

PLASMONICS FROM METAL NANOPARTICLES FOR SOLAR CELL APPLICATIONS

A THESIS

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in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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In today's economy, need for development in energy is essential. Solar energy is safe, and at the same time is one of the cleanest, cheapest choices of energy alternative to fossil fuels. In this perspective, using the sun light effectively is in fundamental importance. One of the problems, because of the indirect band gap of the material Si, is small energy conversion ratios of various solar cell structures and limited absorption of red light. Because of the material properties, Si cells cannot absorb red light, which contributes great amount of the sun light. One of the recent developed techniques to use red light is using metal nanoparticles (MNP) embedded in a semiconductor medium as sub-wavelength antennas or MNP scatterers, hence increasing the effective path length of light in the cell.

Absorption and scattering are mostly in plasmon resonances. Shifting the plasmon resonance peaks is possible by changing various parameters of the system like the size of the MNPs. In this work, Finite-Difference Time-Domain (FDTD) method is used to analyze various systems worked. Mainly the MEEP package, developed at MIT, is used to simulate systems and other codes, related to analytical work, have also used to compare results. The plasmon resonances of various sizes of Ag MNPs embedded in different mediums at different positions are analyzed. Critical parameters like particle size, shape, dielectric medium, film thickness are discussed for improved solar cell applications.

Keywords: Solar Cells, Plasmonics, metal nanoparticles, Ag nanoparticles, FDTD, MEEP, Drude, Lorentz..

ÖZET

GÜNEŞ PİLLERİ İÇİN METAL NANOPARÇACIK PLAZMONİK UYGULAMALARI

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Günümüzde, gelişen ekonomiyle enerji kullanımı da artmaktadır ve bu durum enerji kaynaklarında önemli geliştirmeler gerektirmektedir. Güneş enerjisi fosil yakıtlara kıyasla, güvenli, sağlıklı ve aynı zamanda ucuz bir seçenektir. Bu bağlamda güneş ışığını verimli kullanmak oldukça önemlidir. Birçok güneş pili yapısının enerji dönüştürme oranının düşüklüğü ve özellikle kırmızı ışığı soğuramama gibi karşılaşılan sorunlar, silisyum malzemesinin yasak enerji bant yapısının direk olmamasından kaynaklanmaktadır. Kırmızı ışığın soğurulmasını sağlayacak yeni geliştirmelerden birisi de; güneş piline yerleştirilen metal nanoparçacıkların (MN) saçıcı özelliklerini kullanarak, ışığın güneş pili içerisindeki efektif yolunun uzatılmasıdır.

Soğurum ve saçılım en çok plazmon rezonans durumlarında gerçekleşmektedir. Plazmon rezonans dalga boylarını istenen aralığa taşıma sistemdeki çeşitli değişkenleri, örneğin MN boyutlarını, değiştirerek mümkün olabilmektedir. Bu çalışmada zamanda sonlu farklar (FDTD) metodu çeşitli sistemlerin analizleri için kullanıldı. Simülasyonlarda ağırlıklı olarak MIT’de geliştirilen FDTD kodu MEEP [1] kullanıldı ve ek olarak analitik çözümlere karşılık gelen çeşitli kodlarla kıyaslandı. Çeşitli malzemelere, farklı pozisyonlarda yerleştirilen değişik boyutlardaki Ag nanoparçacıkların plazmon rezonans durumları incelendi. Parçacık boyutu, şekli, dielektrik malzeme özelliği ve film kalınlığı gibi farklı değişkenler geliştirilmiş güneş pili uygulamaları için incelendi.

Anahtar sözcükler: Güneş pilleri, plazmonik, metal nanoparçacıkları, Ag nanoparçacıkları, FDTD, MEEP, Drude, Lorentz.

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Chapter 1

Solar Cells

1.1 Working Principles

Working principle behind the solar cell is the photovoltaic effect. Considering the basic solar cell structure, a simple p-n junction; light falling on top of a semiconductor material work as the generator of free electric charge carriers in the material. Separated charges, electron and holes, attracting each other can not combine by crossing the junction but they follow an outside circuit. The reason why those charge carriers can not follow a path inside of solar cell to combine is the formation of depletion region in between the p-n junction interface.

Majority carriers of the semiconductor materials diffuse into opposite parts and then combine with the opposite charges. After this process the remaining minority carriers forms an opposite electric field through the junction which do not allow the flow of majority carriers. This region, at the junction interface, where minority carriers take the control called depletion region.

Apart from this principle, which just describes the steps how a basic p-n junction solar cell works, there exist several different types of solar cells to convert light to electricity as much efficient they designed.

The solar spectrum has a peak around 550 nm. Due to this reason, the band-gap of silicon (1.2 eV) and its abundance on earth makes it the primary material for most solar cell applications. However, silicon has also some disadvantages for solar cell applications. One of the problem is its poor absorption of red light. This is the fact that silicon is an indirect band-gap material. The requirement for the absorption of red light is that; there should be phonons in the material so that their momentums match the condition to conserve crystal momentum.

Despite the world abundance of certain solar cell materials, there will not be enough of them in future, if the production rate of solar cells grows as it is predicted. Statistics show that by the year 2020 [5] we will be finishing our sources. This will also lead to financial problems that the cost of the solar cells will increase huge amounts [5].

Engineers, scientists foreseen the problem and researches go on to overcome it in different ways. The usage of materials other than silicon is one way but not promising since world reservoir of silicon is still the highest. Another solution is to reduce the amount of silicon used in the solar cell. This idea lead to the 2nd generation solar cells, which are thinner compared to the ones of first generation. However this has not solved the problem but directed to another form. Thinner solar cells, which are made of silicon, have less efficiencies compared to the thicker ones, since silicon is already a indirect bandgap material.

Solutions for the problem are continuing under the topic of 3rd generation solar cells. These new solar cell structures are thin compared to the 1st generation ones and they are have comparable efficiencies with the 1st generation solar cells.

There are several solutions to increase the light conversion efficiencies of solar cells. Since the Silicon material can not absorb red and infrared spectrum of sun light, thinner solar cells has disadvantage of reduced optical path length. One of the solutions to overcome this situation is by means of usage of photoelectric effect. Materials with different bandgap energies, corresponding to different energies of light, are sandwiched in order to absorb more light. These structures are called tandem solar cells and each layer in the solar cell responsible to absorb corresponding light. Efficiency of solar cell can be increased in that manner.

Since the normally incident sun light falling on a solar cell will have very small distance to be absorbed the another method is established to increase the effective path length of light in the solar cell structure. The key to increase optical path length is plasmonics. Up to now, almost all the conventional solar cell structures are builded so that they function by use of a photo electric effect, which is the quantum nature of light. The field of plasmonis provides the light to be concentrated in these thinner solar cell structures. Structures could trap the light which is scattered into the film at resonances of nanoparticles located on top of a solar cell structures. Alternatively nanoparticles embedded in solar cell form strongly oscillating electric fields at resonances, which extract electrons. Moreover structure can be used to form Surface Plasmon Polaritons in the metal dielectric surfaces, which are again responsible to extract electrons through their travel on metal dielectric interface.

1.2 Plasmonics

The quantum of collective electron oscillations in matter are called plasmon. So plasmons are kind of quasiparticles like photons and phonons. It is the reason that most metals in their bulk form are shiny. Since their plasmon frequencies are in ultraviolet region of spectrum, electrons are able to respond the light below these wavelengths, making them shiny. There was certain limitations regarding the control of light but; the field plasmonics make it possible to confine the light into sub-diffraction limit. So it is one of the great interest on the subject, plasmonics, today since it allows materials to be characterized in nanometer scale. Materials characterized their plasmonics properties are being used and suggested to be used in many areas of technology today like; photovoltaics [5], surface enhanced raman spectroscopy [6], data storage [7] and biosensing [8].

There are variety of theories, models examining the above problems under the topic of plasmonics. In this thesis mostly the nanoparticles to scatter light is studied and FDTD method is used in simulations.

Chapter 2

Theory

For the sake of convenience, before starting to show the results obtained in this thesis, brief mentions to the methods are given in below sections. These are not the work done in this thesis, but since they form the theories behind the simulations, they must be known.

2.1 Mie

Scattering by spheres (similar in size to light wavelength) in uniform media, usually referred to Mie, was originally a work started by Ludvig Lorenz [9]. In 1908, Gustav Mie is the one who has rediscovered it and improved the theory to calculate scattering of radiation from spherical particles [10]. So the work started by Lorenz developed by Mie to its final form and the solution is named Mie Scattering. After establishment of the Mie theory there became a lot of approaches to electromagnetic problems but Mie solution preserves its importance. The reason might be that it is the exact solution of spherical particles with sizes similar to light wavelength.

Mie solution uses Maxwell's equations to explain the scattering phenomena of spherical particles with similar sizes of the light wavelength. Form of the solution

includes infinite series of spherical bessel functions.

In order to solve the problem, incident plane wave is expanded to spherical vector wavefunctions since the system is spherically symetric.

The main considerations in the problem is that; medium is isotropic and homogeneous. The basic steps of the theory is given below are taken from the known source from literature [11]:

Electromagnetic fields should satisfy the wave equation in a linear, isotropic and homogeneous medium as below:

$$\nabla^2 \mathbf{E} + k^2 \mathbf{E} = 0 \quad (2.1)$$

$$\nabla^2 \mathbf{H} + k^2 \mathbf{H} = 0 \quad (2.2)$$

Where $k = \omega\sqrt{\epsilon\mu}$ is the wavevector and $\mathbf{E}$ and $\mathbf{H}$ are coupled each other through the curl equations:

$$\nabla \times \mathbf{E} = i\omega\mu\mathbf{H} \quad (2.3)$$

$$\nabla \times \mathbf{H} = -i\omega\epsilon\mathbf{E} \quad (2.4)$$

Analogous to fields in a divergenless medium, there could be generated vector function $\mathbf{M}$ to represent them:

$$\mathbf{M} = \nabla \times \mathbf{c}\psi \quad (2.5)$$

So that:

$$\nabla \cdot \mathbf{M} = 0 \quad (2.6)$$

Using vector identities, the vector equation is satisfied by $\mathbf{M}$

$$\nabla^2 \mathbf{M} + k^2 \mathbf{M} = \nabla \times [\mathbf{c}(\nabla^2 \psi + k^2 \psi)] \quad (2.7)$$

Furthermore, analogous to the relations between $\mathbf{E}$ and $\mathbf{B}$ another vector function can be generated:

$$\mathbf{N} = \frac{\nabla \times \mathbf{M}}{k} \quad (2.8)$$

and it also satisfies the wave equation:

$$\nabla^2 \mathbf{N} + k^2 \mathbf{N} = 0 \quad (2.9)$$

so that:

$$\nabla \cdot \mathbf{N} = 0 \quad (2.10)$$

Representations to vector wave equations is completed in this manner and stands for electromagnetic fields.

Determining the generating functions, ψ , will solve the problem. Considering the solutions of ψ to be in the form $\psi_{(r,\theta,\phi)} = R_{(r)}\Theta_{(\theta)}\Phi_{(\phi)}$,

Equation 2.9 in spherical coordinates gives 3 separate equations:

$$\frac{d^2 \Phi}{d\phi^2} + m^2 \Phi = 0 \quad (2.11)$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + [n(n+1) - \frac{m^2}{\sin^2 \theta}] \Theta = 0 \quad (2.12)$$

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + [k^2 r^2 - n(n+1)] R = 0 \quad (2.13)$$

Linearly independent solutions to equation 2.11 are:

$$\Phi_1 = \cos m\phi, \Phi_2 = \sin m\phi \quad (2.14)$$

Linearly independent solutions to equation 2.12 are associated legendre functions of first kind $P_n^m(\cos \theta)$.

And introducing dimensionless variable $\rho = kr$ and the function $Z = R\sqrt{\rho}$ linearly independent solutions to equation 2.13 are the Bessel functions of first and second kind:

$$j_n(\rho) = \sqrt{\frac{\pi}{2\rho}} J_{n+\frac{1}{2}}(\rho) \quad (2.15)$$

$$y_n(\rho) = \sqrt{\frac{\pi}{2\rho}} Y_{n+\frac{1}{2}}(\rho) \quad (2.16)$$

Then the generating functions satisfying the wave equation are in the form:

$$\psi_{mn}^1 = \cos m\theta P_n^m(\cos \theta) z_n(kr) \quad (2.17)$$

$$\psi_{mn}^2 = \sin m\theta P_n^m(\cos \theta) z_n(kr) \quad (2.18)$$

where z_n stands for any of the Bessel functions first and second kinds.

The $\mathbf{M}$ and $\mathbf{N}$ are then:

$$\mathbf{M}_{mn}^1 = \frac{-m}{\sin \theta} \sin m\phi P_n^m(\cos \theta) z_n(\rho) \hat{\mathbf{e}}_{\hat{\cdot}} - \cos m\phi \frac{dP_n^m(\cos \theta)}{d\theta} z_n(\rho) \hat{\mathbf{e}}_{\mathbf{e}} \quad (2.19)$$

$$\mathbf{M}_{mn}^2 = \frac{m}{\sin \theta} \sin m\phi P_n^m(\cos \theta) z_n(\rho) \hat{\mathbf{e}}_{\hat{\cdot}} - \sin m\phi \frac{dP_n^m(\cos \theta)}{d\theta} z_n(\rho) \hat{\mathbf{e}}_{\mathbf{e}} \quad (2.20)$$

$$\begin{aligned}
\mathbf{N}_{mn}^1 &= \frac{z_n(\rho)}{\rho} \cos m\phi n(n+1) P_n^m(\cos \theta) \hat{\mathbf{e}}_{\mathbf{r}} + \cos m\phi \frac{dP_n^m(\cos \theta)}{d\theta} \frac{1}{\rho} \frac{d}{d\rho} [\rho z_n(\rho)] \hat{\mathbf{e}}_{\theta} \\
&| -m \sin m\phi \frac{P_n^m(\cos \theta)}{\sin \theta} \frac{1}{\rho} \frac{d}{d\rho} [\rho z_n(\rho)] \hat{\mathbf{e}}_{\phi}
\end{aligned} \tag{2.21}$$

$$\begin{aligned}
\mathbf{N}_{mn}^2 &= \frac{z_n(\rho)}{\rho} \sin m\phi n(n+1) P_n^m(\cos \theta) \hat{\mathbf{e}}_{\mathbf{r}} + \sin m\phi \frac{dP_n^m(\cos \theta)}{d\theta} \frac{1}{\rho} \frac{d}{d\rho} [\rho z_n(\rho)] \hat{\mathbf{e}}_{\theta} \\
&| +m \cos m\phi \frac{P_n^m(\cos \theta)}{\sin \theta} \frac{1}{\rho} \frac{d}{d\rho} [\rho z_n(\rho)] \hat{\mathbf{e}}_{\phi}
\end{aligned} \tag{2.22}$$

Above formulas are then evaluated to express scattering and extinction cross sections given below:

$$C_{sca} = \frac{2\pi}{k^2} \sum_{i=1}^{\infty} (2n+1) (|a_n|^2 + |b_n|^2) \tag{2.23}$$

$$C_{ext} = \frac{2\pi}{k^2} \sum_{i=1}^{\infty} (2n+1) \text{Re}(a_n + b_n) \tag{2.24}$$

At this step, interested reader is advised to check the relevant sections of the books [12, 13, 11] to find more on light and Mie scattering theory.

2.2 FDTD

Electromagnetics became a complete theory after Maxwell's contributions. In its simple understanding, electromagnetics describes the forces exerted by charges and charges in motion. Developments in computer technology lead to solve complex electromagnetic problems that could not be dealt before.

One of the way to deal with electromagnetic problems is to make use of Finite Difference Time Domain method (FDTD). Fundamental idea behind FDTD is

the discretization of space and time. Basic steps below show, how to discretize space and time in 1–dimension in an FDTD algorithm.

FDTD algorithm requires a lot of spatial and temporal derivatives of fields. In order to see and understand the approximations, let's start with the Taylor's series expansions of function $f(x)$ around point x_0 with an offset of $\pm \frac{\delta}{2}$:

$$f(x_0 + \frac{\delta}{2}) = f(x_0) + \frac{\delta}{2}f(x_0)' + \frac{1}{2!}(\frac{\delta}{2})^2 f(x_0)'' + \dots, \quad (2.25)$$

$$f(x_0 - \frac{\delta}{2}) = f(x_0) - \frac{\delta}{2}f(x_0)' + \frac{1}{2!}(\frac{\delta}{2})^2 f(x_0)'' - \dots, \quad (2.26)$$

Using above equations one can lead to find the differentiation of function $f(x)$:

$$\frac{df(x)}{dx} = \frac{f(x_0 + \frac{\delta}{2}) - f(x_0 - \frac{\delta}{2})}{\delta} + O(\delta^2) \quad (2.27)$$

So for sufficiently small δ it is plausible to omit $O(\delta^2)$. Since, the highest power omitted in δ is second order, this is called the second-order accuracy. For higher resolution in space (smaller δ) we get a better approximation and in the limit δ goes to zero we have the exact case.

Kane Yee proposed the method FDTD in his 1966 paper [14] by make use of second–order accuracy in Maxwell equations, such that:

$$\frac{df(x)}{dx} = \frac{f(x_0 + \frac{\delta}{2}) - f(x_0 - \frac{\delta}{2})}{\delta} + O(\delta^2) \cong \frac{f_{(i+1/2)} - f_{(i-1/2)}}{\delta x} \quad (2.28)$$

On the other hand, considering the Maxwell's equations:

Faraday's law says that,

$$\nabla \times \mathbf{E} = -\mu \frac{\partial \mathbf{H}}{\partial t} \quad (2.29)$$

Ampere's law says that,

$$\nabla \times \mathbf{H} = \epsilon \frac{\partial \mathbf{E}}{\partial t} \quad (2.30)$$

In order to see how the second order accuracy applied to equations 2.29 and 2.30, let's focus on a 1-D problem and consider that the wave travelling in x-direction. So let it's electric field to be in y-direction and magnetic field is in z-direction. Considering these conditions we have the equalities regarding the equations (2.29 and 2.30);

$$\frac{\partial E_y}{\partial x} = -\mu \frac{\partial H_z}{\partial t} \quad (2.31)$$

and

$$-\frac{\partial H_z}{\partial x} = \epsilon \frac{\partial E_y}{\partial t} \quad (2.32)$$

Numerically these are corresponding to:

$$\frac{E_{y(i+1/2)}^n - E_{y(i-1/2)}^n}{\Delta x} = -\mu \frac{H_{z(i)}^{n+\frac{1}{2}} - H_{z(i)}^{n-\frac{1}{2}}}{\Delta t} \quad (2.33)$$

$$\frac{H_{z(i+1/2)}^n - H_{z(i-1/2)}^n}{\Delta x} = \epsilon \frac{E_{y(i)}^{n+\frac{1}{2}} - E_{y(i)}^{n-\frac{1}{2}}}{\Delta t} \quad (2.34)$$

Where 'i' shows the spatial indices and 'n' stands for the time indice.

Above relations show that time derivative of electric field depends on space derivative of the magnetic field and vica versa. These makes it possible to calculate a field by using the knowledge of the ones before. At each step calculated fields allow it possible to calculate the fields at further steps and progression in the method, simulation goes on this way.

$$E_{y(i+1/2)}^n = E_{y(i-1/2)}^n - \mu \frac{\Delta x}{\Delta t} (H_{z(i)}^{n+\frac{1}{2}} - H_{z(i)}^{n-\frac{1}{2}}) \quad (2.35)$$

$$H_{z(i+1/2)}^n = H_{z(i+1/2)}^{n-1} + \epsilon \frac{\Delta x}{\Delta t} (E_{y(i)}^{n+\frac{1}{2}} - E_{y(i)}^{n-\frac{1}{2}}) \quad (2.36)$$

Apart from the 1-D problem described above one of the most important point that should be highlighted about the FDTD is the Courant factor (S). Courant factor originates from the Courant–Friedrichs–Lewy Condition that is developed to solve certain kinds of partial differential equations by the method of finite differences [15]. In our FDTD method Courant factor builds the consistency between space and time resolution.

Courant Factor, S, is a condition such that:

$$\Delta t = S \Delta x \quad (2.37)$$

and there is a restriction on it says that:

$$S < \frac{n_{min}}{\sqrt{d}} \quad (2.38)$$

‘ n_{min} ’ is the minimum refractive index in the system being worked and ‘d’ is the dimensionality of the space.

Equations basically says that light in an FDTD algorithm, simulation can not be greater than that of the light. So one must take care of S to make the algorithm working and get realistic results.

Another important issue to be known about FDTD is the Yee Lattice. Different field components are stored at different grid locations in the FDTD cell according to the Maxwell’s equations.

Yee proposed to arrange the E–field and H–field components about a rectangular unit cells of a cartesian coordinate system such that E–field vectors located at the midway between H–field vectors so that field vectors do not overlap. In Figure 2.1 the basic Yee lattice in 3–D with all E and H field components is shown.

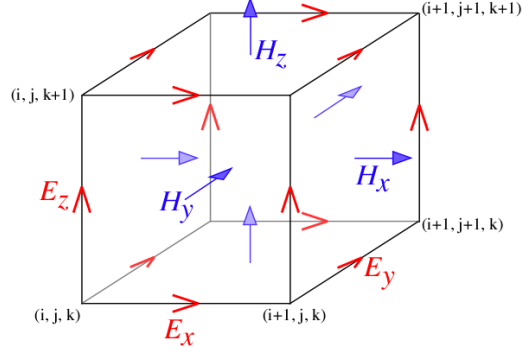


Figure 2.1: Demonstration of Yee lattice [2]

After the foundation of light localization into the diffraction limit, subject Plasmonics gain a popularity among others.

2.3 Drude–Lorentz

In principle, dielectric function of a medium has frequency dependent nature. However, it is not possible to use the dielectric function in that manner all the time. This make the arise of formula defined dielectric functions.

A formula defined dielectric function can be reached by fitting the experimental data. In order to fit dielectric function to experimental datas, method of least squares is determined. The functional for the technique is given as [3]:

$$\chi^2 = \sum_{i=1}^N \left(\frac{y_i - f(x_i, p_1 \dots p_M)}{\sigma_i} \right)^2 = \chi^2(p_1, \dots p_M) \quad (2.39)$$

Statistically better fit corresponds to the smaller value of χ^2 which says that the parameters differ from their deviations smaller. So minimization of the χ^2 term will lead to the best fit of the parameters.

Since the Drude–Lorentz dielectric function is a non–linear function, in order to minimize χ^2 numerically there is the Levenberg–Marquardt algorithm is

required to be used [3].

Another important physical property of dielectric functions to be mentioned is; Kramers–Kronig relations. They require the imaginary and real parts of dielectric function to relate each other by equation:

$$\epsilon_1 - 1 = \frac{2}{\pi} \int_0^\infty \frac{x\epsilon_2(x)}{x^2 - \omega^2} dx \quad (2.40)$$

This fact can be used to ensure for the reliability of dielectric function.

The Drude–Lorentz dielectric function is then expressed as sum of infinite frequency dielectric constant, Drude term and Lorentzian terms as many as needed to model.

$$\epsilon = 1 + \epsilon(\omega)^D + \epsilon(\omega)^1 + \epsilon(\omega)^2 + \dots \quad (2.41)$$

In principle, taking too many Lorentzian terms in modelling dielectric function will lead to a better fit to experiment datas. However, too many terms will cause numerical difficulty in the simulation, which we already encountered during the experience of AZO modelling in this thesis work.

So Drude–Lorentz is one of the most used formula defined dielectric functions of this type. Drude–Lorentz model make use of set of harmonic oscillators to describe the optical response of the medium.

$$\epsilon = \epsilon_\infty - \frac{\omega_p^2}{\omega_0^2 + i\gamma\omega} + \sum_i \frac{\omega_{pi}^2}{\omega_{oi}^2 - \omega^2 - i\gamma_i\omega} \quad (2.42)$$

Where the first term stands for the Drude term and the others are Lorentzian terms representing the interband transitions. ϵ_∞ is the response of the material at infinite frequency, dielectric constant. ω_{pi} is the plasma frequency, ω_{oi} is the eigenfrequency and γ_i is the damping rate of the i^{th} oscillator.

Chapter 3

Initial Problems

In all FDTD simulations in this thesis, freely available MEEP package is used [1]. Parallel-MEEP version is used for simulations in 3-D. Drude-Lorentz parameters for silver taken from literature relevant to our problems [16]. Typical run takes 10 hours CPU time in 4×8 AMD core PC system.

3.1 Reflection and transmission through a dielectric slab

3.1.1 Reflection and Transmission Through a Dielectric Slab

In order to start working with FDTD calculations, basic simulations ran under the code. First simulation is the reflection and transmission of a slab in reference to the work [17].

Reflection and transmission curves through a dielectric slab of thickness $d = 10 \mu\text{m}$, relative permittivity $\epsilon = 12$ is calculated under AM1.5 light of wavelengths between 723nm to 779nm. Cross sectional view of the simulation setup is shown

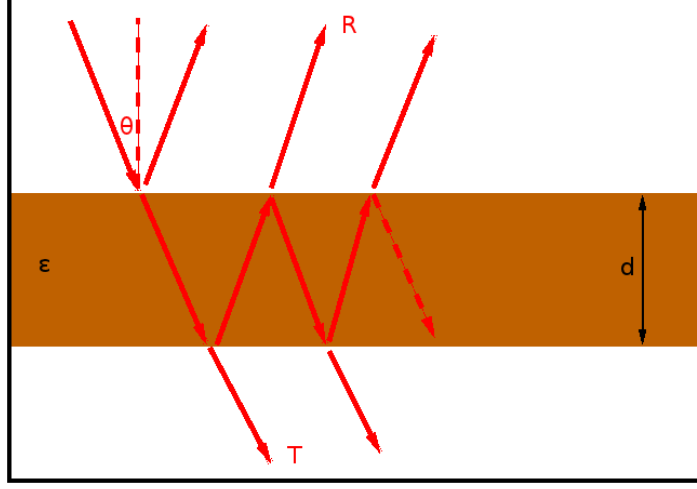


Figure 3.1: Cross sectional view of the simulation setup

Figure 3.2. In order to compare the simulated value of Free Spectral Range (FSR), which is described as the wavelength (or frequency) range between two successive maximum (or minimum) intensities in the reflection (or transmission) spectrum for a system under study, to that of in the work of others approximated formula is used [17]:

$$FSR \cong \frac{c}{2d \cdot \sqrt{\epsilon(f)' \cdot \cos \theta}} \cdot [1 + \frac{f}{2\epsilon(f)'} \cdot \frac{d\epsilon(f)'}{df}]^{-1} \quad (3.1)$$

Since in our problem, we only work on a frequency independent relative permittivity $\epsilon(f)' = \epsilon$ and second term in the parantheses drops to zero. On the other hand since light used in the simulation is AM1.5 we have $\cos(\theta) = 0$. The equation 3.1 for the values in simulation case give the value of FSR (in frequency) to be approximately: $FSR = 4.3301 \times 10^{12}$.

and FDTD result is found to be $FSR_{FDTD} = 4.045 \times 10^{12}$.

So comparison of the analytical result with MEEP's outcome shows very good aggrement between them.

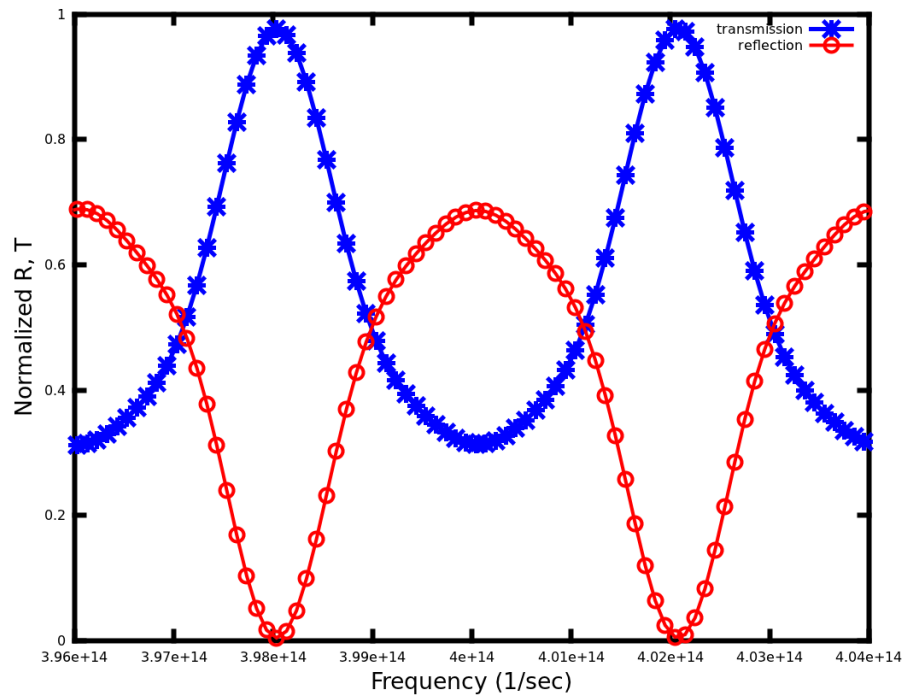


Figure 3.2: Reflection and Transmission through dielectric slab under oblique incidence

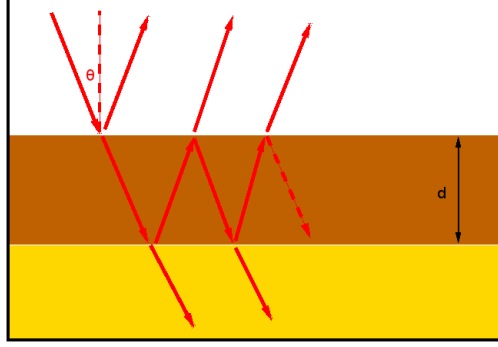


Figure 3.3: Reflection through a slab of 100 nm ITO between air and silicon. Reflection monitor is located in air side where the source is on top.

3.1.2 Dielectric Slab on Substrate

After establishing above simulation, further step for dielectric layer in different medias are simulated. In order to do that, expressions [18] for a dielectric layer are modified so that the equation is reached:

$$E_r = E_0 e^{i\omega t} \frac{r + r' e^{-i\delta}}{1 + r r' e^{-i\delta}} \quad (3.2)$$

and leads to;

$$\frac{I_r}{I_0} \cong \frac{|E_r|^2}{E_o^2} = \frac{r^2 + r'^2 + r r' 2 \cos(\delta)}{1 + (r r')^2 + r r' 2 \cos(\delta)} \quad (3.3)$$

$$r = \frac{n_1 - n_s}{n_1 + n_s}, \quad r' = \frac{n_2 - n_s}{n_2 + n_s}$$

where light coming from one media ϵ_1 reflects and take multiple reflections through a slab of ϵ_s and transmits into another media ϵ_2 . Comparison between the FDTD and above formula for $\epsilon_1 = 1$ (Air), $\epsilon_2 = 3.6$ (ITO) and $\epsilon_s = 11.68$ (Si) is seen in Figure 3.3; where the thickness of the SiO_2 thin film between the air and Si is determined to be $d = 100\text{nm}$:

3.2 Reflectivity of Ag thin films

Second step through the main goal is to implement a metal material to the FDTD. This can only be done with use of the lorentzian parameters since MEEP-FDTD only support this feature for dispersive materials. In order to make use of silver material in the simulations, well known used parameters of Drude-Lorentz dielectric function are taken from literature as it also completes our purposes in simulations [16].

As it is previously stated, MEEP is a code based on scale invariant units (since Maxwell equations allow this feature) which allows user to consider a unit length in the simulations and a very usefull property.

The Drude-Lorentz parameters [16] then converted to the lorentzian parameters into the MEEP units.

Reflectivity of silver thin fim of thickness 100 nm calculated under AM1.5 light of wavelength as it is seen in Figure 3.4 have the same argument with the ones in the literature.

Vacuum wavelengths in the simulation changes between 2 to 8 in scale invariant units in the simulation. Resolution is set to 20 , which means that 40 to 160 pixels per wavelengths 200 – 800 nm in vacuum. Despite we reach results that are observed to be well agree with the ones in literature; simulations thereafter belongs to cases in which units were scaled in same manner, but resolution is set to 40.

3.3 Scattering of Ag nanospheres

Continuing to the main task, scattering efficiencies of Ag nanospheres in air are calculated. Computational cell of volume $500 \times 500 \times 500 \text{ nm}^3$ is employed. Perfectly matched layers introduced as the boundary condition and nanospheres with different radiis, 30 – 45 – 60 – 90 nm, are setted up during simulations.

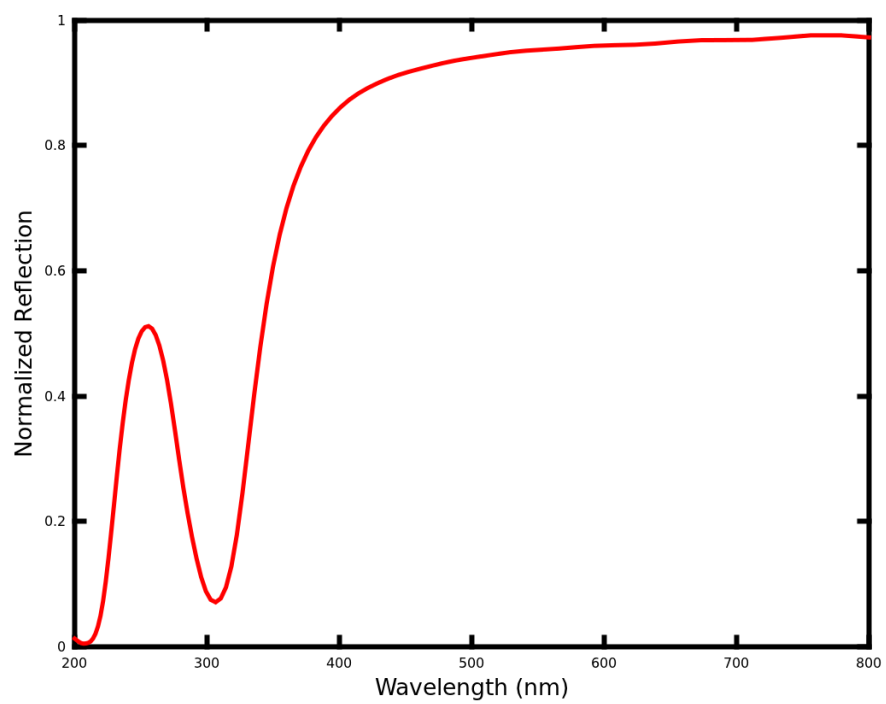


Figure 3.4: Reflection of Ag thin film of thickness 100 nm.

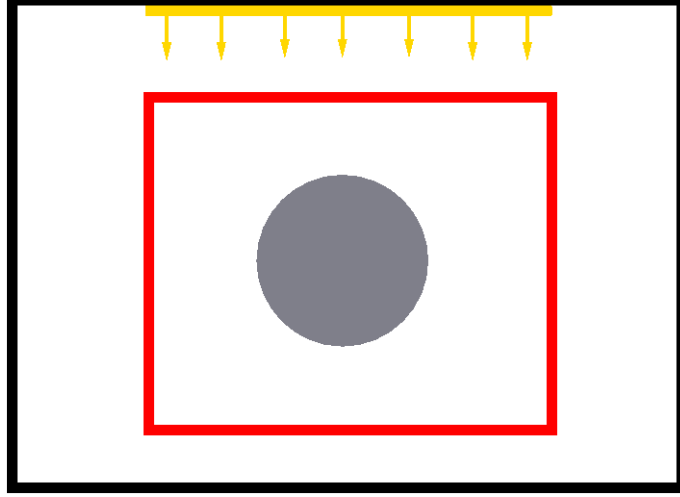


Figure 3.5: Cross sectional view of simulation system. Black lines are PML, sphere is at the center and light shown in yellow arrows. Scattered fields are calculated on planes represented by red lines.

Total scattered flux calculated over all surface of the imaginary box of volume $350 \times 350 \times 350 \text{ nm}^3$ centered origin and silver sphere also located at the center. Total power on the surfaces is then calculated by;

$$P(\omega) = \text{Re} \hat{n} \cdot \oint \mathbf{E}_\omega(x)^* \times \mathbf{H}_\omega(x) d\mathbf{a} \quad (3.4)$$

then the power calculated is used to calculate the scattering cross section by,

$$C_{sca}(\omega) = \frac{P(\omega)}{I(\omega)} \quad (3.5)$$

Where $\hat{n}$ is the outward normal direction to the surface, $I(\omega)$ is the intensity of light.

The cross sectional view of the simulation system is seen in Figure 3.5 with Perfectly Matched Layers (PML) embedded is shown in black lines surrounding the computational cell, flux planes shown in red lines, silver sphere at the center and the source in yellow color.

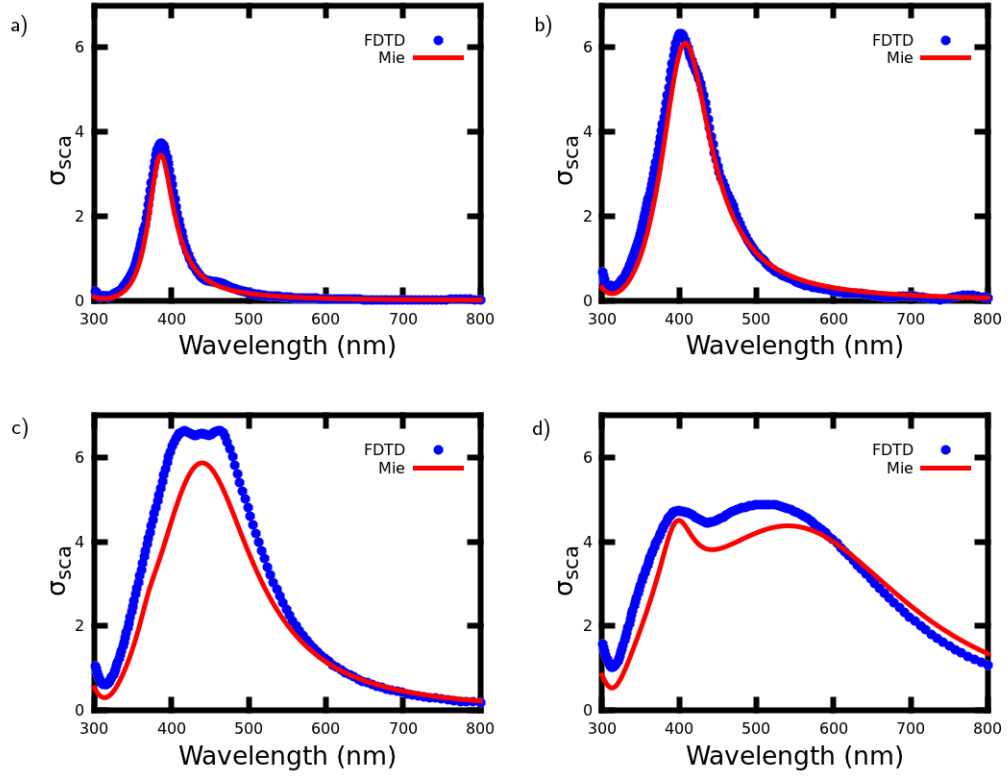


Figure 3.6: Scattering efficiencies of Ag spheres with diameters 60, 90, 120 and 180 nm in air.

Scattering cross section efficiencies, σ_{sca} , can be calculated by dividing the scattering cross section to the geometric cross section of the scatterer object.

In Figure 3.6, the scattering cross section efficiencies are shown for spheres with $r = 30, 45, 60, 90$ nm in air. The range of the wavelength is employed so that only the dipole resonances of the spheres are seen.

To identify the resonances on the systems; images of the near fields for the resonance conditions are determined and it is clearly seen in Figure 3.7 that 90 nm radius of Ag sphere has a dipole resonance under the light of wavelength 512 nm while quadrupolar resonance observed at 400 nm.

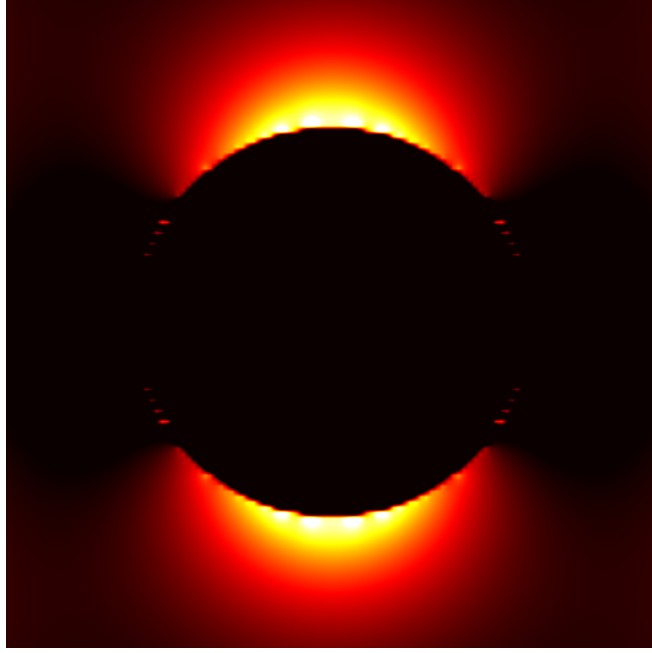


Figure 3.7: Near fields for sphere with radius $r = 30$ nm under resonance condition, $\lambda_{PR} = 390$ nm

Effect of different shapes are also examined. Considering spheroid particles, oblate ellisoids, for which $r_3 = r_2 > r_1$ set of simulations made. Orientation of the object such that the axis r_1 is in the same direction with light propagation as seen in Figure 3.8.

Results are seen in Figure 3.9. For the same aspect ratios of different sizes of spheroid particles; decreasing the radius in light propagation direction, r_1 , leads to red-shifted dipole resonance, but this leads to decrease the scattering efficiencies of particles too.

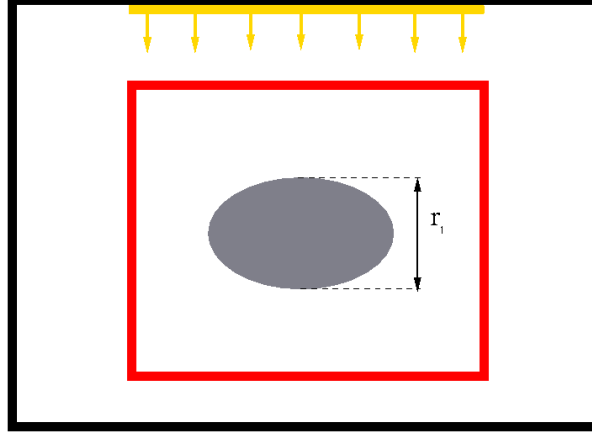


Figure 3.8: Cross sectional view of the simulation system for spheroid particles. Geometric cross section of the spheroids are same with that of spheres', but radius in light propagation direction, r_1 , is changed.

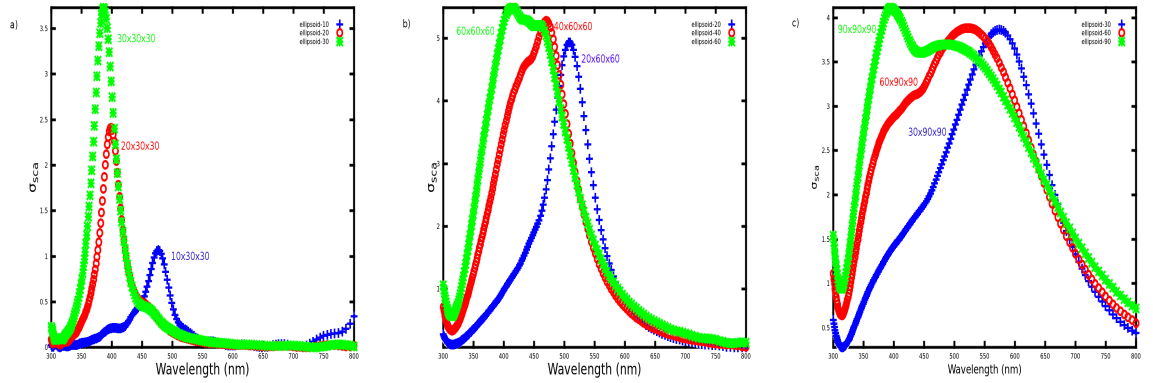


Figure 3.9: Scattering cross section efficiencies of ellipsoidal particles.

3.4 Scattering, absorption and extinction cross sections of silver nanocylinders

In the light of paper [19]; scattering, absorption and extinction cross sections of infinite silver nanocylinder is reproduced. Due to infinity in one dimension, problem could be reduced to 2-D which gives a great advantage in computations since it requires a lot less memory compared to the simulations in 3-D.

Diameter of spheres are determined to be 50 nm. Scattering, absorption and extinction cross section efficiencies are then calculated;

- $C_{sca} = \frac{P_{sca}}{I_{inc}}$
- $C_{abs} = \frac{P_{abs}}{I_{inc}}$
- $C_{ext} = C_{sca} + C_{abs}$

Where P_{sca} and P_{abs} are scattered and absorbed powers. I_{inc} is incident flux; C_{sca} , C_{abs} and C_{ext} are scattering, absorption and extinction cross sections.

As it is seen in Figure 3.10, results obtained are the same with that of the ones in work in [19].

3.5 AZO implementation

After working with Ag nanoparticles on different medias, new simulations required to address the different experimental needs. One of the most studied Transparent Conducting Material for this kind is Aluminium Zinc Oxide (AZO). Since it both transparent to light and conducting to electricity AZO is a very promising material for plasmonic solar cell applications and low cost alternative to ITO [20].

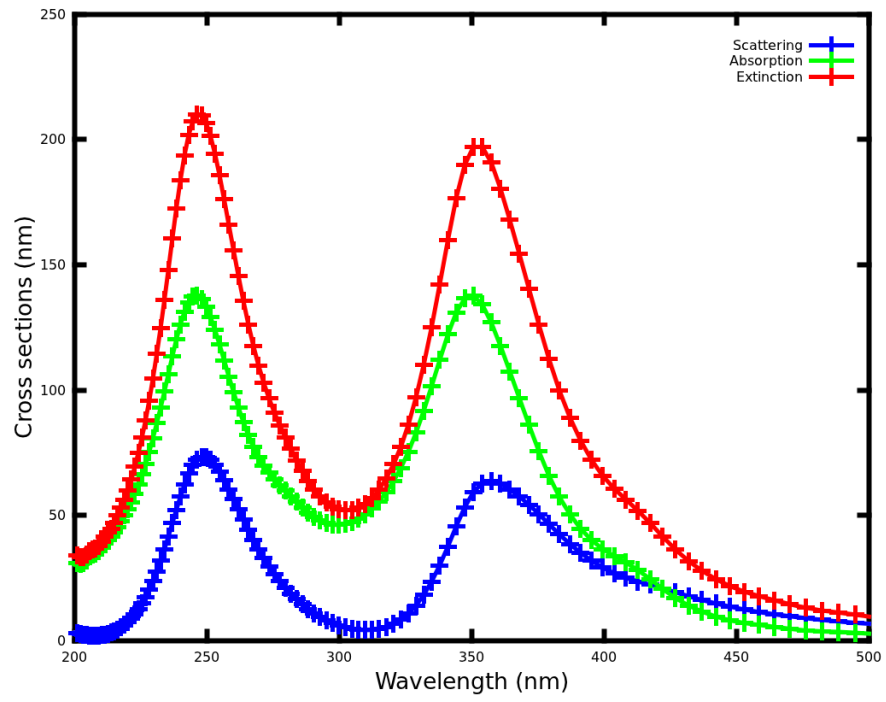


Figure 3.10: Scattering, absorption and extinction cross sections for nanocylinder with radius $r = 25$ nm.

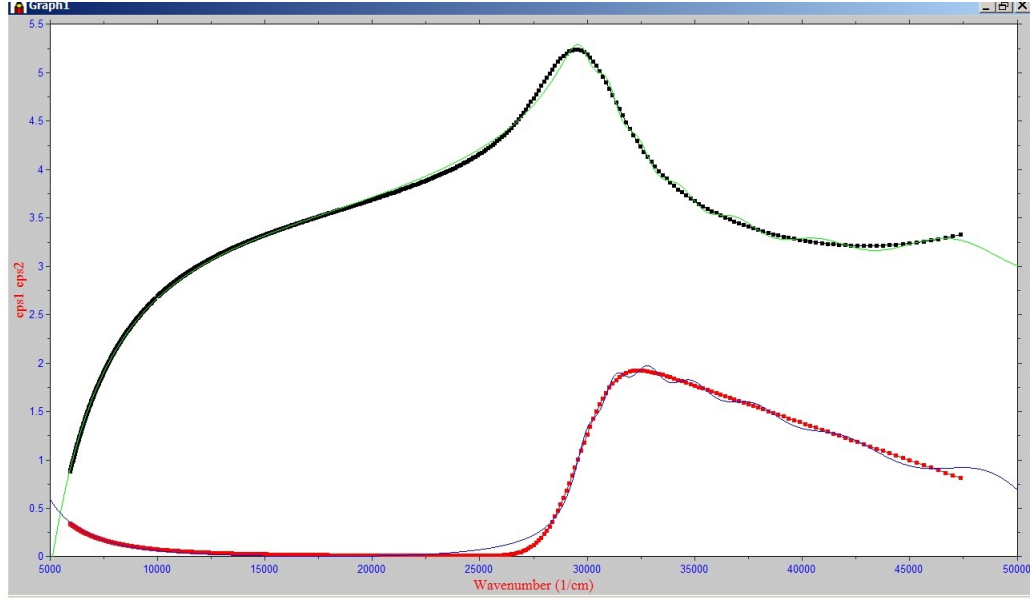


Figure 3.11: Fitting window of AZO sample. Drude-Lorentz fit is made to ellipsometry data [3]. Black is real dielectric constant and red is complex dielectric constant.

The only way to implement frequency dependent dielectric function of this material is to make use of parameters for the lorentzian oscillators. In order to do that; first the experimental ellipsometry data is expressed in terms of optical constants η and κ for a range of photon energies between 0.73 – 5.87 eV. Then optical data is converted to real, ϵ_1 , and imaginary, ϵ_2 , parts of the dielectric function; $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ and expressed in terms of $\frac{1}{cm}$. Then Drude–Lorentz fit is made. For this we used freely available software program [3]. Fit window is seen in Figure 3.11.

Drude–Lorentz fit to AZO data made by 1 Drude and 7 Lorentzian terms, infinite frequency dielectric constant set to be 1. So 8 lorentzian terms converted in the FDTD code to represent AZO material. As seen in Figure 3.11 AZO material has almost zero contribution to the complex part of dielectric function through the wavelength region between 300 and 1400, which means no light absorption. Additionally ϵ_1 changes smoothly in this interval, makes it reasonable, possible to determine constant permittivity for this interval under study.

Chapter 4

Results

The necessity of extending optical path length of light inside the solar cells for efficient light absorption calls for a refined method other than the surface texturing commonly applied in both wafer based and thin film solar cells. One viable option is to utilize plasmonic scattering from metal nanoparticles placed on the front or back surface of the cell. Although plasmons in homogenous media are well understood [21] inhomogeneities caused by substrate interface or influences of other proximate metallic nanoparticles are not so well, yet those play important role in optical response which must be taken into account in order to interpret the experimental data more realistically. The aim of work in this chapter is to show how plasmonic resonances are affected by the various inhomogeneities including those originating from the substrate material, submerging behavior of nanoparticles into the substrate and influences of other neighboring particles, and provide insight into how we can positively manipulate these features for improved solar cell applications.

4.1 Ag nanospheres on different matrices

Interesting behaviours of Ag nano particles in inhomogeneous medium are examined. This is an important design parameter for solar cell applications. Nano

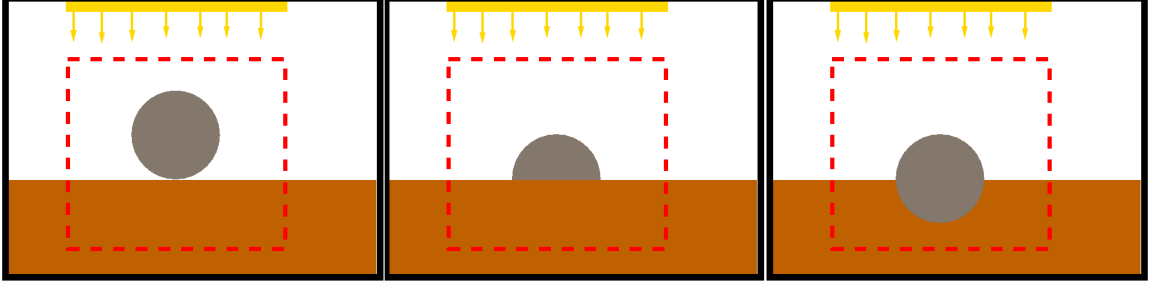


Figure 4.1: Cross sectional views of simulation systems a) Sphere on ITO b) Hemi-Sphere on ITO c) Sphere dipped in ITO

particles near or inside a semiconductor interface are studied using FDTD. Then FDTD results compared with experimental results.

In experiments, de-wetting technique is used to form silver nanoparticle islands [4]. Since the aim of work is to study and understand scattering characteristics of metal nanoparticles for solar cell applications; it is important to have more scattering compared to absorption. It has been shown that the average nanoparticle size should be at least 70 nm in diameter to fulfil this necessity [22]. For this purpose, Prof. Turan's Group at GÜNAM coated different substrates; Si, SiO₂, Si₃N₄ and ITO; with 12 nm thickness of Ag film and then annealed at 400 °C. Average nanoparticle sizes that are greater than 70 nm is reached, in all substrates, under these conditions. Sample pictures and results for scattering are shown in Figure 4.2.

To simulate silver nanoparticle, approximation to the experimentally available parameters of silver in terms of a Drude-Lorentz series as in the literature [16] are determined. Sample for calculation systems is shown in Figure 4.1 with the inset describing geometric boundaries and the imaginary surfaces to calculate the scattering cross section. A radius 30 – 60 – 90 nm spheres placed near the center of computational cells of sizes 600X600X600 nm³, 700X600X600 nm³ for sphere diameter of 180 nm. We determine Perfectly Matching Layers as the boundary conditions so 100 nm thick reflectionless region is set at the outermost region shown black. Then we choose an imaginary surface, a cube of size 350X350X350

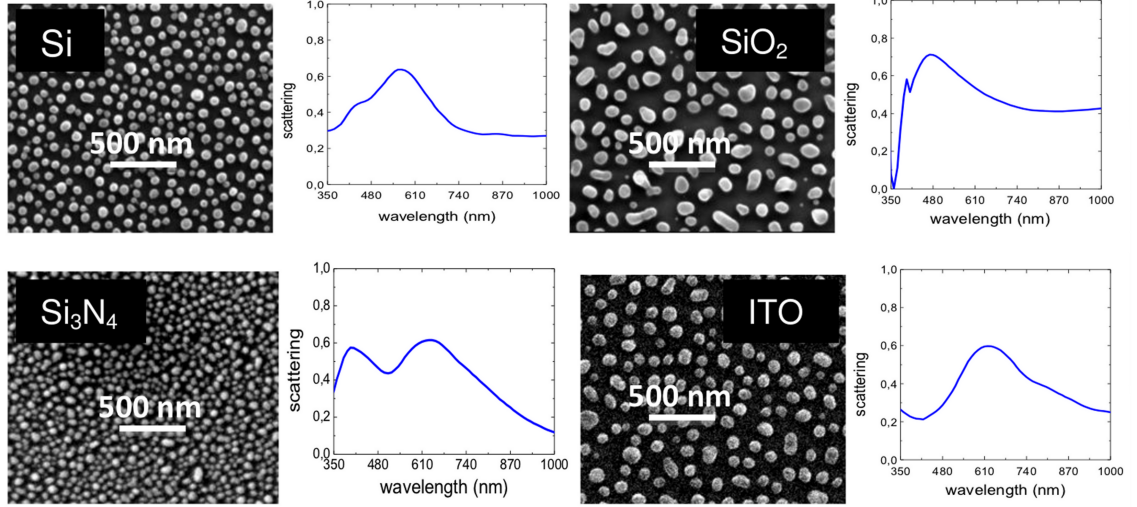


Figure 4.2: Silver islands on Si, SiO₂, Si₃N₄ and ITO. This figure is reproduced from Ref. [4].

nm^3 ($425 \times 350 \times 350 \text{ nm}^3$ for spheres with 180 nm diameter), shown as red line, to calculate the scattering cross section. Source is just at the edge of PML region and sends gaussian wave.

We calculate the ponyting vector at the surface of an imaginary box of $350 \times 350 \times 350 \text{ nm}^3$ before and after the scatterer exists in the system. After this two run, we find the scattering cross section and scattering cross section efficiency given by the ratio of scattering cross section and geometrical cross section of the sphere.

A typical simulation run for ITO matrice is shown in Figure 4.3. We see that the plasmonic scattering spectrum is greatly influenced by the contact area and geometry at the interface. Compared to the spheres in air case magnitudes of total scattering efficiencies decrease; but it is possible to red shift the dipole resonance wavelength by embedding nanoparticles on substrates.

Results obtained by a series of experiments on plasmonic metal nanoparticles are compared with theoretical results generated by FDTD method.

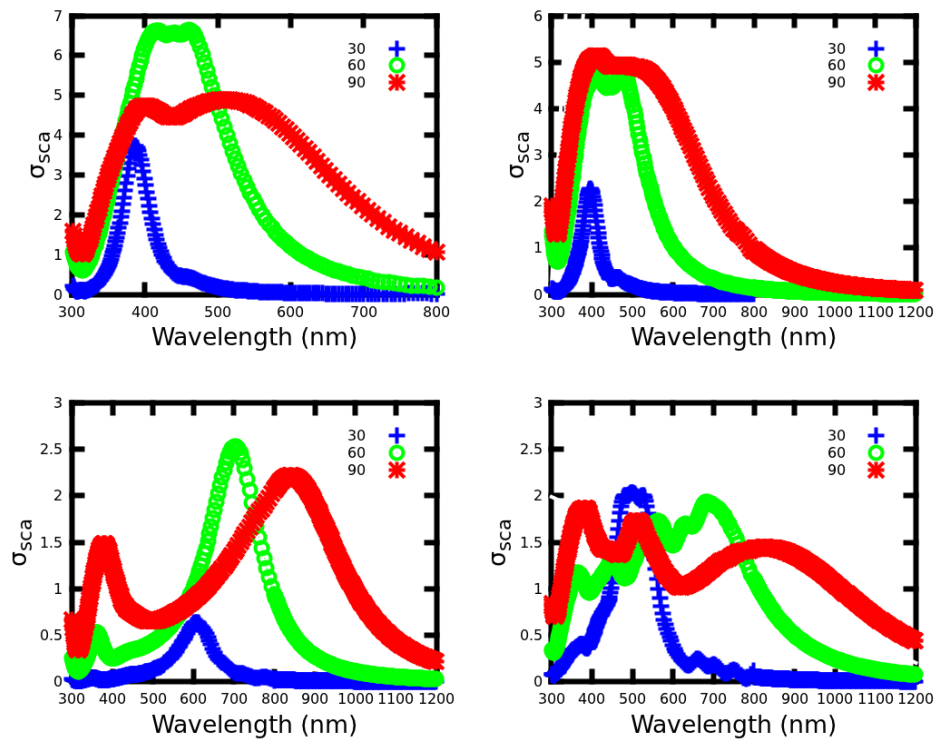


Figure 4.3: a) Spheres in Air. b) Spheres on ITO touching in one point. c) Hemi-Spheres on ITO. d) Spheres dipped in ITO

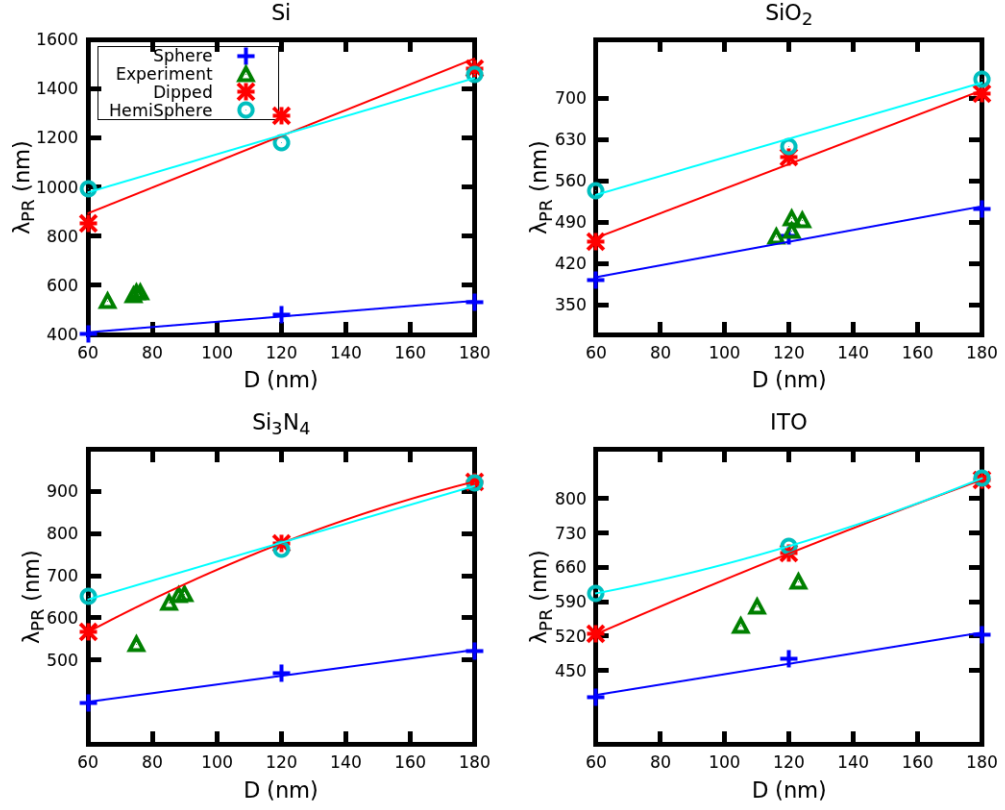


Figure 4.4: Comparison of plasmon resonance peak positions, λ_{PR} , between experiment (green triangles) and FDTD. Spheres with different diameters, D ; for various positions (blue cross—touching in one point, red star—sphere half dipped into substrate and magenta circle—hemisphere on substrate) on substrates a) Si b) SiO₂ c) Si₃N₄ d) ITO.

The comparison between experimental data and theoretical plasmon resonances, λ_{PR} , calculated for a series of realistic conditions is seen in Figure 4.4. The experimental data were obtained from the samples annealed at different temperatures. As seen from the results; plasmon peaks shift to red with increasing particle size as predicted by the theoretical calculations. In order to match the theoretical data to the experimental one, three different conditions are taken into the account: the Ag nanoparticle is a sphere touching the surface at one point, or a hemisphere with a large interacting interface with the substrate, or entirely dipped sphere into the substrate. It is observed that the theoretical results approach the experimental data reasonably well in all cases when all three configurations are considered. This is reflecting the inhomogeneous nature of the Ag particle formation by de-wetting. However, in the case of Si and SiO₂ substrates, there is a better agreement with one configuration only, indicating a more homogenous distribution. The SEM pictures are indeed showing a more uniform distribution for these two substrates.

Considering the effect of changing refractive index of underlying substrate, good relations is observed between FDTD and experimental results. As it is seen in Figure 4.16 increasing the dielectric constant of underlying substrate clearly shift the plasmon resonance to red region of the spectrum.

4.2 Effect of dielectric interlayer

Despite it is mentioned that the effect of dielectric interlayer between scattering objects and substrate material plays essential role [23], it is not adequately studied to understand the nature and role of the layer. In this section, systematic increase in the thickness of dielectric interlayer is considered as research of it's function. Spheres with different diameters, 35 nm and 120 nm, conducted to ensure experimental needs. SiO₂ is considered as a dielectric film for all simulations.

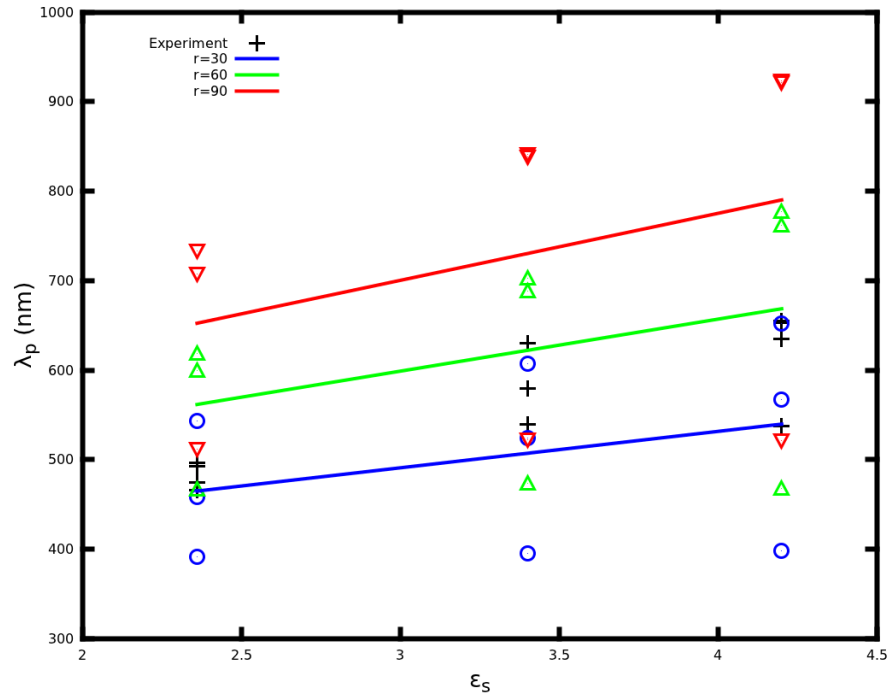


Figure 4.5: Comparison between FDTD and experiment. Plasmon resonance peak position, λ_p versus dielectric constant of substrate. Black cross experiment, spheres with radius, $r = 30$ nm shown in blue; $r = 60$ nm in green and $r = 90$ nm in red.

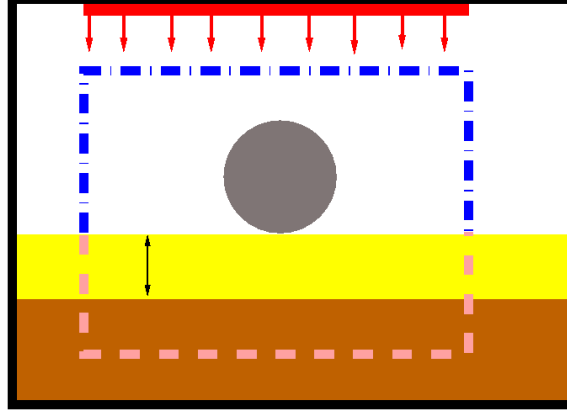


Figure 4.6: Cross sectional view of simulation system. Silver sphere stands on SiO_2 (yellow) both of them are on silicon (brown). Forward scattered fields are calculated on planes represented by dashed pink lines and the back scattered fields are calculated on planes represented by dashed and dotted blue lines. Simulation cell is surrounded by PML (black lines) in all directions. Sphere diameter is $r = 70$ nm.

4.2.1 70 nm Diameter

In Figure 4.6 cross sectional view of the simulation setup is shown. In order to deal with the most efficient system, back and forward scattered fields are determined separately for above (dashed and dotted blue line) and below the dielectric layer (dashed pink line). The thickness of dielectric layer (yellow color) increased gradually from 10 nm to 200 nm. The position of Silicon substrate (brown color) kept fixed and again PML introduced in all boundaries of the simulation cell.

Calculated forward scattering efficiencies for the range of wavelengths 300 – 700 is shown in Figure 4.7. As it is seen; resonances are observed at two different wavelengths closer to each other and the largeness of the scattering efficiency shifts between those two resonant wavelengths as the thickness of the dielectric layer increases.

The back scattering efficiencies, in Figure 4.8, are observed in the same order in magnitude with that of forward scattering. Compared to forward scattering

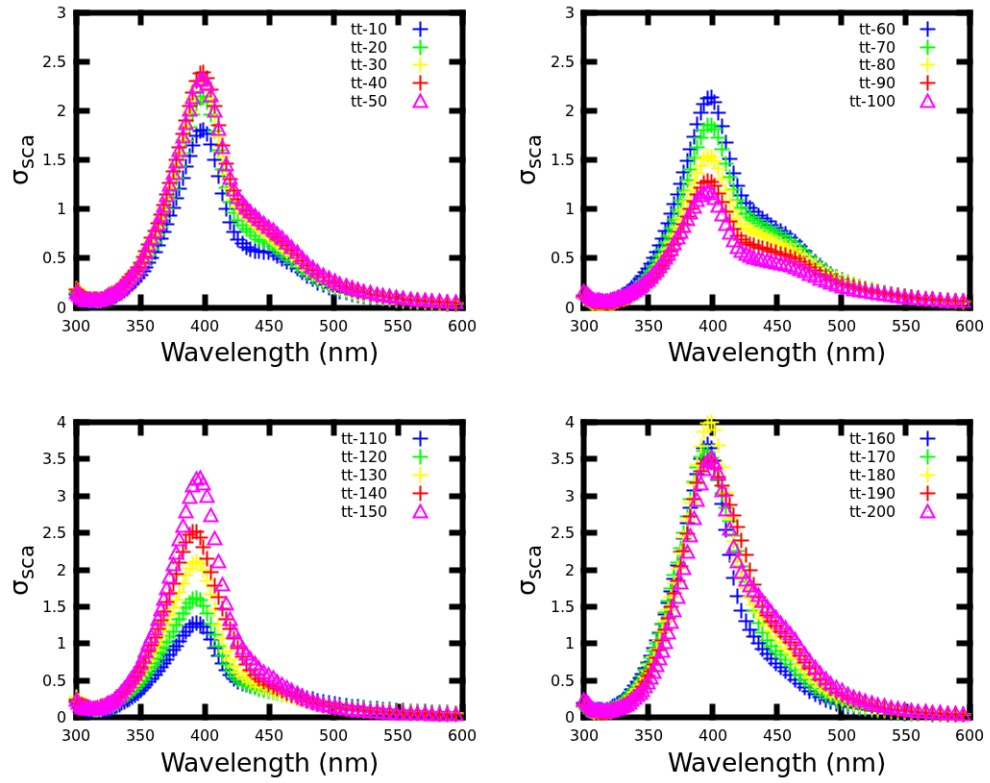


Figure 4.7: Forward scattering efficiencies for silver sphere with 70 nm diameter on SiO_2-Si substrate. Thickness of SiO_2 increased is gradually.

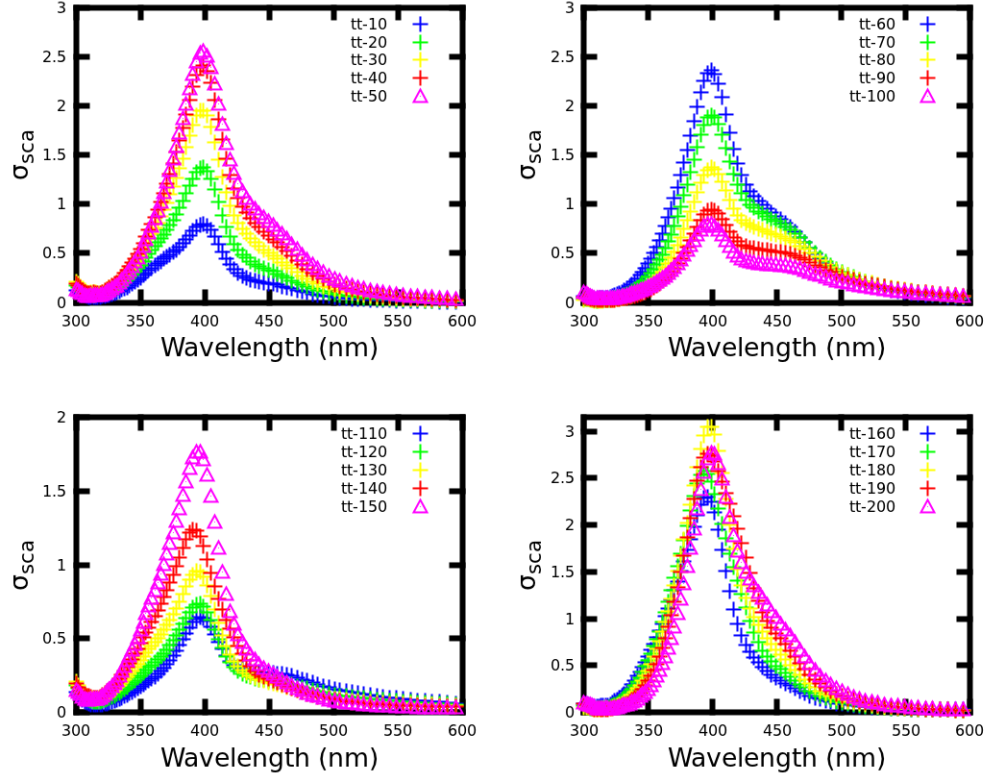


Figure 4.8: Back scattering efficiencies for silver sphere with 70 nm diameter on $SiO_2 - Si$ substrate. Thickness of SiO_2 is increased gradually. Sphere diameter is $r = 70$ nm.

efficiency, similar behaviour in the shift between wavelengths makes the total scattering efficiency twice the magnitude to that of back (or forward) scattering one.

In order to better see the the shift between resonances, σ_1 and σ_2 ; the ratio of magnitudes of scattering efficiencies is shown in Figure 4.10 for changing thickness of SiO_2 layer. Considering the importance of red-shifted resonance scatterings, both back and forth scattering cases have a peak of ratio $\frac{\sigma_2}{\sigma_1}$ observed around 80 nm thickness of SiO_2 layer.

However, considering the 80 nm thickness of SiO_2 layer, these peaks do not

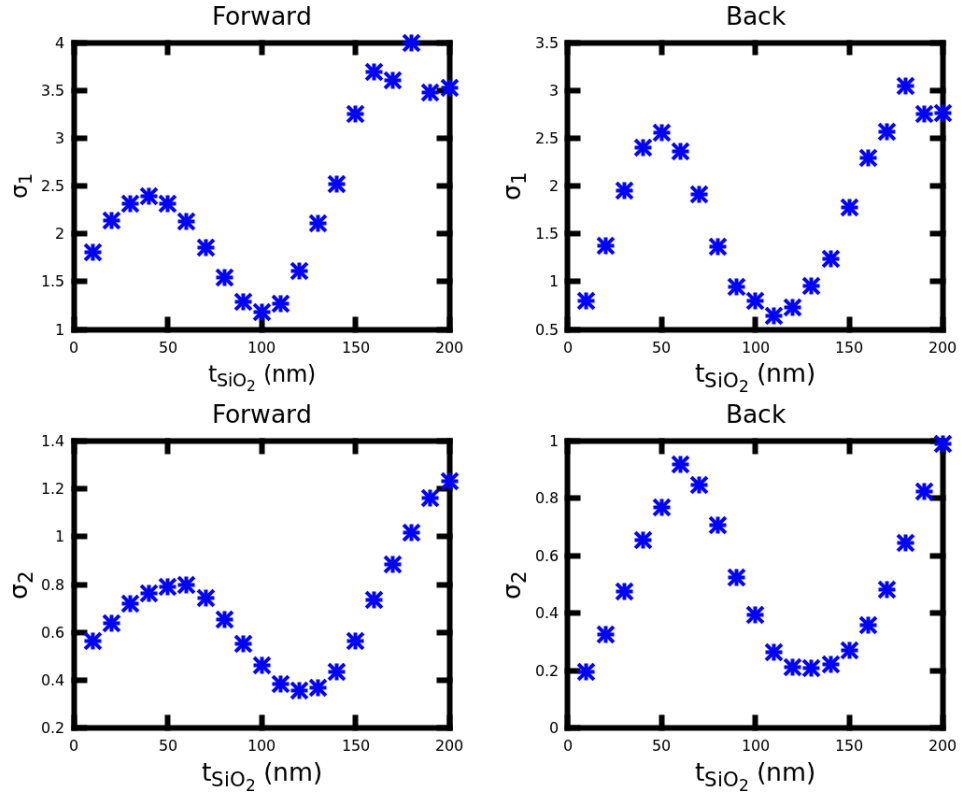


Figure 4.9: Magnitudes of resonance plasmon scattering efficiencies for different thicknesses of SiO_2 . σ_1 represents first plasmon peak (400 nm) and σ_2 represents second plasmon peak (450 nm). Results are shown for back and forward scatterings separately. Sphere diameter is $r = 70$ nm.

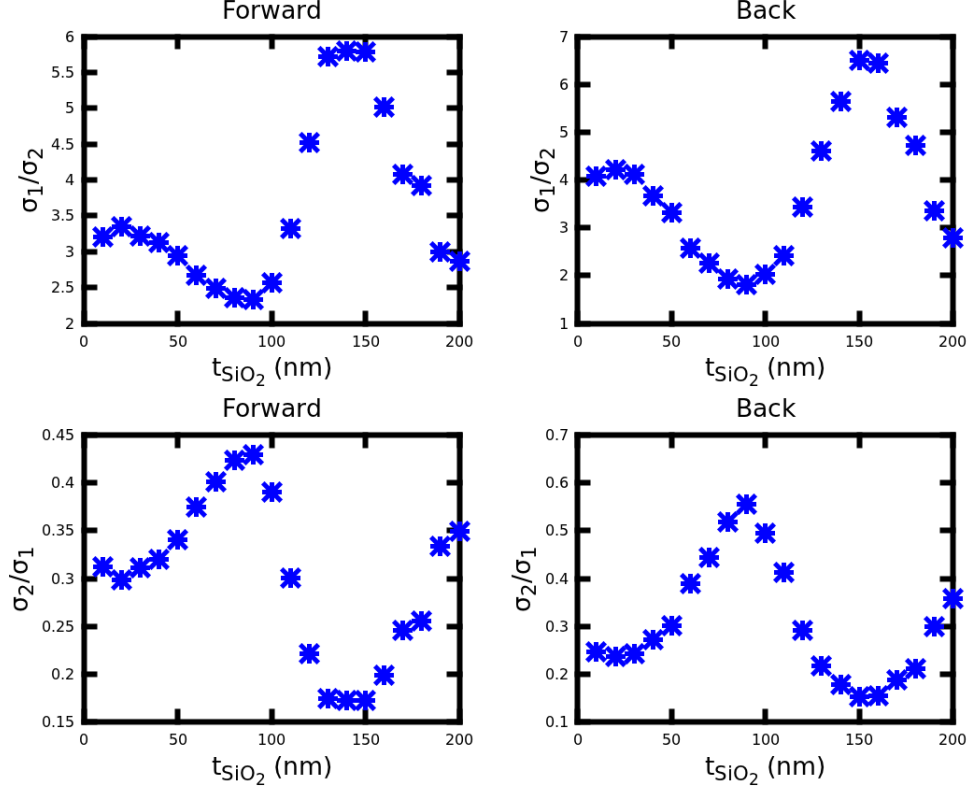


Figure 4.10: Ratios of magnitudes of plasmon resonant scattering efficiencies (σ_1 , σ_2) for different SiO_2 thicknesses. Back and forward scatterings are shown separately. Sphere diameter is $r = 70$ nm.

correspond to maximum scattering efficiencies, as seen in Figure 4.9. The maximums of both peaks, σ_1 and σ_2 , are observed around same wavelengths for both back and forward scattering conditions.

Finally the anomalous character of back and forward scattering situations is seen in different perspective in Figure 4.11. The value of total forward scattering to total back scattering decreases for increasing SiO_2 thickness. However, dip is observed around 120 nm thickness of SiO_2 layer.

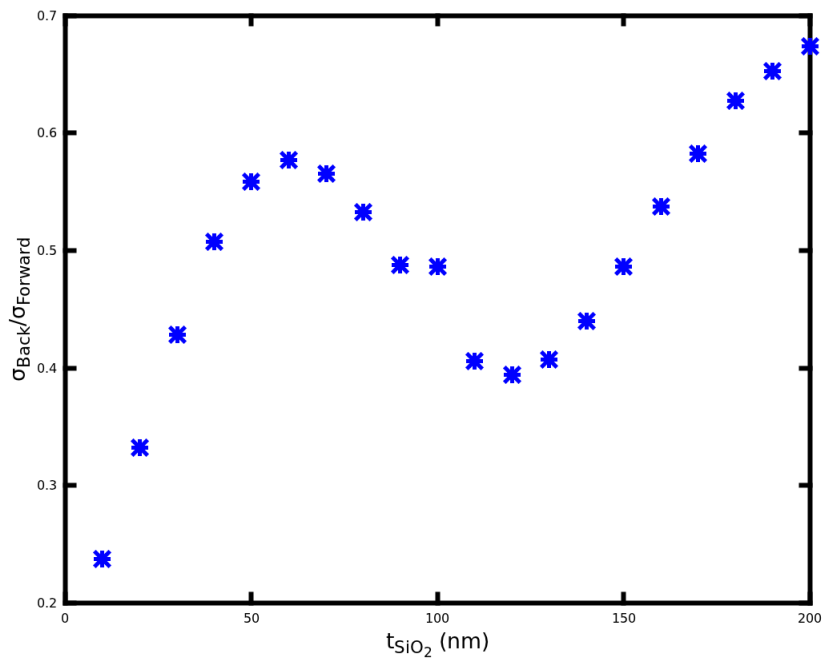


Figure 4.11: Ratio of total back scattering to total forward scattering for changing SiO_2 thickness. Sphere diameter is $r = 70$ nm.

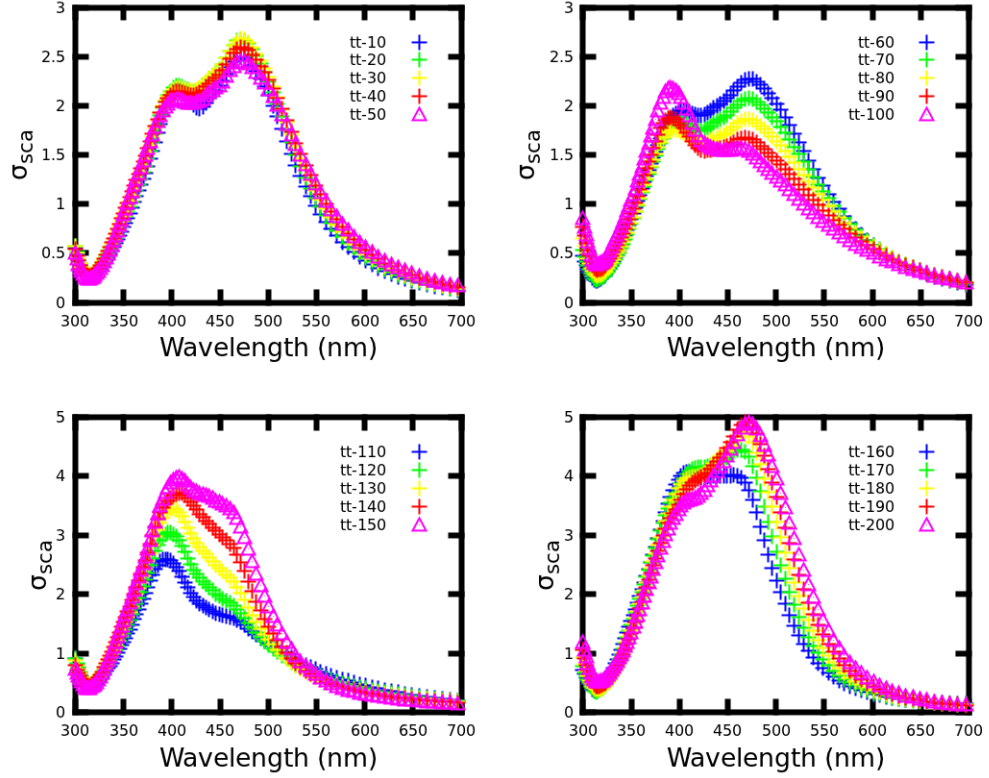


Figure 4.12: Forward scattering efficiencies for silver sphere with 120 nm diameter on $SiO_2 - Si$ substrate. Thickness of SiO_2 increased gradually.

4.2.2 120 nm diameter

Simulations for a sphere with 120 nm diameter are conducted in same manner with that of 70 nm diameter. Compared to results for 70 nm sphere; scattering efficiencies for 120 nm sphere have broader peaks in wavelength and greater in magnitude. Considering the need of red light scattered into the substrate, spheres with 120 nm are more promising.

The main difference of 120 nm diameter sphere is observed in the second plasmon peak, σ_2 , as it is seen in Figure 4.13. Second plasmon peak is in the same order, even bigger, compared to the first one, σ_1 . Greatness of second

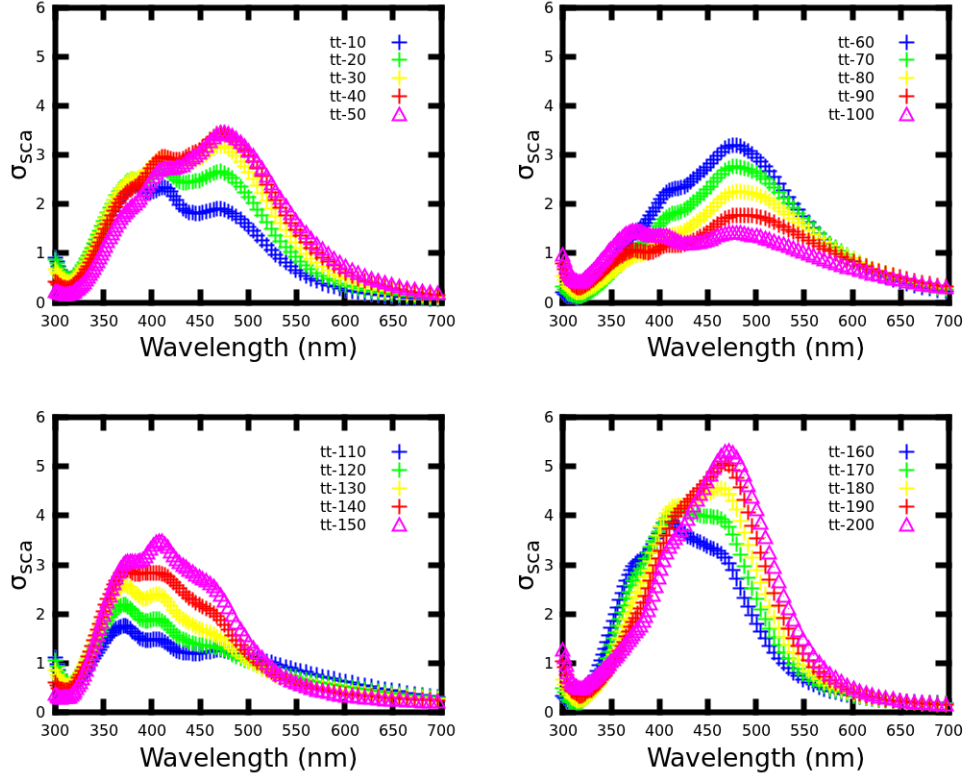


Figure 4.13: Back scattering efficiencies for silver sphere with 70 nm diameter on $SiO_2 - Si$ substrate. Thickness of SiO_2 increased gradually. Sphere diameter is $r = 120$ nm.

plasmon peak is due to the red shifted dipole resonance of bigger spheres. This feature is also very valuable considering the light with smaller wavelengths already absorbed and need of light absorption for higher wavelengths, red and infrared.

Comparing the ratio of magnitudes of σ_1 and σ_2 there is no large difference with respect to sphere with 70 nm diameter. However, maximum effective light scattering, $(\frac{\sigma_2}{\sigma_1})_{max}$, is reached for smaller thickness of SiO_2 layer. The ratio of total back scattering (σ_{back}) to total forward scattering efficiency ($\sigma_{forward}$) has similar behaviour as in the case for smaller diameter. This time however, the maximum of ratio $(\frac{\sigma_{back}}{\sigma_{forward}})_{max}$, is observed to be at smaller value of SiO_2 , around 40 nm thickness of SiO_2 .

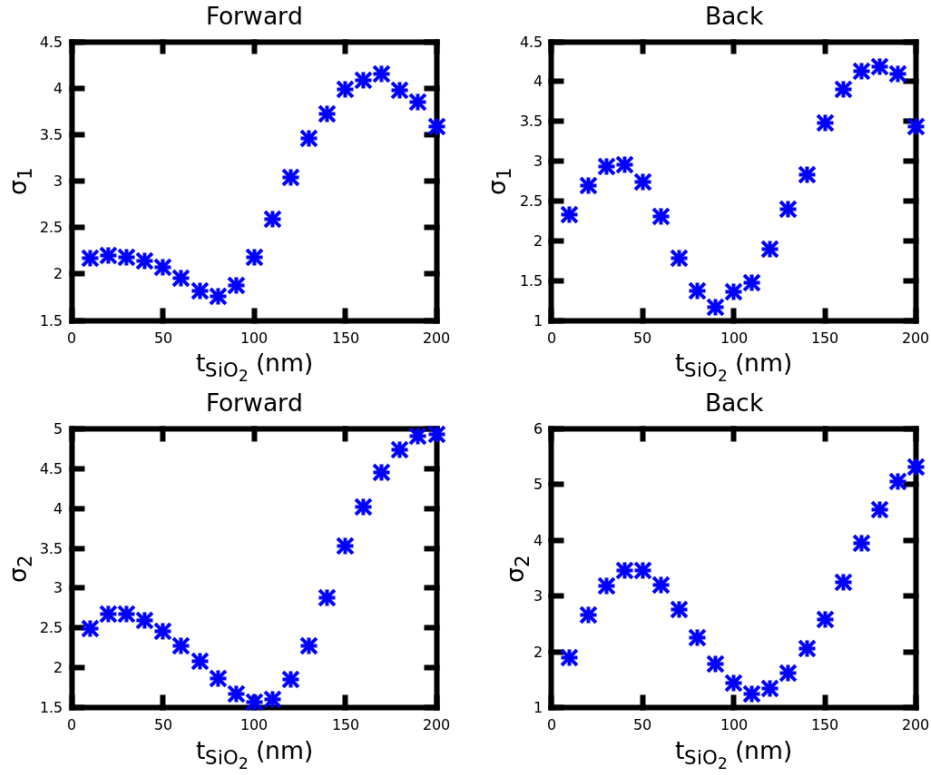


Figure 4.14: Magnitudes of resonance plasmon scattering efficiencies for different thicknesses of SiO_2 . σ_1 represents first plasmon peak (400 nm) and σ_2 represents second plasmon peak (450 nm). Results are shown back and forward scatterings separately. Sphere diameter is $r = 120$ nm.

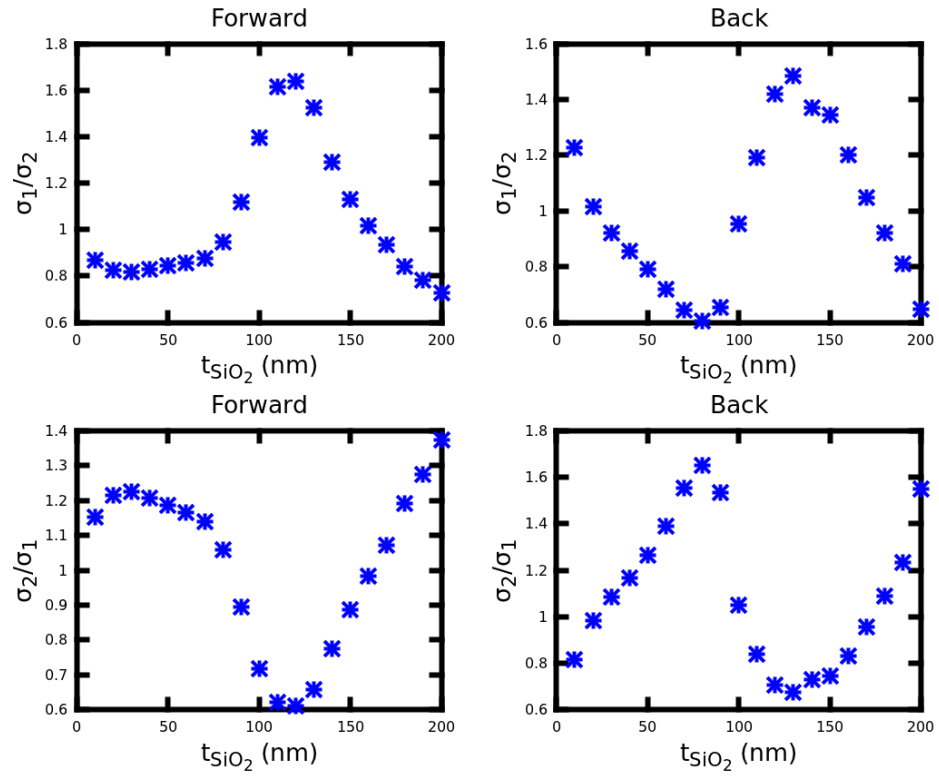


Figure 4.15: Ratios of magnitudes of plasmon resonant scattering efficiencies (σ_1 , σ_2) for different SiO_2 thicknesses. Back and forward scatterings shown separately. Sphere diameter is $r = 120$ nm.

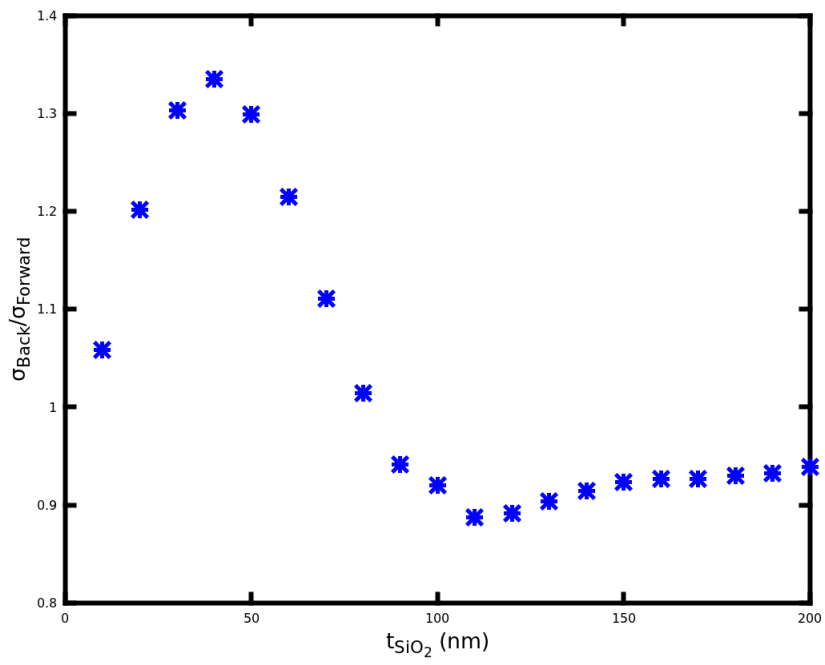


Figure 4.16: Ratio of total back scattering to total forward scattering for changing SiO_2 thickness. Sphere diameter is $r = 120$ nm.

Chapter 5

Conclusion

In this thesis, plasmonic scattering behaviours of several structures are worked, which are also possible experimental applications. First basic functions of solar cell have been introduced, the need of development and brief information about plasmonic applications to solar cell structures have been mentioned. Then basics of methods related to electromagnetic theory is shown which are needed to be known for numerical computations. Then fundamental examples of light scattering, reflection, transmission and absorption from particles in various media have been given. Examples compared with their counterparts in literature, give valuable aggrement in working of FDTD code.

In the following chapter, effects of inhomogeneous media on plasmonic scattering behaviours of nanoparticles and interactions with substrate have been introduced. Comments on the locations and shapes of nanoparticles which were uncertain in experiments have been given. Effects of nanoparticle size and permittivity of underlying medium to plasmonic scattering have also been shown.

Later it has been shown that; despite the need of dielectric underlayer to increase red light scattered into the substrate. Thickness plays important role in various considerations. It has been observed that the thickness of dielectric layer between silver island and substrate plays essential role increasing the forward scattering compared to that of back scattering.

Computational research on plasmonic scattering behaviours of nanoparticles in this thesis led to submission of one journal paper and preparation of additional three journal papers.

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