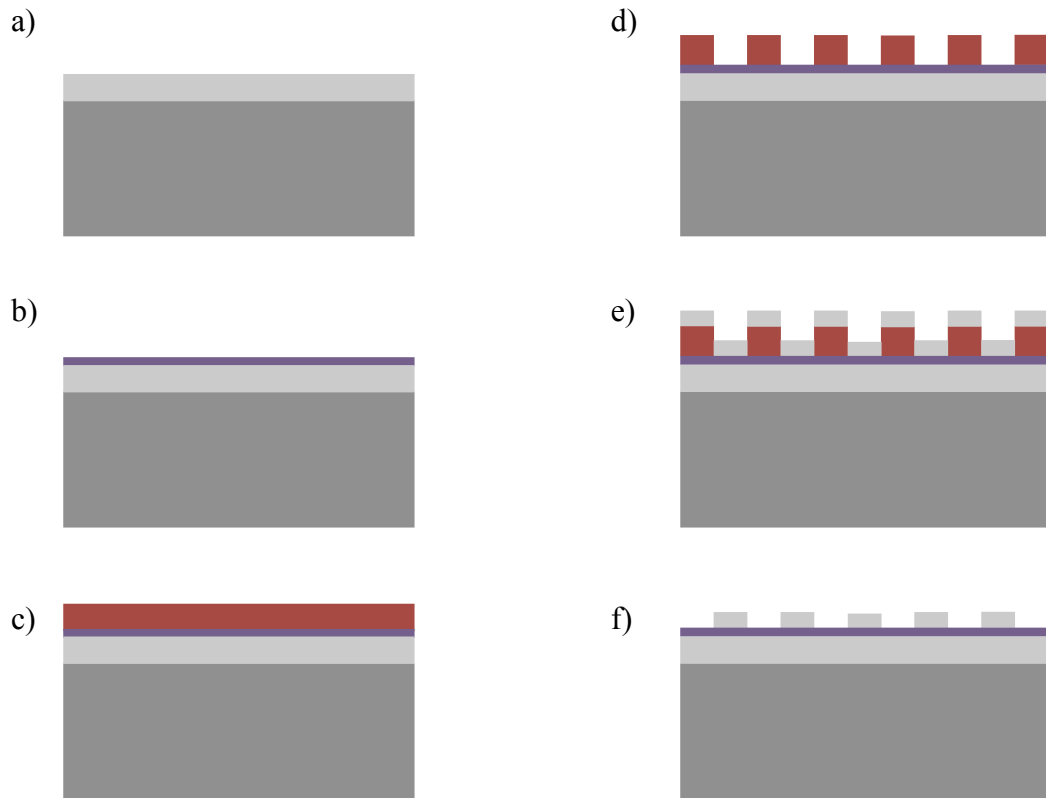


Figure 4. 23. Fabrication of metal stripes using e-beam lithography. a) Thermal deposition of Ag on Silicon (Ge wetting layer of 3 nm thickness not shown). b) 15 nm HfO₂ is deposited by ALD. c) ~100nm PMMA is spin coated and annealed for 90 seconds at 180°C. d) Pattern is formed using e-beam lithography system, and then the resist is developed. e) 50nm of Ag is deposited using thermal deposition. f) Lift-off to obtain the final patterns.

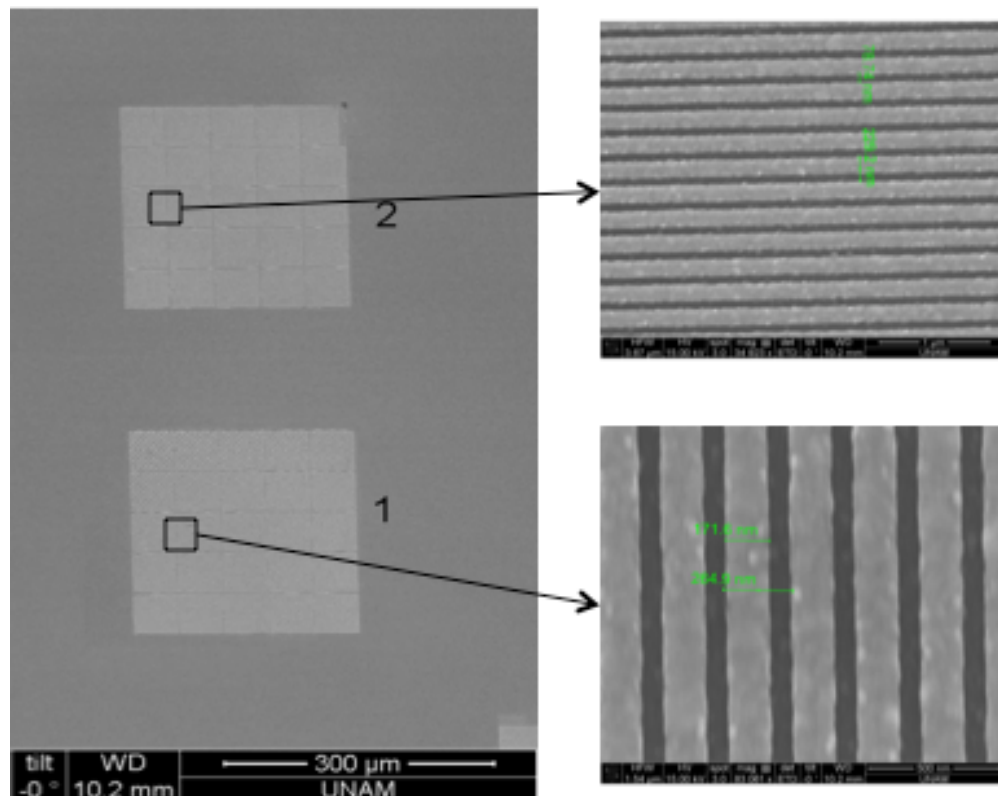


Figure 4. 24 Figure 4.24. SEM image of the gratings. Width of the gratings is 150 nm and period is 250 nm, length of each strip being 50 μm. The dimensions of each set are 250μm X 250μm, and each set contains an array of 5X5 groups of gratings, and there are 200 strips in each grating.

Origin of the Resonances

In the previous sections, ellipsometer results showed that resonances can be tuned by changing fabrication conditions. This will change overall plasmonic properties due to the interaction of metal nanoparticles with the metal film and with each other. The FDTD simulation methods and results are explained in details and can be found in the in the last paper we published [26]. Origin of the resonances is coupling of nanoparticles between each other (dipolar coupling) and coupling between the nanoparticles and the bottom metal. The first one is known as electrical resonance, where magnetic field is confined between the nanoparticles. The particle-metal film coupling is typically referred to as the magnetic resonance and it has the magnetic field confined to the spacer layer [27,28]. Absorption enhancement observed in the region between the two resonances is due to coupling of the two types of resonances.

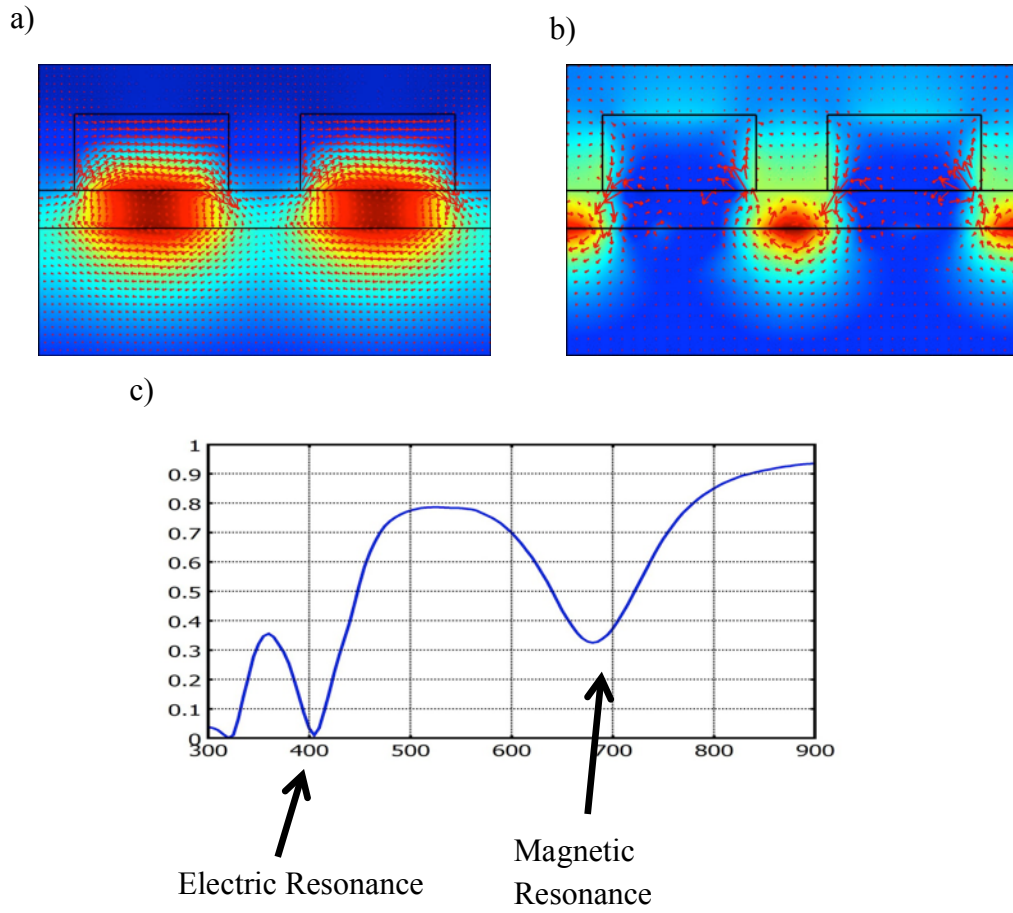


Figure 4. 25. a) Magnetic mode; Magnetic field is confined between nanoparticle and ground plane, b) Electric mode; Magnetic Field is confined to inter-particle spacing and c) magnetic and electric resonances shown in a reflection spectra.

Chapter 5

X-ray Photoelectron Spectroscopy Experiments, Results and Discussion

In the previous chapter, methods used to fabricate the plasmonic surfaces were explained in details. Characterization of optical properties of the samples in the visible spectrum is performed. Our interest in the visible spectra is because of many reasons. Firstly, these surfaces have applications at this range (energy conversion or photodetection). There is also a technical detail related to the Laser used that takes our interest towards the visible part of the electromagnetic spectrum. Three different continuous wave (CW) Lasers with wavelengths of 445 nm, 532 nm and 650 nm and rated powers of 10-30 mW are used.

In this chapter, the experiment setup will be explained, and results obtained from the experiments will be discussed. The results from the previous chapter will also be used to explain the shifts, and simulation results (LUMERICAL) are also utilized to support our arguments.

Using of XPS in characterization of electrical properties of the sample is extremely complicated. The nature of x-rays themselves makes things complicated. XPS spectra are obtained by irradiating a solid surface with a beam of X-rays while simultaneously measuring the kinetic energy of the photoelectrons emitted from the top 1-10 nm of the material being analyzed. Despite this fact, x-rays penetrate to larger distances in the material, causing ionization of atoms way below the surface and creating electron-hole pairs there. A systematic study of the dependence of the XPS spectra on excitation wavelength, light intensity, polarization, insulator thickness and nanostructure geometry is presented. Effects of using different materials as substrate and insulator are also studied in symmetric and asymmetric tunnel junctions.

5.1 Experimental setup

The experiments are based on the X-ray photoelectron spectroscopy. The equipment was slightly changed so that it allowed for the Laser light to be aligned illuminating the sample inside the chamber. The setup is shown in figure 5.1.

Laser used during the experiments (shown in Figure 5.2) has the following technical specifications: [2]

- Wavelength: 532nm(30mW)+650nm(100mW)+445nm(100mW)
- Combined Optical Power output: >200mW
- Operating Voltage: 12VDC
- Warm-up Time: <2 minutes
- Operating Lifetime: >5000hrs
- Operating temperature: 0 - 40 °C
- Modulation: TTL 30kHz
- Laser Head Dimensions: 86mm x 42mm x 80mm
- Beam Characteristics :(Near to TEM)) model, Divergence<2.5mrad, Spot roundness >85%.

The experiment method used is as follows. Firstly one of the monochromatic Laser was switched on. We waited until the Laser stabilized and the intensity remained constant. Then the Laser was aligned, and from the camera of the equipment we made sure the Laser hits the data collection spot. Figure 5.3 shows the alignment of the Laser light with the samples.

When Laser light illuminates plasmonic surfaces, a shift in the spectra towards higher energies is observed. In our case, since the metal particles on top of the insulator are not grounded, the shift caused by Laser illumination will add to the shift of the spectra due to the x-ray measurement. Both the Laser light and the X-ray photons extract electrons from the metal nanoparticles. In addition to the structures explained in the previous chapter, in some samples Al has also been used as bottom metal. Also Al_2O_3 has been used as insulator instead of HfO_2 in some experiments. Shifts on the XPS spectra and the dependence of these shifts on excitation wavelength, light intensity, polarization, and insulator thickness and nanostructure geometry are studied

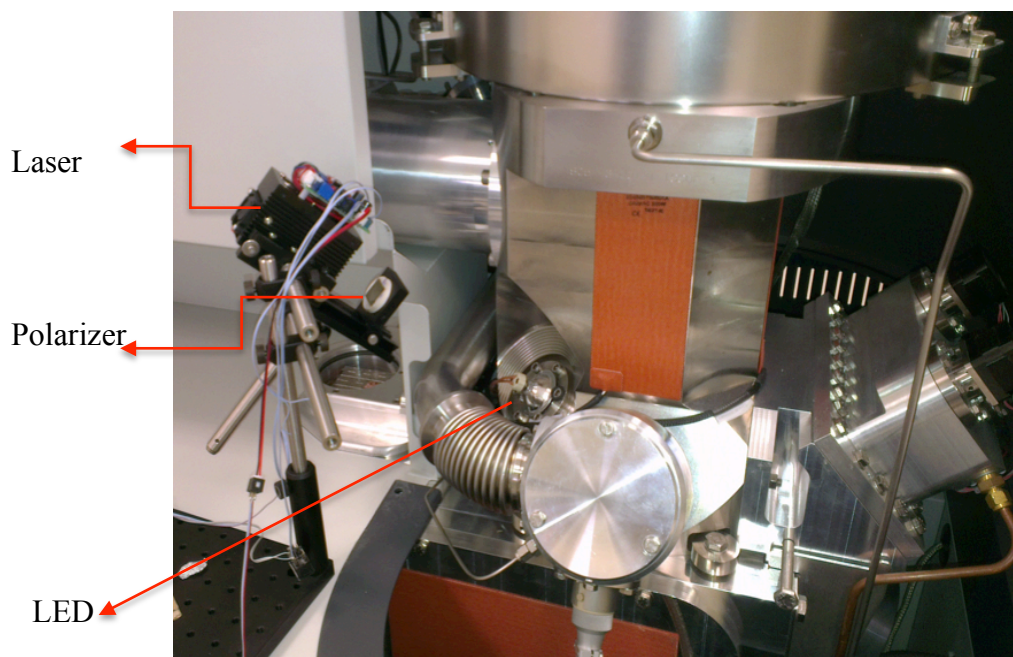


Figure 5. 1. Experimental setup. Shown is the Laser aligned with the help of the optical setup. The LED is removed so that the Laser light can enter the chamber of the XPS. The vacuum is not affected since thick glass is placed normally after the LED. Reflection of the Laser light from the glass is neglected.

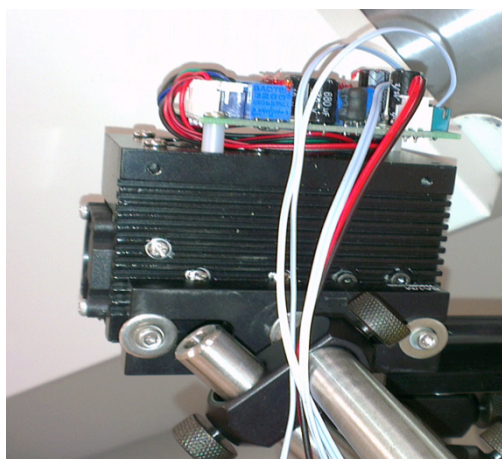


Figure 5.2. Laser used during the experiments

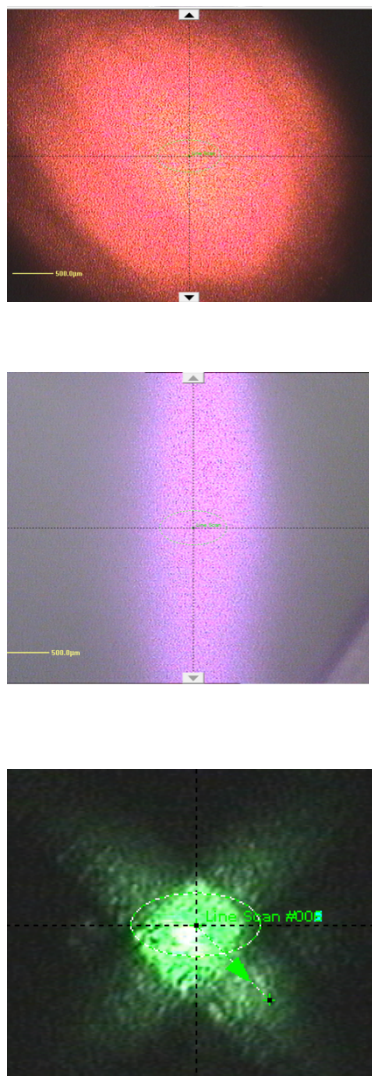


Figure 5. 3. The Laser is aligned in the beginning of the experiment. Red, blue and green Laser spots are shown. XPS data is taken only from the green circle shown in the middle.

5.2 Effect of the top metal Nanostructure geometry

Samples having 5 nm ALD deposited HfO_2 (100C) and Silver of 1, 3, 5 nm evaporated on that layer are studied here. As shown in the SEM images in the previous chapter, the upper Ag layer does not form a film for the 1 and 3 nm mass layer deposition. Due to the surface forces, nanoparticles are formed in these cases. On the other hand, almost a film is formed when 5 nm Ag is deposited and this will have its effect on the plasmonic properties of the sample. During this part of the experiment, the Laser light intensity was held constant. Blue Laser light (445 nm) was used to illuminate the samples. The vacuum of the XPS chamber was kept unbroken during the experiment. The fabrication conditions were same for all the samples.

Hence all the three samples can be considered to be identical in terms of the bottom metal and insulator thickness, and also in material properties. Figure 5.4 shows the native binding energy spectra of Ag3d. Two peaks are shown, one at 374.35 eV ($3d_{3/2}$) and the other at 368.24 eV ($3d_{5/2}$). During the dark and illumination spectra experiments these two peaks shift equally, so any of them can safely be used when studying the shifts. In this study we use the values of the $3d_{5/2}$ peaks. Below, spectra obtained from samples having 1nm Ag, 3 nm Ag and 5 nm Ag deposited are shown. All the samples have 5nm HfO_2 insulating layer.

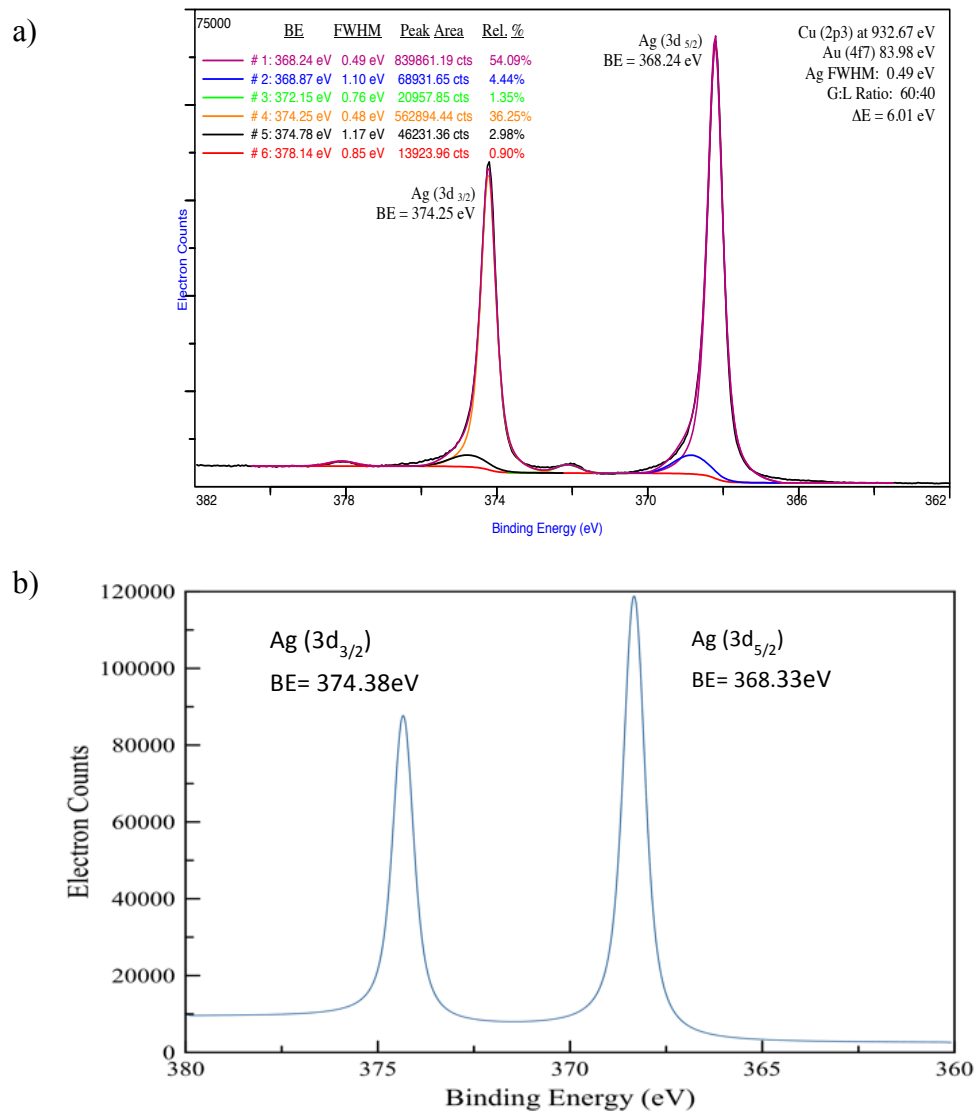


Figure 5.4. Native binding energy spectra of Ag3d from literature a)[29] and from our experiments b) . Here the metal is grounded and electrons lost via photoelectric effect will immediately be replaced by electrons from the ground, preventing shifts in the spectra.

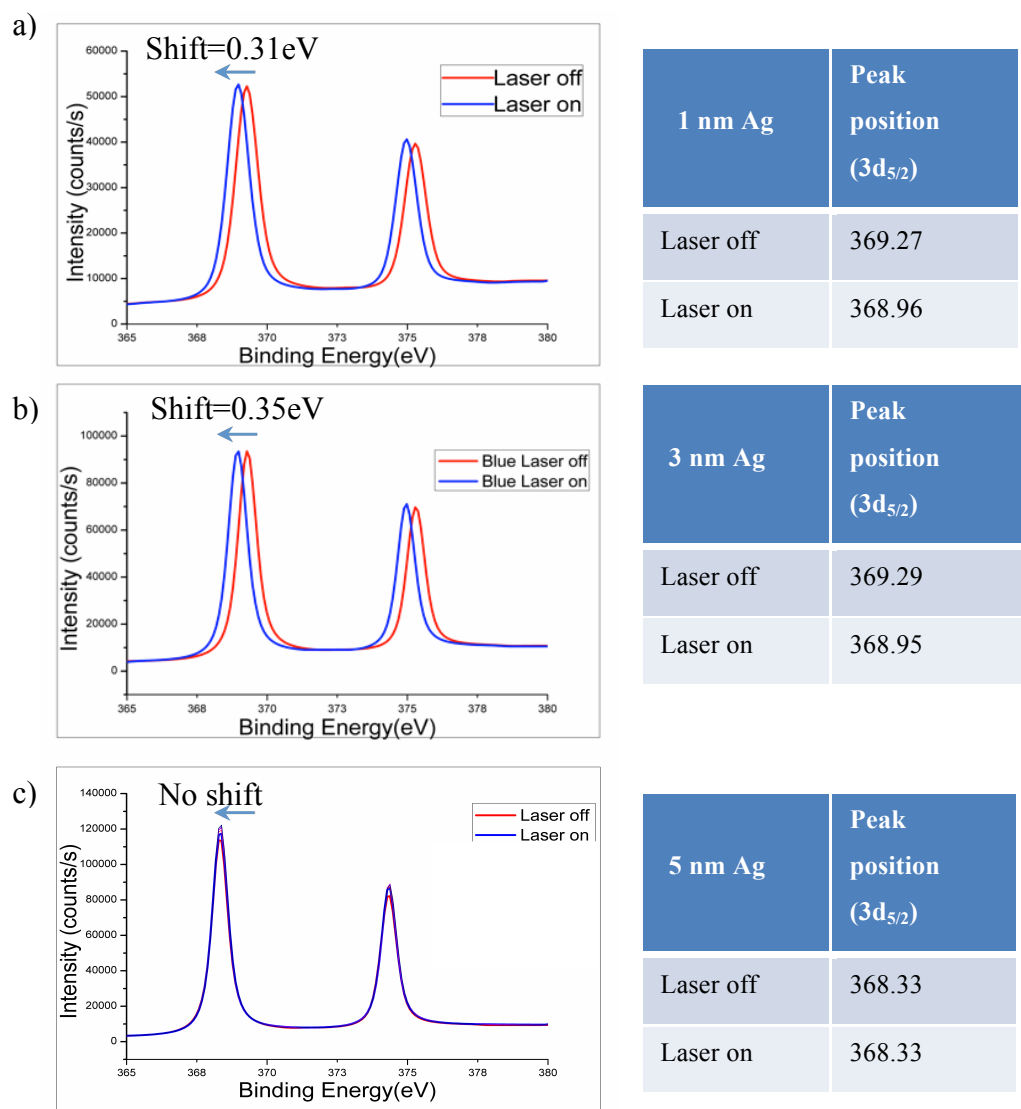


Figure 5.5. Shifts of the Ag 3d spectra when illuminated by blue Laser light ($\lambda=445\text{nm}$) for top metal 1nm, 3nm and 5nm thick deposited. For 5 nm thick top metal film the binding energy is very close to native value of B.E. The reason of this is explained later.

The shifts in the XPS binding energy for the three cases are shown in figure 5.5. Dark spectrum is first taken (red), and after that Laser light is shined on the surface to take illumination spectrum data. Blue light is used because photons at this wavelength can provide, via photoelectron effect, enough energy (2.78 eV) to the electrons to pass the barrier (2.01 eV). Energy band diagram can be used to explain the shift of the binding energy towards lower energies. The band diagram when no light or x-rays hit the surface is shown in figure 5.6. The band diagram is symmetric.

Three cases will be studied. In the first case, only Laser illuminates the plasmonic surface. In the second case, only x-rays and in the third case both x-rays and Laser hit the surface. Firstly, shown schematically in figure 5.6, we investigate what happens when the surface is exposed to x-rays during the dark spectra data acquisition. Electrons are excited and lost to vacuum, leaving the top metal positively charged. This will cause the band of the top metal to shift to lower energies. As more and more electrons are removed from the top metal nanoparticles, the bending of the band will increase, making it easier for the bottom metal electrons to tunnel the barrier (becoming thinner as the top metal band lowers). These electrons tunneling from the bottom metal bulk to the top metal nanoparticles compensate the lost electrons, and this process continues until equilibrium is reached. At equilibrium point, tunneling electrons totally compensate the lost electrons and prevent the top metal band from further bending. The process explained so far is totally a consequence of the nanoparticle nature of the top metal. The number of electrons available in the nanoparticles is limited and the oxide insulator barrier prevents electrons to pass, playing a crucial role as well. Effect of the X-rays can be considered similar to applying a positive voltage to the top metal. It can be quantified by comparing the native binding energy peaks position (taken from bulk Ag) and the light off position of the spectra in figure 5.5 taken from the silver nanoparticles. Position of dark $3d_{5/2}$ peak for both the 1nm Ag and 3 nm Ag mass cases (nanoparticle) is approximately same, ~ 369.3 eV. For the bulk case this peak is observed to be at

368.33 eV. The difference is about 1 eV, and other results that we will show in the proceeding chapters reveal similar peak position for dark data acquisition.

Next, the situation where plasmonic substrate is illuminated by blue Laser light is considered (Figure 5.7). In this case, band diagram preserves its symmetry, and incoming photons cause excitation of hot electrons from the surface of both metals, up to a maximum energy equal to the energy of the incoming photon (2.78 eV for $\lambda=445\text{nm}$).

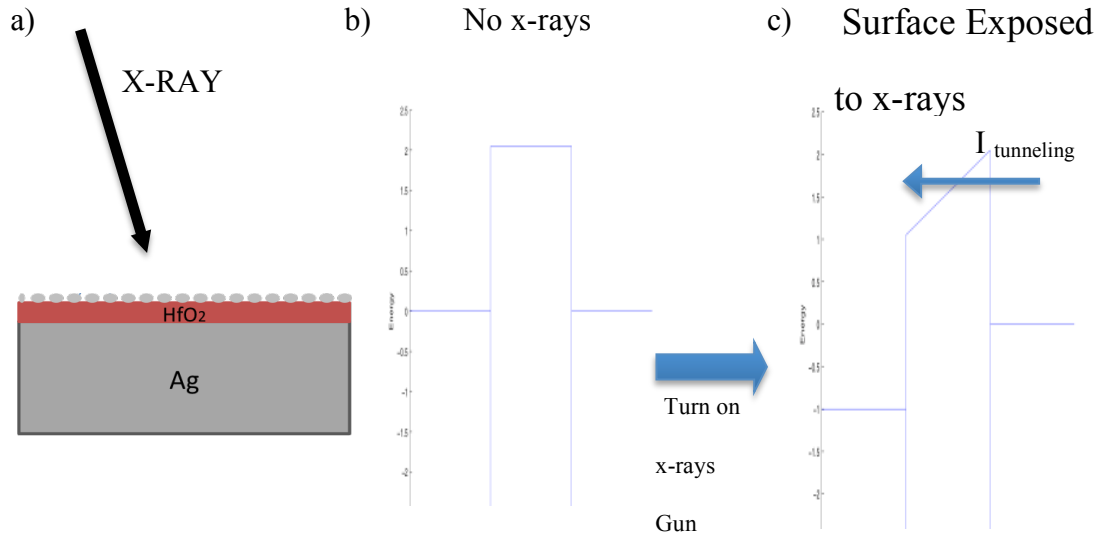


Figure 5.6 Schematic view of the effect that x-rays have on the band diagram of the MIM structure. The surface is exposed only to x-rays a), in b) the symmetric band diagram is shown for Ag-HfO₂-Ag plasmonic structure. X-rays change the band diagram structure, and tunneling electrons from the bottom metal compensate the lost electron in the top metal nanoparticles, causing for equilibrium to be reached at about 1 eV lowering of top metal band. The bottom metal Fermi level is taken as a reference (0 eV).

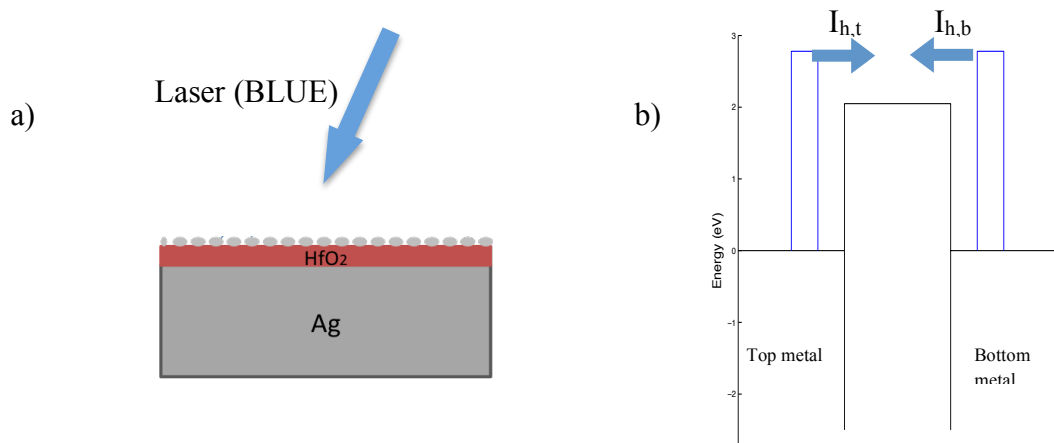


Figure 5.7. Band diagram of the structure, only Laser light is shined on the surface. Hot electrons cause a current flow in both directions. Due to the symmetry of the band diagram, these currents are equal and the net current sums to zero.

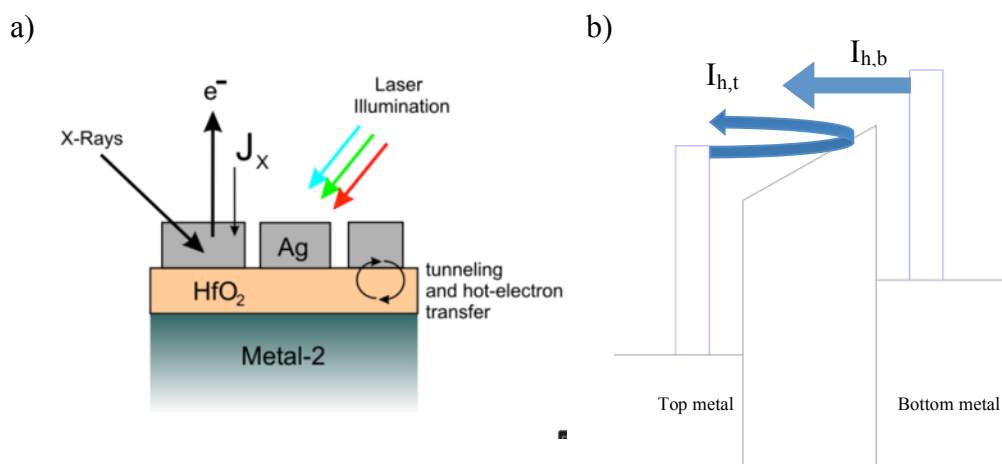


Figure 5.8. Both x-rays and Laser light hit the surface. Shown is band diagram of Ag-HfO₂-Ag MIM structure at this case b). During x-ray exposure, positive charges accumulate in the top metal, lowering the top metal band and bending the insulator band by approximately 1 eV.

In the third case we study, the x-rays and Laser hit the sample simultaneously. This is a combination of cases one and two. The first data is dark spectrum (Figure 5.5). Then the Laser light is allowed to illuminate the substrate and the XPS data is retaken. During x-ray exposure, positive charges accumulate in the top metal, lowering the top metal band and bending the insulator band by approximately 1 eV. This will prevent hot electrons from top metal ($I_{h,t}$) directly pass the barrier, because maximum kinetic energy given from the photoelectric effect is not enough to overcome the barrier any more (barrier height for top metal electrons becomes $2.01+1=3.01\text{eV} > 2.78\text{ eV}$, maximum kinetic energy given to electrons by blue Laser light photons). Only tunneling is possible for the electrons from the top metal. Even though tunneling current passes, due to a certain tunneling probability of the electron, this current is small compared to the ballistic passing electrons from the bottom metal leading to $I_{h,b}$. Hence shifting of the top metal band towards lower energies causes the hot electron current flowing from the bottom metal towards the top metal $I_{h,b}$, be the governing current as can be seen from the band diagram in figure 5.8 b). This is the reason why XPS binding energy spectra of the top metal nanoparticles shifts towards lower energies when Laser light illuminates the surface.

In the 5 nm Ag case no shift is seen. This can be explained with the fact that a quasi-continuous film is formed, and if somewhere in the film there is a leakage to the bottom metal, all the film would be short. Any accumulation of charges in the top metal would then be compensated by charges from the bottom metal. Another explanation may be related to the plasmonic properties of the surfaces. In the sample containing 5nm Ag as the top metal (the quasi-film) and 5 nm HfO_2 , plasmonic modes are not excited, leading to smaller field enhancement. Electric field enhancement is calculated by the FDTD program (LUMERICAL). SEM images were used and imported to LUMERICAL to set the form of the top metal. The results show enhancements of the electric field at 445 nm, corresponding to blue wavelength.

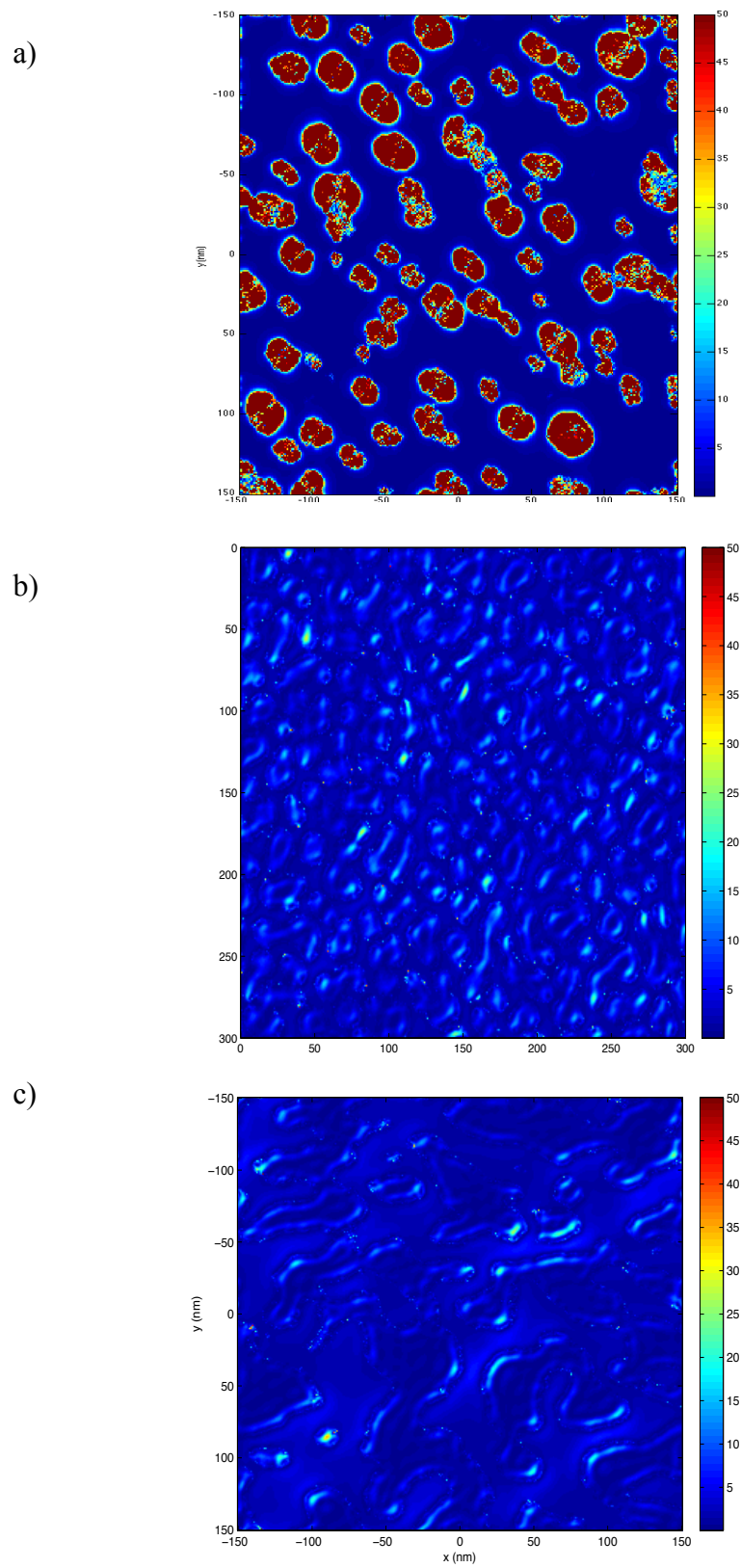


Figure 5.9. FDTD simulation results for the electric field enhancement shown for samples having 5nm insulator and 1 a), 3 b) and 5 nm c) Ag on top.

It can be seen that field enhancement for 1 and 3 nm is large, while in the case of 5 nm Ag, enhancement of electric field is very small.

Combining this fact with the reflection spectra shown in figure 5.9, it would be expected that the shift for 5 nm would be much smaller than in the 1 and 3 nm cases. The plasmonic surface containing 3 nm Ag mass layer deposited is a better absorber than the one containing 3 nm Ag mass deposited. This may be the reason why the shift in binding energy spectra is larger for the 3 nm Ag mass layer than for the 1 nm one. This is clearly seen in the ellipsometre and simulation results shown in figure 5.10 a) and b).

To be sure that the results are repeatable, the Laser off-on process was repeated for three times consecutively for the three cases. The resulting Ag3d spectra and the shifts are shown in figure 5.11.

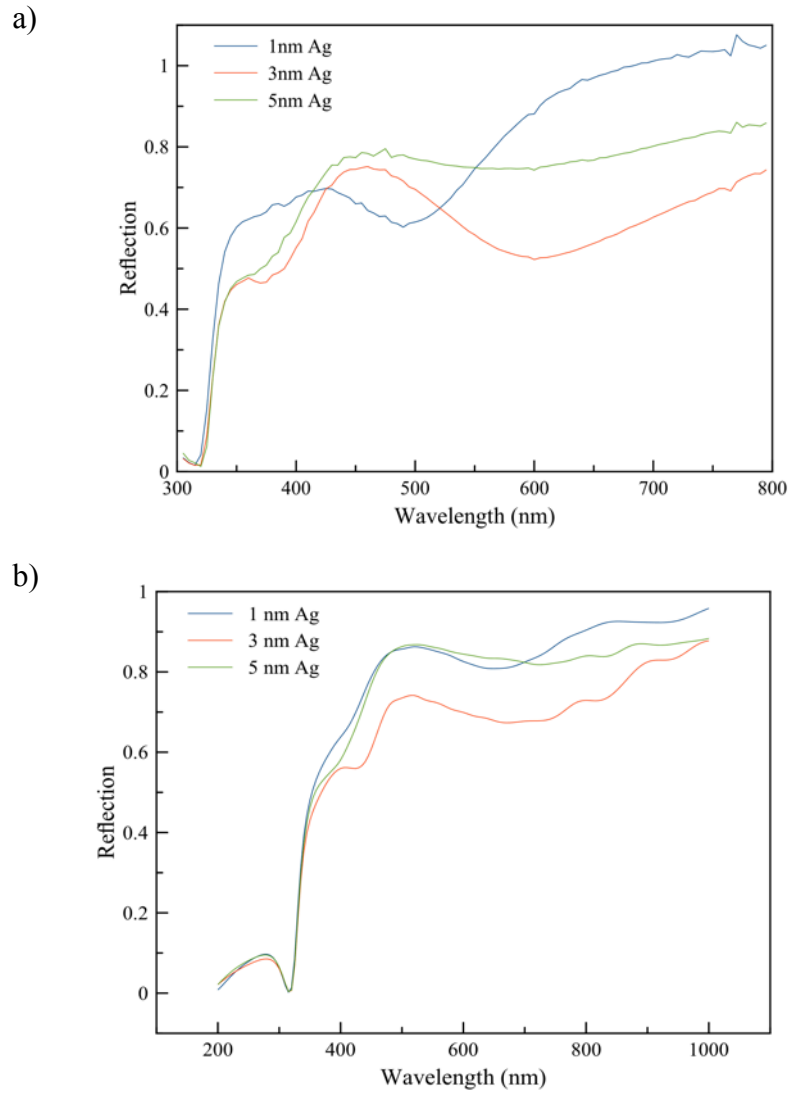


Figure 5.10. a) Spectroscopic results for the 15 degree reflection spectra (p-polarization) of the Ag(70 nm)-HfO₂(5nm)-Ag(1,3,5 nm) MIM structure samples. Resonances shift towards higher wavelengths with increasing the nanoparticle sizes. b) FDTD simulation results.

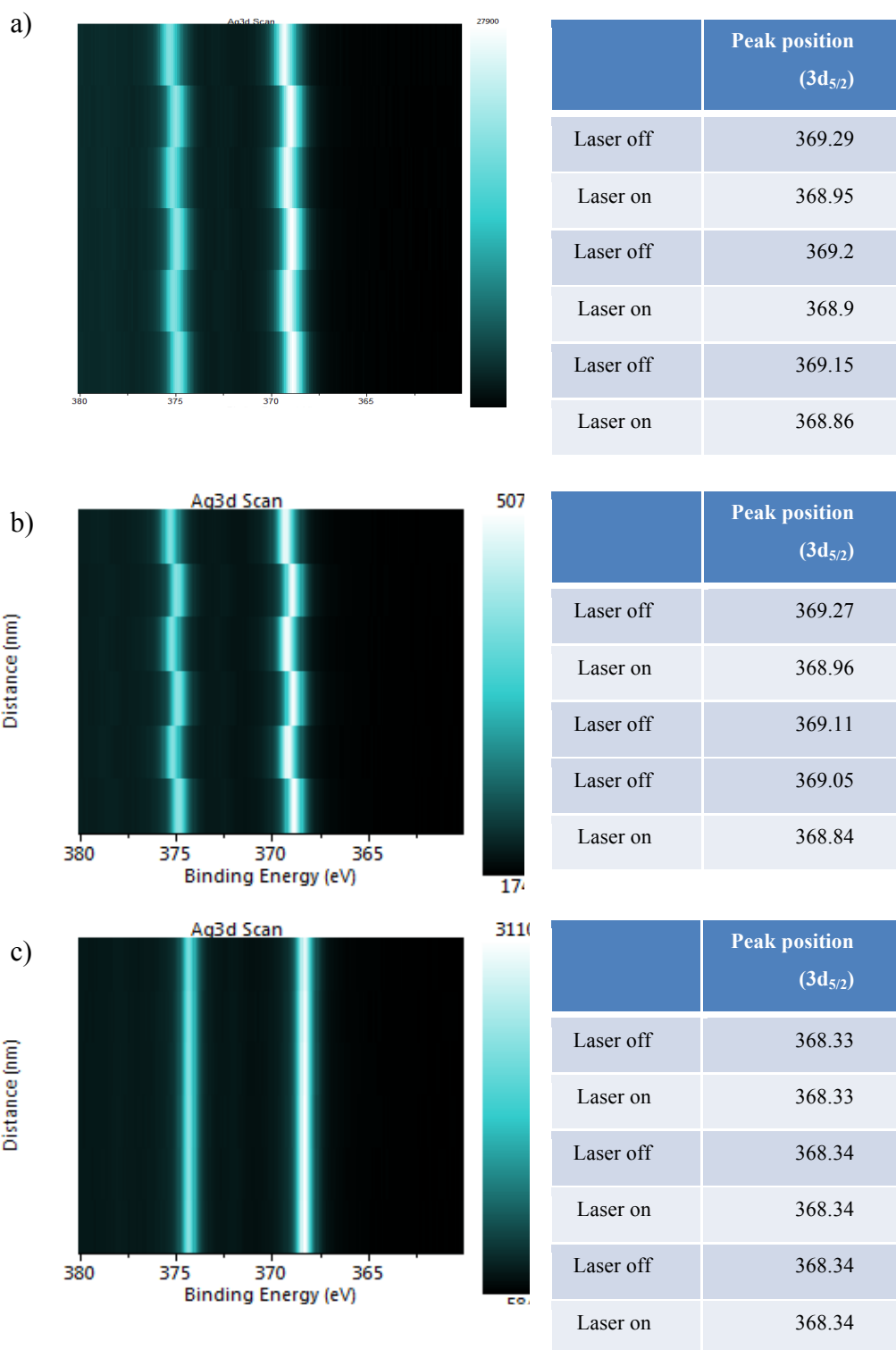


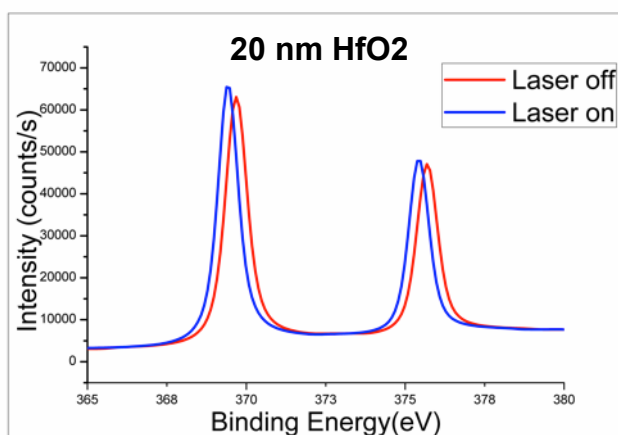
Figure 5.11. Laser off-on process was repeated 3 times consecutively for the 1nm a), 3nm b) and 5nm Ag c) on top of 5 nm HfO₂. The process is repeatable, and the peaks continue to shift towards lower energies approaching Ag's native Binding energy value, 368.3 eV.

5.3 Effect of the insulator spacer thickness

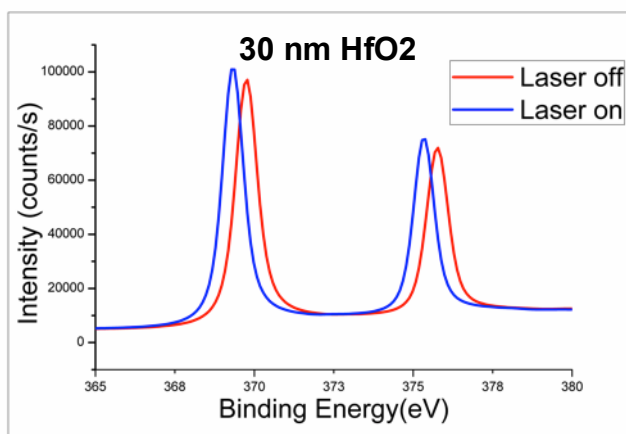
In this part of the experiment, blue Laser is used to illuminate samples having same Ag thicknesses on both bottom and top (3nm) layers, but having different insulator thicknesses (20 and 30 nm). This is done to check the dependence of the binding energy spectra shifts on the insulator thickness. Fabrication procedures for the samples are identical, except for the insulator deposition step that was done in different processes.

This experiment was conducted while both the samples were inside the XPS chamber. Blue Laser was held at constant intensity throughout the experiment.

The band diagram representation is similar to that shown in figure 5.8 b). Binding energy spectra shift for the sample having 30 nm HfO₂ thickness (0.42 eV) is larger than for the sample having 20 nm HfO₂ (0.26 eV). The ellipsometre reflection result gives a better insight to why this is so.



3 nm Ag 20 nm HfO ₂	Peak position (3d _{5/2})
Laser off	369.68
Laser on	369.42



3 nm Ag 30 nm HfO ₂	Peak position (3d _{5/2})
Laser off	369.75
Laser on	369.33

Figure 5.12. Shifts of the Ag 3d spectra when sample having 70nm bottom Metal, 3nm top metal and a) 20 nm and b) 30nm insulator thickness is illuminated by Blue Laser light ($\lambda=445\text{nm}$).

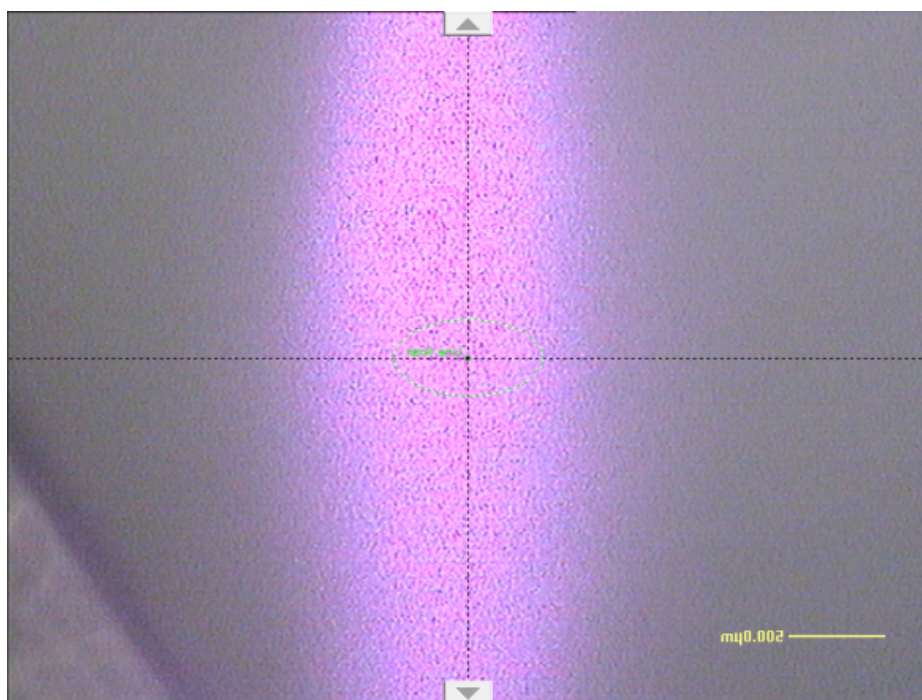


Figure 5. 13. Intensity of the blue Laser light was held constant during the XPS data acquisition. XPS collects data only from the area marked with a green circle.

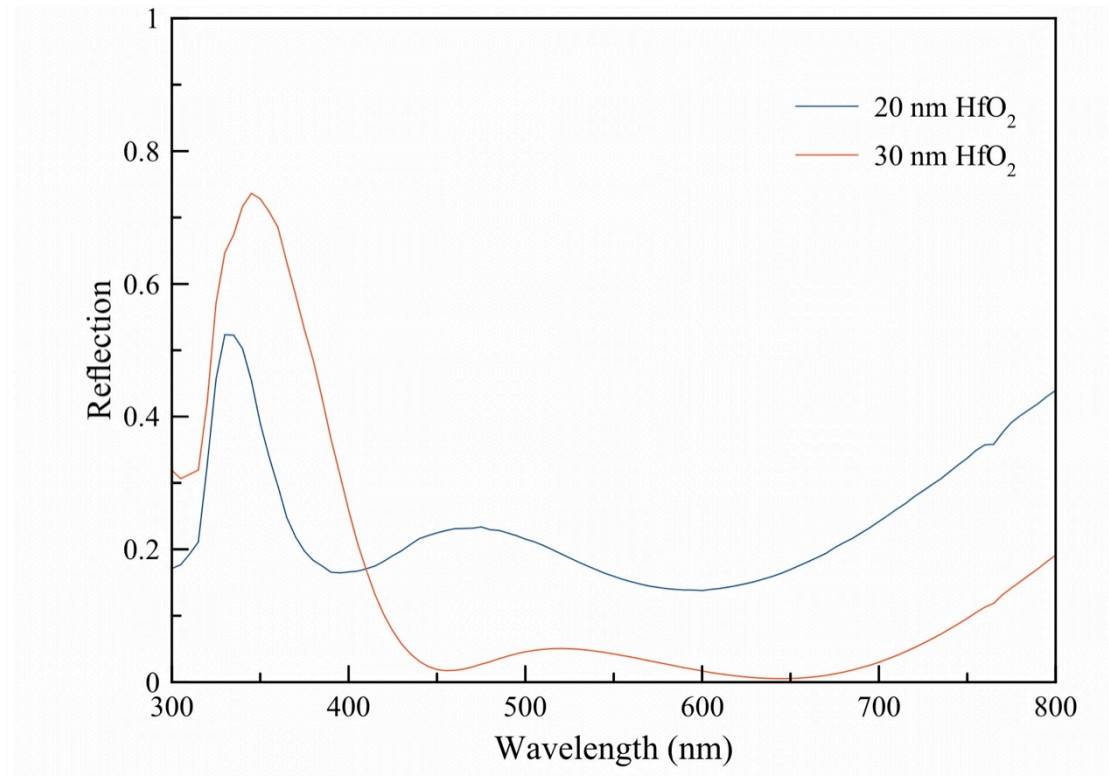


Figure 5. 14. Reflection results from ellipsometre measurement. The result is shown for p-polarized light, 15° angle of incidence. The sample having 30 nm insulator layer is better absorber than the one having 20 nm insulator layer.

As seen from the reflection measurements (figure 5.14), the sample having 30 nm HfO_2 absorbs light better than the sample having 20 nm HfO_2 . The sample having 30 nm HfO_2 has a resonance at wavelength 450 nm, coinciding with the blue light. Reflectance is almost zero at this wavelength, meaning that it is perfect absorber and it will absorb all the photons coming at this wavelength. On the other hand, the sample having 20 nm HfO_2 at 450 nm absorbs less than 80% of the incoming photons. Less photons absorbed means less hot electrons excited, and in turns that would mean less electrons available to pass the barrier from the bottom metal toward the top metal. As a result, the biding energy will shift less for the less absorbing sample having 20 nm HfO_2 than for the perfect absorber having 30 nm HfO_2 thickness.

This part of the experiment was repeated with the red Laser light instead of the blue one. This case is a little different than the previous. Maximum kinetic energy of the hot electrons does not exceed the barrier. Hence, ballistic transport of the electrons over the barrier is not possible. Instead, tunneling current governs. The band diagram is shown in figure 5.15.

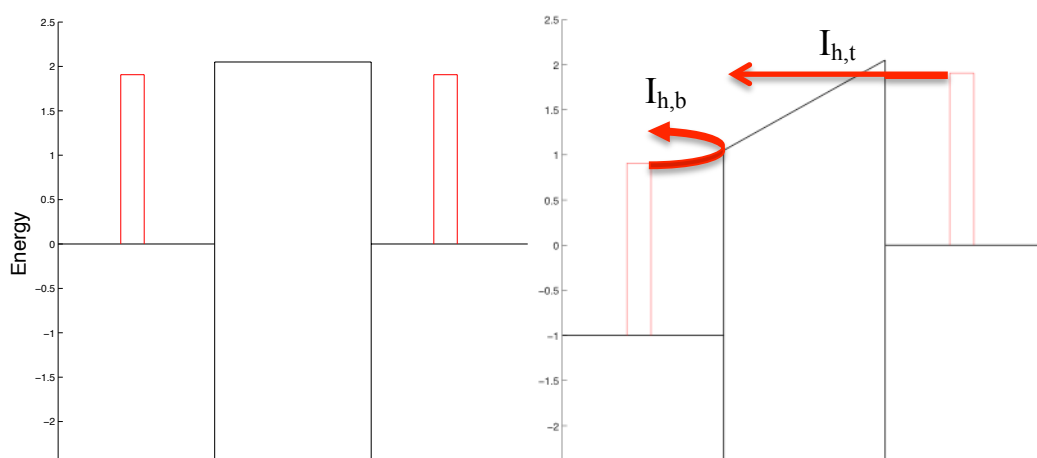


Figure 5. 15. Red Laser illuminates the sample (a), exciting hot electrons up to a kinetic energy equal to the incident photon energy 1.907 eV. This is not enough to overcome the barrier. When the x-rays gun is turned on (data acquisition), the insulator band is bent (b) and the barrier becomes thinner in the bottom metal side. It is then easier for the hot electrons excited in the bottom metal to tunnel the barrier (Fowler-Nordheim tunneling).

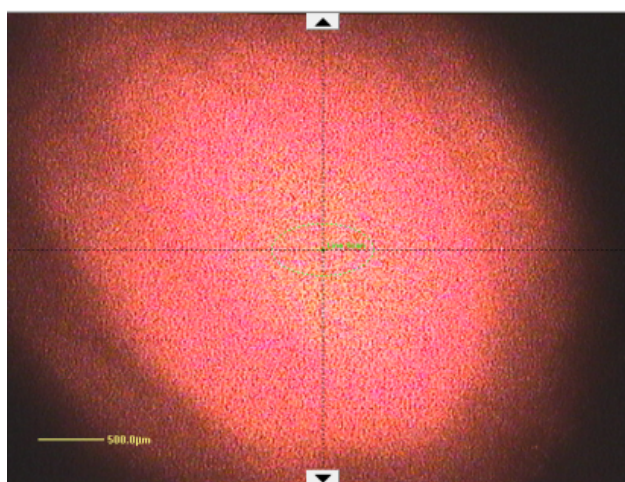
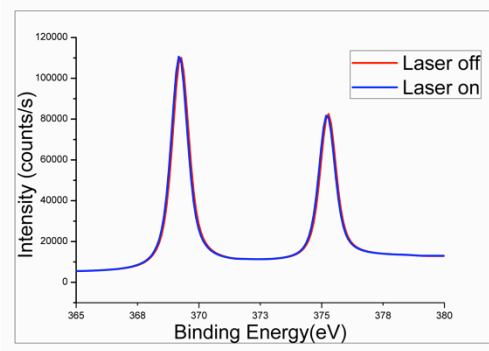
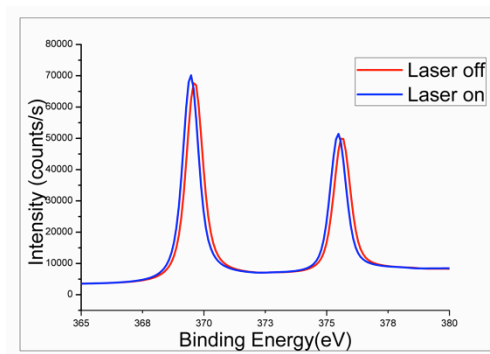


Figure 5.16. Intensity of the red Laser light was held constant during the XPS data acquisition. XPS collects data only from the area marked with a green circle.



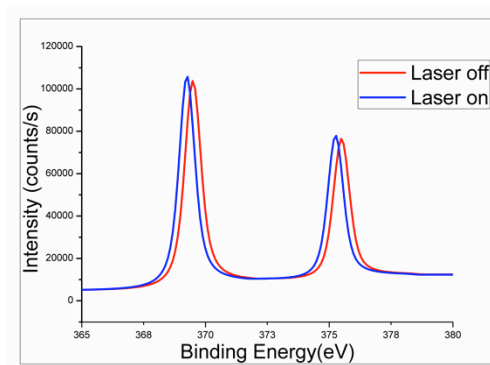
	Peak position (3d _{5/2})
Laser off	369.25
Laser on	369.2

10 nm HfO₂
Shift= 0.05 eV



	Peak position (3d _{5/2})
Laser off	369.62
Laser on	369.46

20 nm HfO₂
Shift=0.16 eV



	Peak position (3d _{5/2})
Laser off	369.49
Laser on	369.25

30 nm HfO₂
Shift=0.24 eV

Figure 5.17. Shifts of the Ag 3d spectra. Samples having 70nm bottom metal, 3nm top metal and a) 10 nm, b) 20nm and c) 30 nm insulator thicknesses are illuminated with red Laser light ($\lambda=650\text{nm}$). The shift in spectra increases with increasing spacer thickness. The explanation given for the blue light illumination case is valid here too, with the difference that here the Fowler-Nordheim tunneling mechanism is responsible for the current, hence for the shifts in binding energies too.

Results of the XPS binding energy spectra are shown in figure 5.17. All the samples have 3nm Silver deposited on different (10, 20, 30 nm) HfO_2 thicknesses.

5.4 Polarization dependence

Here we check if the spectra shifts are polarization dependent or not. The sample used has 10 nm HfO_2 and 3 nm Ag on it. XPS data was firstly taken for unpolarized light. Then a polarizer is placed in front of the laser and illumination xps data is taken. The polarizer is rotated by 90 degree after 1 cycle (off-on). Results are shown in the following below. Spectra shifts are expected to be polarization independent. Though, our polarizer is not perfect and it also splits the intensity unevenly and more intensity is provided peak slightly more shifting. Difference in the binding energy spectra shift between the cases when polarizer was at 0° and 90° is because of the polarizer imperfection. It does not split the light intensity evenly.

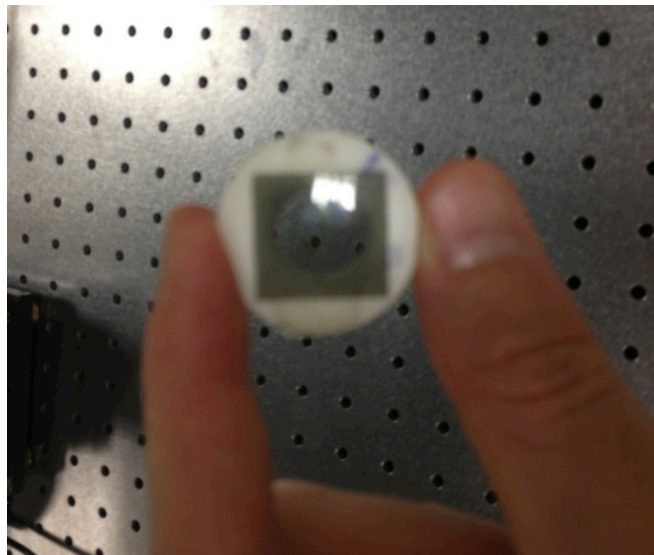
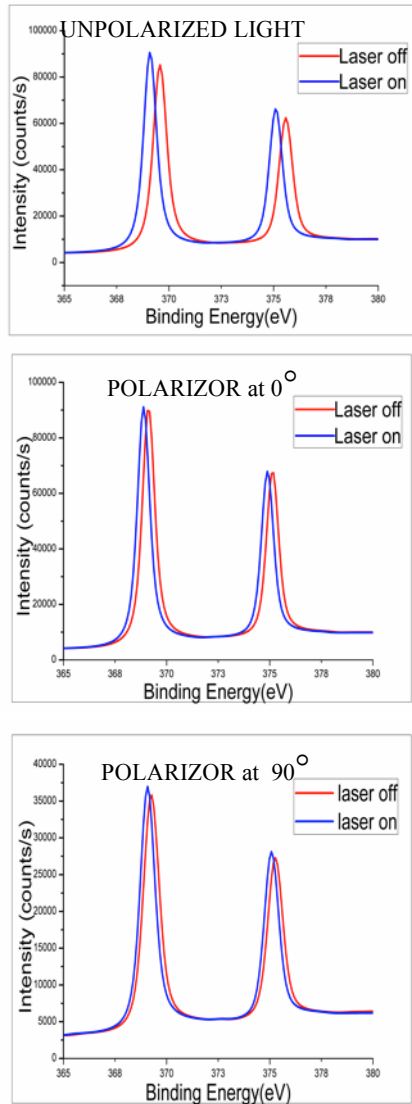


Figure 5.18. Polarizer used in the experiment.



Unpolarized light	Peak position (3d _{5/2})
Laser off	369.57
Laser on	369.1
Polarization 0°	Peak position (3d _{5/2})
Laser off	369.12
Laser on	368.88
Polarization 90°	Peak position (3d _{5/2})
Laser off	369.19
Laser on	368.91

3d_{5/2} peak
shift=0.47eV

3d_{5/2} peak
shift=0.24eV

3d_{5/2} peak
shift=0.18eV

Figure 5.19. Energy shifts are polarization independent. Non-perfection intensity splitting of the polarizer is responsible for the differences in the shifts between 0° and 90° polarizer rotation cases.

5.5 Effect of Laser wavelength

Up to now, energy band diagram of the structures studied was symmetrical, having same metal in both sides of the insulator. In this part a junction having nonsymmetrical energy band diagram is studied. The idea is to use an identical sample in identical conditions, by changing only the wavelength (color) of the used Laser. Intensity of the Laser lights is calibrated by means of a power meter. Sample studied has 3nm Ag evaporated on 5 nm Al_2O_3 , which in turns was deposited by ALD on 80 nm Al. As seen from the energy band diagram, none of the lights possesses enough energy to excite hot electrons over the barrier. Shifts in the binding energy when Laser lights of blue, green and red color hit the sample are shown in figure 5.21.

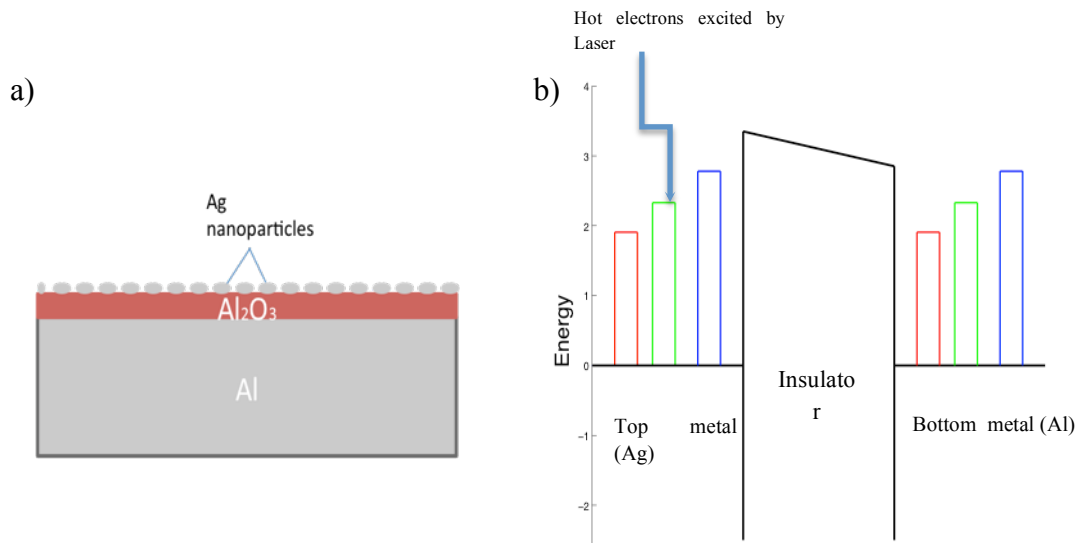


Figure 5. 20.The schematic view of the sample used shown in a) and the band diagram when Laser lights of different wavelengths illuminate the sample shown in b). Note the built in potential of 0.5 V in the insulator band.

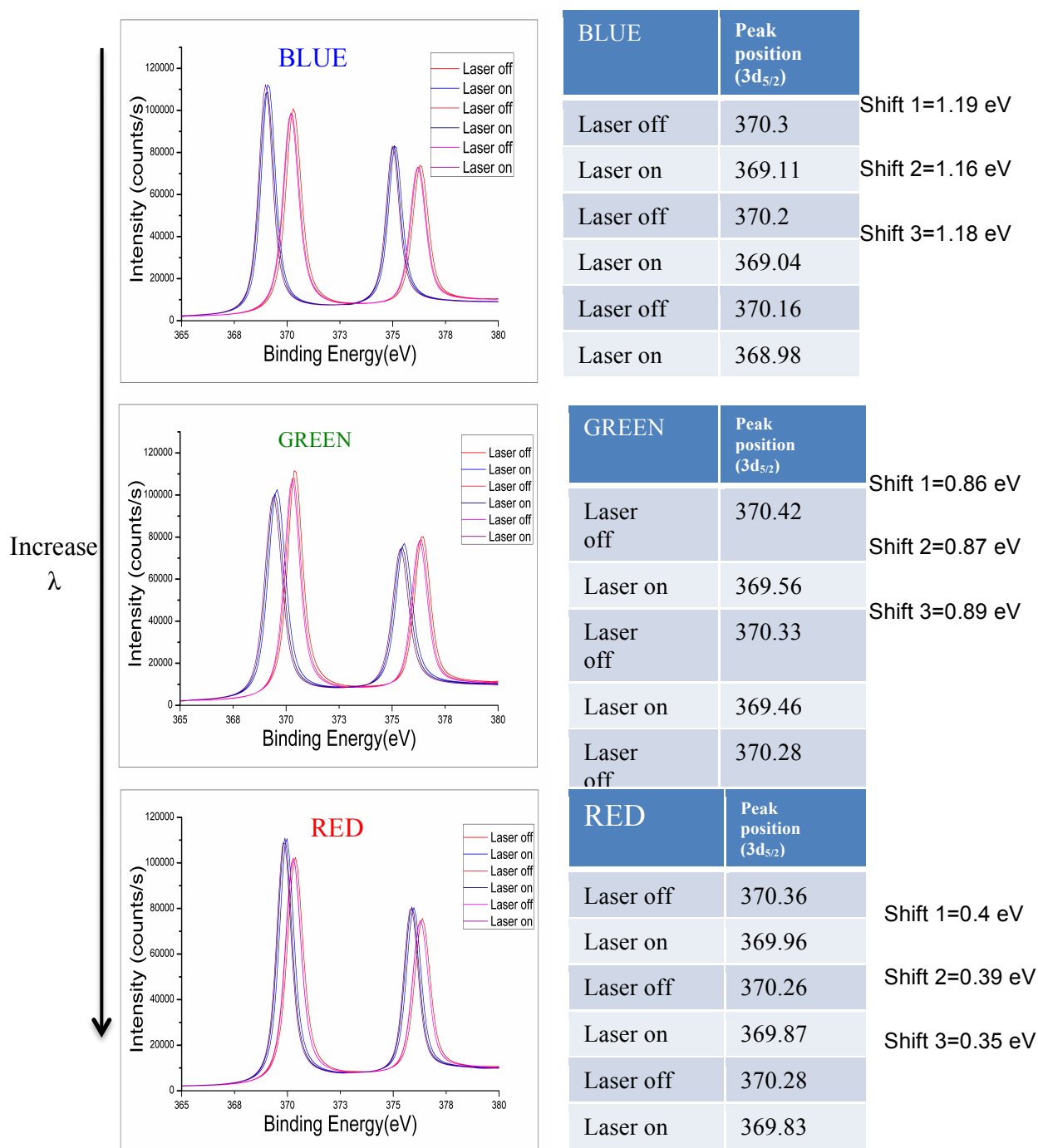


Figure 5. 21. Shifts of the Ag 3d spectra when samples having 80 nm bottom Al metal, 3nm top metal and 5 nm Al₂O₃ insulator thickness are illuminated by Blue, Green and Red Laser light of equal intensities (445nm, 530 nm and). The shift in spectra decreases with increasing wavelength (increasing photons energy).

Intensity (number of photons falling per meter square per second) is same for all three Laser lights. The band bending due to the x-rays in this case is different from the previous because energy band diagram has changed with change of the materials used. By comparing the dark spectra in the previous page to the native binding energy spectra, a shift to x-rays of 2 eV (370.3eV - 368.3eV) is observed. Hence in the band diagram, the top Ag metal band will be lowered by 2 eV as shown below.

As said earlier, energy of the incoming photons is not enough for the excited electrons to flow over the barrier. As in the case of the sample studied in part 5.4, only tunneling is possible for all wavelengths. It can be direct tunneling or Fowler-Nordheim tunneling. It should be kept in mind that direct tunneling is important for thin insulator layers, and it is generally kept responsible for the current in these cases. Still the shifts shown in figure 5.21 are too high to be explained only by direct tunneling mechanism. In this case we think that trap assisted tunneling is responsible for the shifts as well. All these tunneling mechanisms existed in the previously explained cases too, but here, because the insulator layer has been changed, more traps are available in the Al_2O_3 insulator. Larger shift is observed for the blue light. This is intuitive because hot electrons excited at this wavelength are excited to energies higher than the electrons excited by radiation of longer wavelengths. Hence the effective barrier electrons see (figure 5.22) is thinner than for the hot electrons excited to lower energy levels by the green or red light. Hence direct tunneling current will be larger for the blue illumination case. Current from the trap assisted tunneling of the electrons through defects in the oxide layer adds to this current, and in the blue Laser case trap assisted current would be larger too. The same logic is valid for trap assisted tunneling too. Excitation of hot electrons to higher energies leads to a larger number of tunneling electrons through the trap assisted mechanism.

To check the impact of each of these mechanisms in the current we repeated the same experiment with a sample having a thicker insulator than in the previous case. If XPS shifts are smaller for the sample having a thicker insulator than for one having a thinner insulator, then it can be claimed that direct tunneling mechanism is the main responsible for the tunneling.

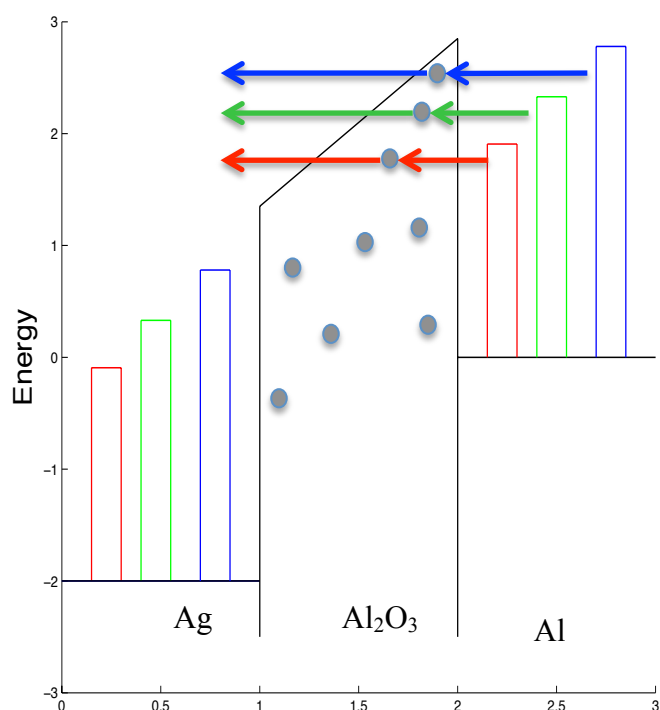


Figure 5. 22. Band diagram representation during the x-ray measurement, immediately as the Laser is turned on. Trapp assisted tunneling is shown for the blue, red and green Laser light excited hot electrons.

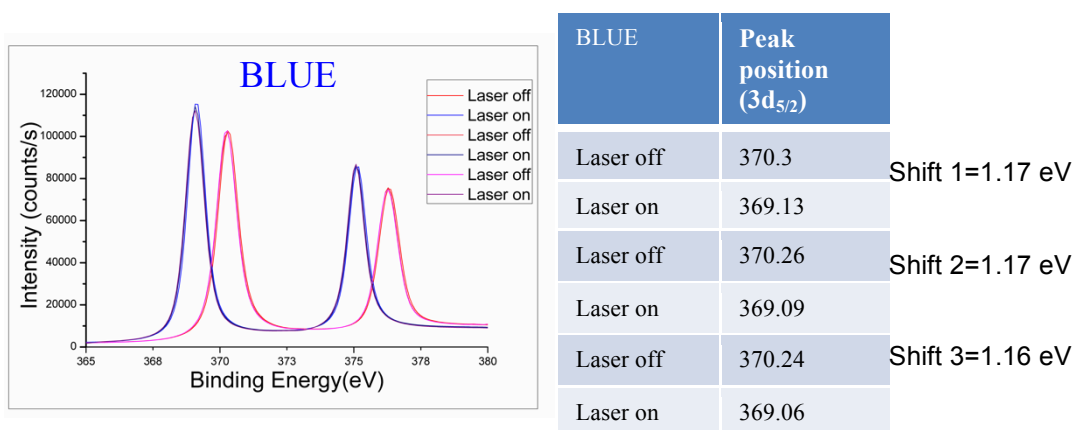


Figure 5. 23. Shifts of the Ag 3d spectra when samples having 80 nm bottom Al Metal, 3nm top metal and **10 nm Al₂O₃** insulator thickness are illuminated by blue Laser light.

On the other case, if there is observed no change in the shifts, then it can be implied that trap assisted tunneling is the main source of current. The experiment was repeated with the blue Laser light illumination of the sample having 80 nm bottom Al Metal, 3nm top metal and 10 nm Al₂O₃ insulator thickness.

The shifts of the Ag 3d spectra for the sample having 10 nm thick insulator thickness are same to the shifts in the sample having 5 nm thick insulator, as can be seen by comparing figure 5.23 and figure 5.21.

Direct tunneling mechanism is highly affected by the thickness of the insulator. Since increasing insulator thickness did not decrease the shifts in the Ag 3d spectra, the governing mechanism concludes to be trap assisted tunneling.

5.6 Effect of electron flood gun

Electron flood gun is used to compensate emitted electrons during the photoelectric effect. It is usually employed used when insulating samples are studied. In our case it will serve to compensate the lost electrons by photoelectric effect caused by Laser light and x-rays, and at some point equilibrium will be set. The sample used here is different than the previously used ones. It has 3nm Ag thermally evaporated on 5nm HfO₂. HfO₂ is deposited by ALD at 100°C on 80 nm Al bottom metal. The experiment flow is as follows: the Laser light is switched off and on in cycles while XPS data acquisition takes place. For every off-on cycle of the Laser, the voltage of the flood gun is increased in 0.15 V steps. Increasing the voltage of the flood gun increases the compensation of lost electrons by the top metal, and at some point the flat-band condition will be achieved. Increasing the flood gun voltage further than this will revert the current mechanism, and this is seen in the results shown in figure 5.25. The same experiment was repeated with the green and red Laser lights, using the same sample. The results are shown in figure 5.26.

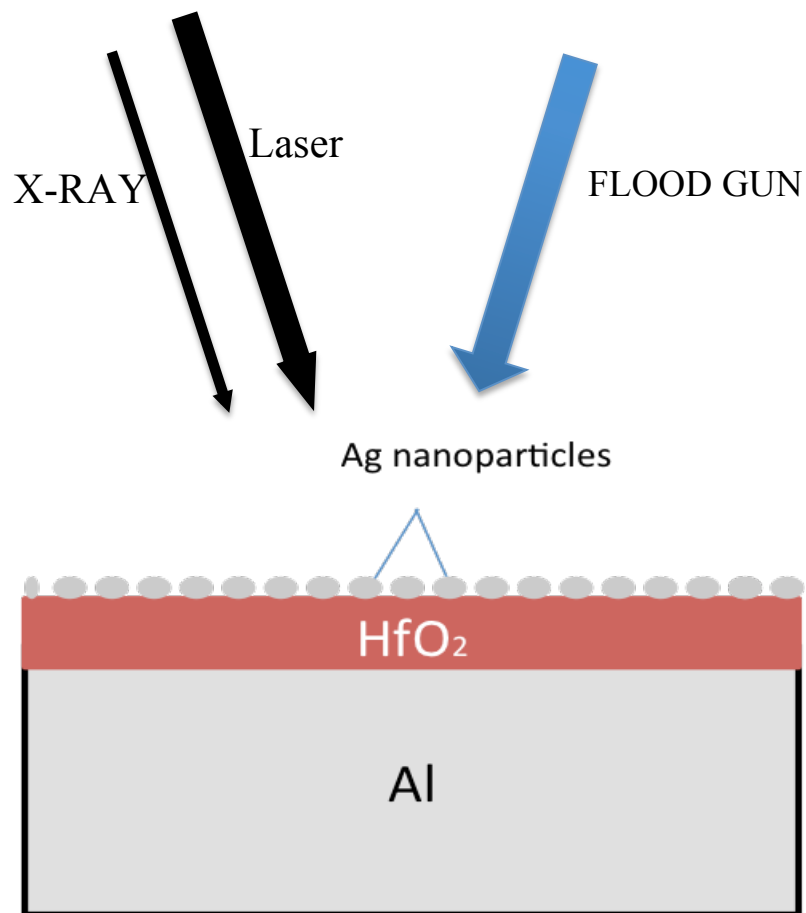


Figure 5.24 Flood gun provides electrons to compensate the loss due to the photoelectric effect.

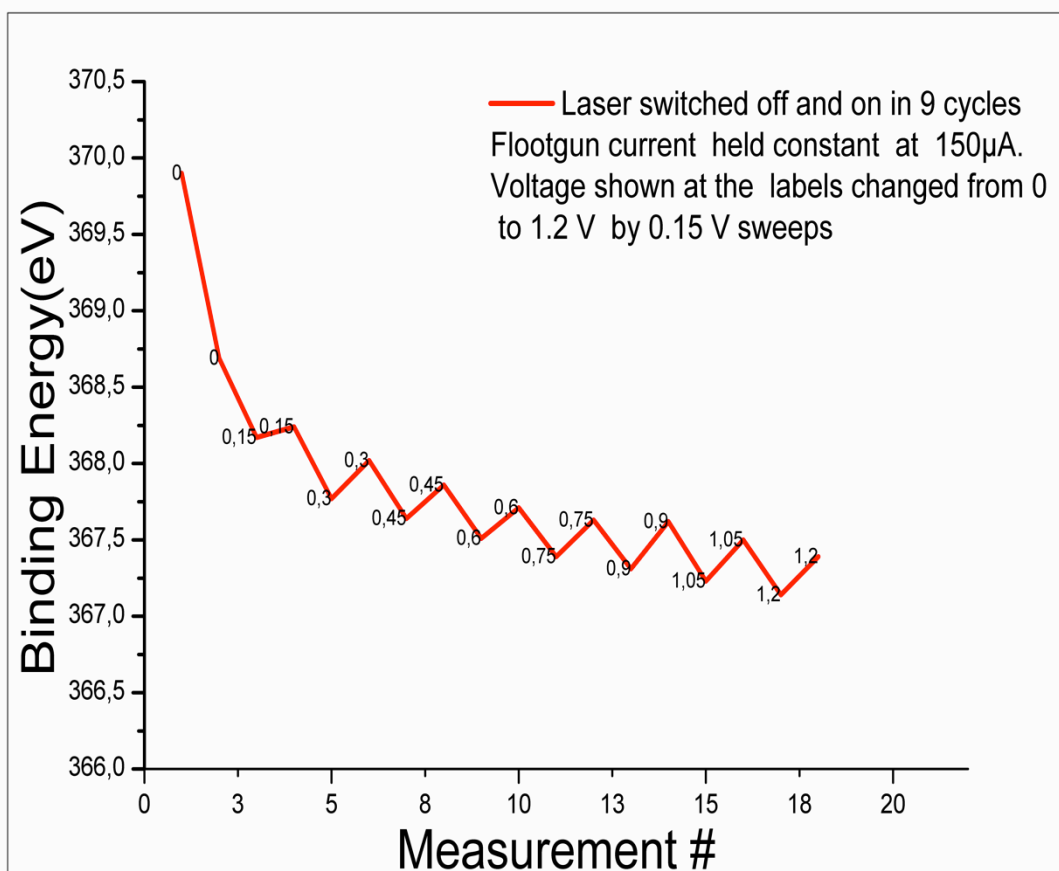


Figure 5.25. Position of the $3d_{5/2}$ peak of Ag 3d spectra. Flood gun was turned on to compensate the lost electrons in the top Ag nanoparticles. Data is taken during off-on cycles of the blue Laser illumination. While the Laser light and x-rays extract electrons to vacuum, floodgun provides extra electrons, balancing and finally reverting the electron flow as shown. Flat band condition is achieved at 0.15 V of applied flood gun voltage.

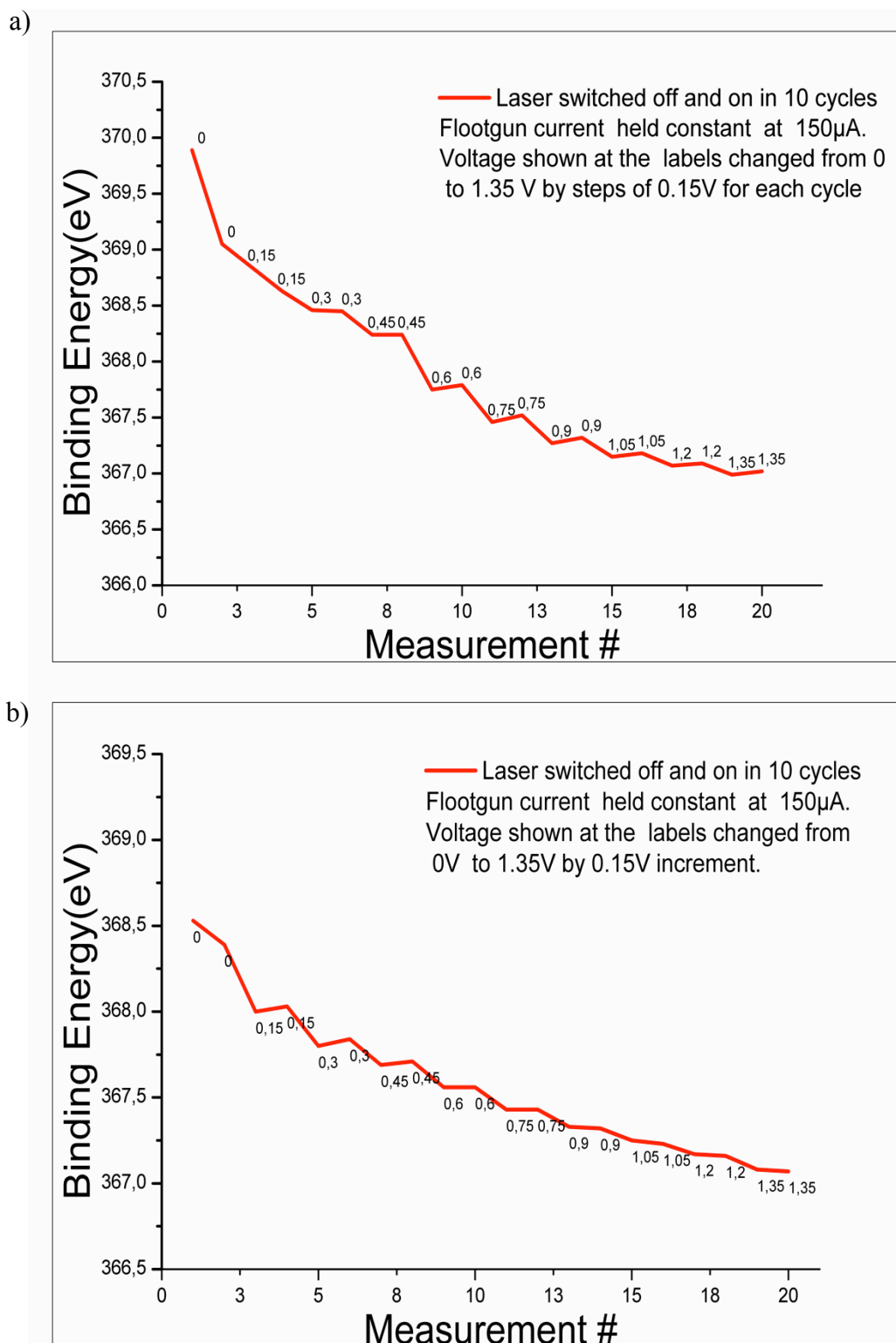


Figure 5.26. Process explained in caption of figure 2.25 is repeated for the a) Green and b) Red Laser lights. For the green Laser light, flatband condition was achieved at 0.3 eV of applied flood gun voltage. For the Red Laser case, current is reverted at 0.15 eV of applied flood gun voltage.

5.7 Effect of changing Laser light intensity

Here the dependence of XPS shifts on the Laser intensity is studied. the sample used in the previous section is used (MIM structure having from bottom to top: 80 nm Al, 5 nm HfO₂, 3nm Ag). The flood gun is turned off. The Laser intensity is increased after every Laser off-on cycle, and the 3d_{5/2} peak positions of Ag for 3 cycles are shown in figure 5.25 Normally a build-in voltage exists due to the difference in the work function of the top and the bottom metals (4.7eV-4.2eV=0.5eV). The shift due to the x-ray charging of the top metal band in the band diagram is (from the data in figure 5.25, first off data measurement) 369.8-368.3= 1.5eV. Hence a positive voltage of 1.5eV is applied on the top metal during XPS data taking. The band diagram alignment changes from the situation 5.28 a) to 5.28 b).

The reason why more shift is observed for the blue Laser case can be understood by looking at the figure 5.28. Hot electrons excited at the bottom metal have kinetic energy exceeding the barrier by a maximum of 1.23eV for the blue light and 0.78 eV for the red one. Since ballistic traveling of the hot electrons over the barrier is the mechanism governing the current, this difference in kinetic energy is the cause of the difference in the shifts.

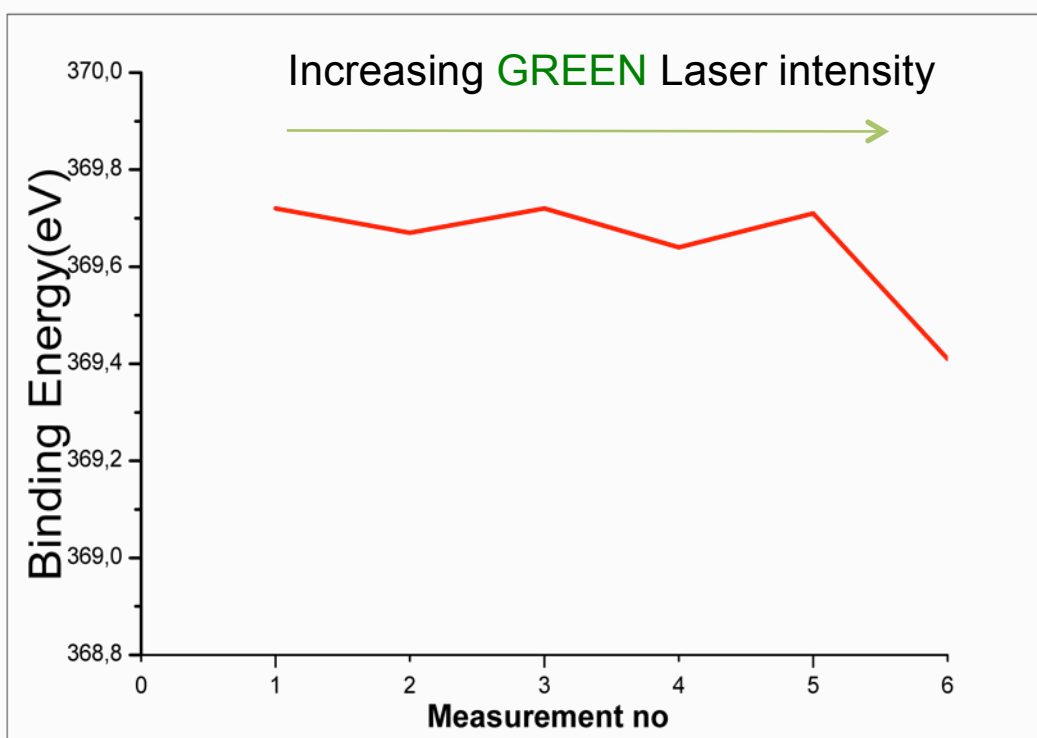
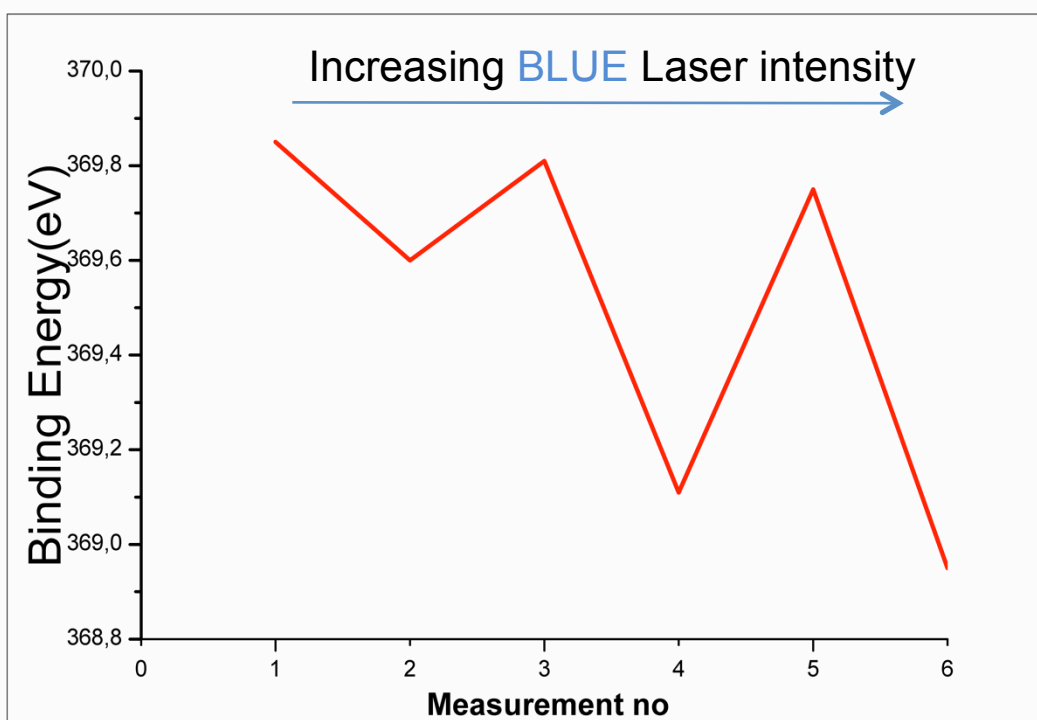


Figure 5. 27. Position of $3d_{5/2}$ peak of Ag for 3 cycles of switching the Laser off-on. Laser intensity is increased after every step, results shown for the blue and green blue and green Lasers.

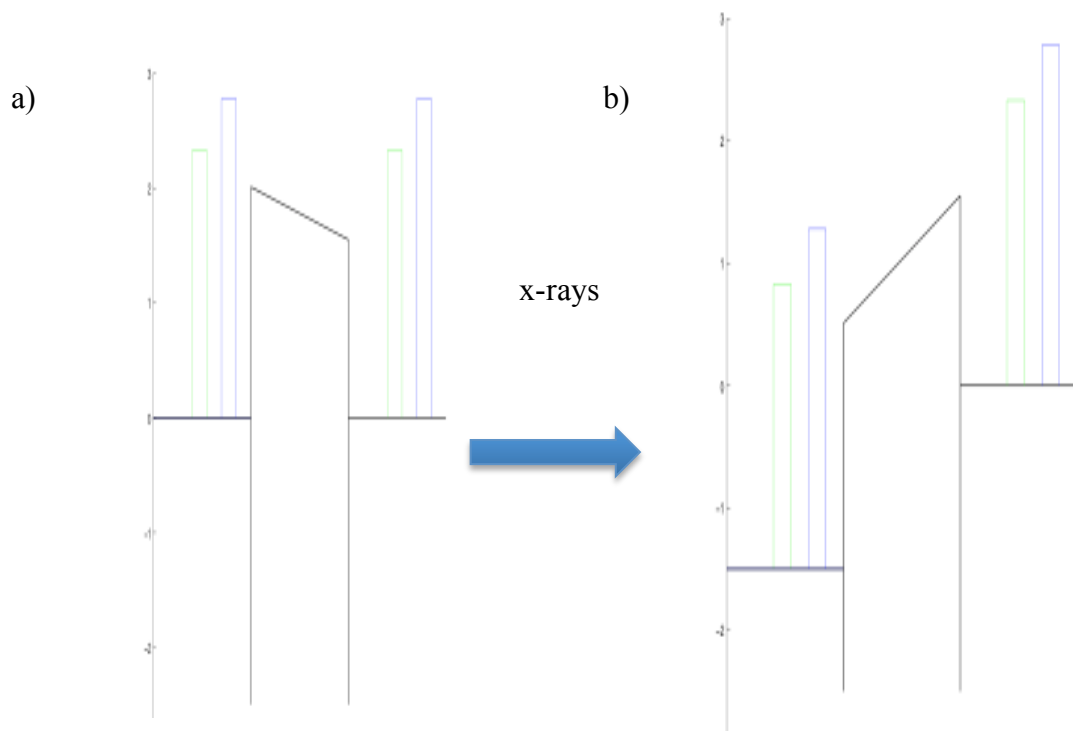


Figure 5. 28. Change in the energy band alignment caused by the X-rays, Laser light illuminates in both the cases

5.8 Gratings experiment

Up to here, dependence of the shifts on the polarization, wavelength, light intensity, polarization, insulator thickness and nanostructure geometry is studied. Still, there is no clear evidence that the shift is due to plasmonic effects. Therefore, the need of a mechanism that would give a clear idea about the plasmonic nature of the binding energy spectra shifts leads to the use of gratings. The plasmonic modes at the gratings are excited by light whose B-field is parallel to the gratings (TM). Otherwise the plasmonic modes in the gratings will not be excited. Hence shift of the binding energy spectra peaks is expected to be seen only when TM polarized light hits the sample.

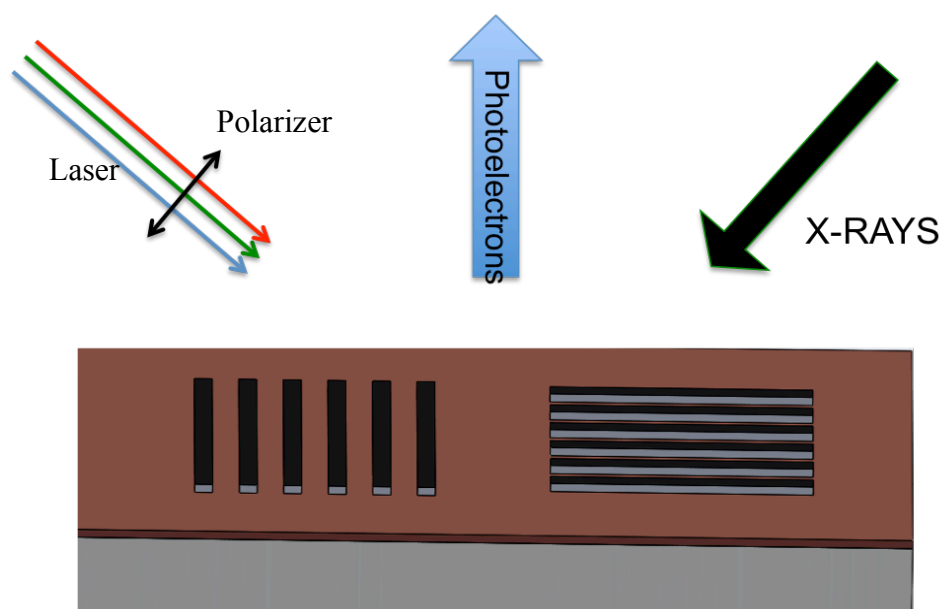


Figure 5.29. Schematic view of the experimental setup. The polarizer polarizes light perpendicular (parallel) to one grating (the other) and vice versa.

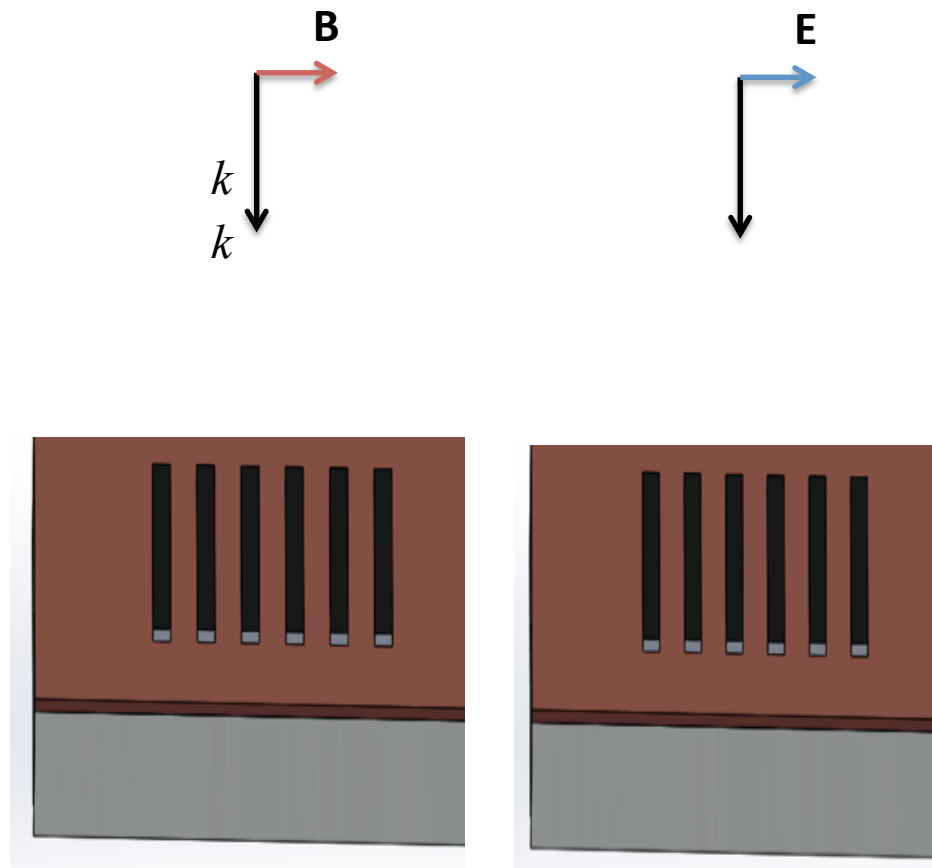


Figure 5.30. Plasmonic modes in gratings are excited by TE polarized light a), but not by TM polarized light, b).

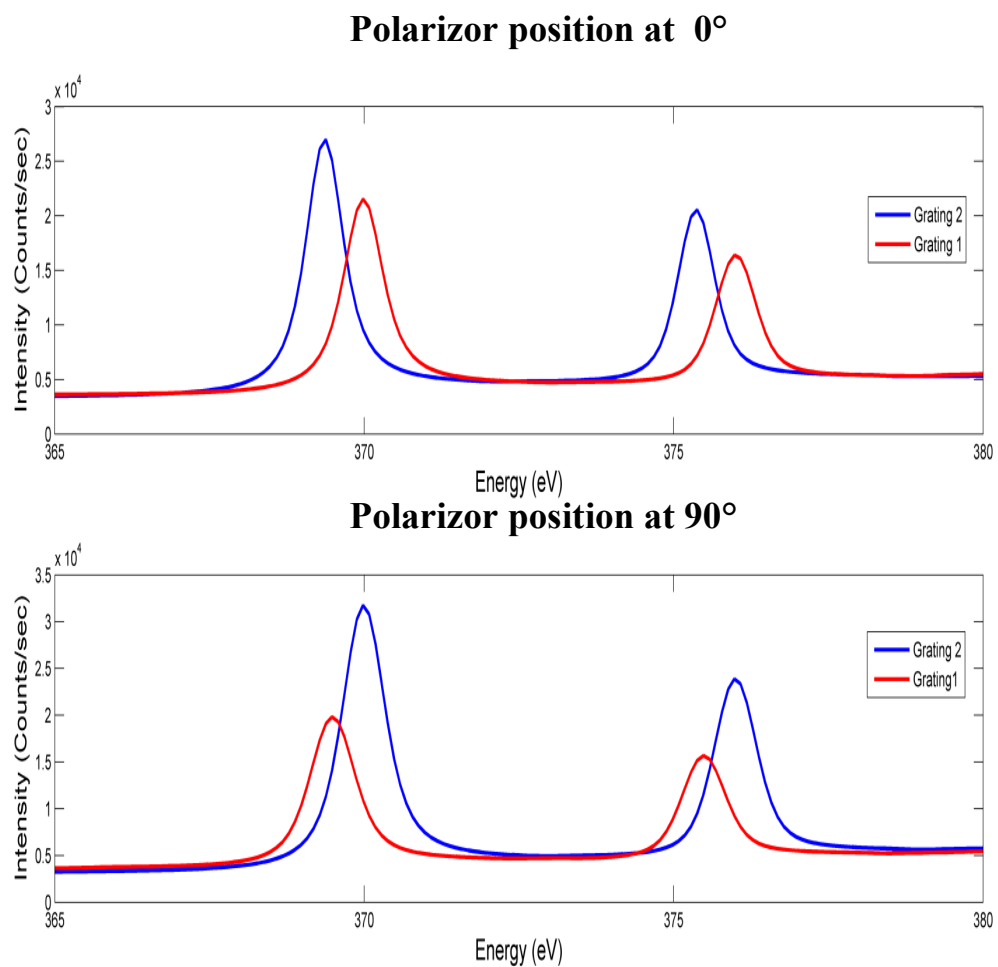


Figure 5.31. Shifts of the binding energy spectra for two different polarizations, for two perpendicular to each other sets of gratings.

The results of the experiments are as expected. When polarizer is at 0° and both the gratings are illuminated consecutively, there is a shift at the binding energy spectra of grating 2 (on the right at Figure 5.27) while no shift is observed for grating 1 (left).

When the polarizer is rotated by 90° and the experiment is repeated, the opposite happens. Binding energy spectra of grating 2 do not shift, while a shift is seen for grating 1 case.

This totally supports the statement that the shifts in the binding energy, and hence the current are due to plasmonic effects. The fact that shift is dependent on polarization implies that plasmonic modes have to be activated for shift to be observed.

Chapter 6

Conclusion

In this thesis, plasmonic and hot electron effects in MIM junctions were studied by means of x-ray photoelectron spectroscopy. Samples having different combination of bottom metal choice and insulator choice were fabricated. The top metal instead was always Ag. Electric resonance and magnetic resonance, and the coupling of both were the cause of the totally absorbing substrate. Resonances of the surface can be tuned by changing fabrication conditions. Optimization of the fabrication process lead to a perfect broadband omnidirectional absorber, that was an improvement of the earlier work done by our group.[31] The surfaces presented here are easy to fabricate over large areas because they require no lithography. This makes this fabrication method used very practical.

Here a new method to probe the plasmonic effects is introduced. X-ray photoelectron spectroscopy is used to record the binding energy spectra shifts. By analyzing the binding energy spectra peak positions in cases where Laser light and floating guns are also used, plasmonic nature of the sample are revealed. Laser light was shined on the plasmonic surfaces to excite hot electrons. Before the Laser light illuminated the samples, dark spectra of the binding energy was taken. It is noticed that due to the electrons lost by photoelectric effect, the top Ag nanoparticles are positively charged. The positive charge accumulation though continues until a certain point, where electrons tunneling from the bottom metal through the barrier compensate for the lost electrons to vacuum. Turning Laser on excites hot electrons, and if their kinetic energy is enough they will traverse the barrier. If no, there is a probability for the hot electrons to tunnel through the barrier or to be reflected.

The samples fabricated were used as SERS substrates. These plasmonic surfaces were shown to exhibit a large density of hot spots, which display blinking

Raman signals. In this manner, these plasmonic surfaces were used to count air molecules by making use of the camera of a mobile phone. [26]

In the last chapter of the thesis, effects on the shifting of the binding energy spectra of Ag of: the top metal Nanostructure geometry, the insulator spacer thickness, polarization dependence and Laser wavelength and Laser light intensity were experimentally studied. Effect of electron flood gun on the binding energy shift was also studied.

As a future work, an electrical circuit model will be used to model and explain the shifts in the binding energy.

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