II
Theory Of Surface Plasmon Resonance (SPR)

II.1 Maxwell equations and dielectric constant of metals

Surface Plasmons Polaritons (SPP) exist at the interface of a dielectric and a metal whose electrons behave like those of a quasi-free electron gas [Kittel96]. SPP are collective longitudinal oscillations of charges which are produced by an external excitation and can be represented as quasiparticles with integer spin, described by the Bose-Einstein statistics[Brennan99]. Quantum Mechanics could be the best tool to describe this phenomenon, but is possible to find a simpler and appropriate description using electrodynamics [Raether77]. The interaction of metals with electromagnetic fields can be described using Maxwell's Equations.
The Maxwell's equations in the matter are [Hecht06]

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \qquad \nabla \cdot \mathbf{D} = \rho_f \tag{1}$$

$$\nabla \times \mathbf{B} = 0 \qquad \nabla \cdot \mathbf{H} = \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t}, \tag{2}$$

where ρ_f is the external charge density and $\mathbf{J}_f$ is the external current density. The constitutive relations for linear, isotropic and nonmagnetic media are defined by [Maier07]

$$\mathbf{D} = \varepsilon_0 \varepsilon \mathbf{E} \tag{3}$$

$$\mathbf{B} = \mu_0 \mu \mathbf{H}, \tag{4}$$

where ε_0 and μ_0 are the electric permittivity and the magnetic permeability of vacuum, ε is the dielectric function of the medium and μ is its the relative permeability. Considering a nonmagnetic ($\mu = 1$) isotropic medium in the absence external stimuli ($\rho_f = 0$, $\mathbf{J} = 0$) it is easy to manipulate the Maxwell's equations to obtain the following generalized wave equation:

$$\mu_0 \frac{\partial^2 \mathbf{D}}{\partial t^2} = \nabla^2 \mathbf{E} \tag{5}$$

The wave equation (5) can be solved only if we know the exact relation existing between the displacement vector $\mathbf{D}$ and the electric field $\mathbf{E}$, that is if we know the behavior with frequency of the dielectric function $\varepsilon(\omega)$ of the material under study. The optical properties of metals can be described by a complex dielectric function. These properties are determined by both the conduction electrons, moving freely within the bulk of material, and the electrons bound to the nucleus which contribute to the dielectric function because of interband excitations [Hecht06].

Inside a material, the presence of an electric field leads to a displacement $\mathbf{r}$ of the electrons which is associated with a dipole moment $\mathbf{p}$. The cumulative effect of all individual dipole moments of all electrons results in a macroscopic polarization per unit volume $\mathbf{P}$ [Hecht06]. The macroscopic polarization is defined as

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}. \tag{6}$$

Using the constitutive relations it is possible to find the relation between the polarization field and the electric fields, that is

$$\mathbf{P}(\omega) = \varepsilon_0 \chi(\omega) \mathbf{E}(\omega). \tag{7}$$

The contribution of electrons to the dielectric function can be obtained using two models. The first phenomenological description of the induced polarization in metals is known as the Drude model[Jackson99], which gives quite accurate results for the optical properties of metals up to the infrared regime (some μm in wavelength of the electromagnetic radiation). The Drude model assumes that the free electrons of the plasma sea of metals are thermalized and interacting one with each other only by elastic collisions. The interactions between the electrons and ions are considered introducing an effective electron mass m_e. The equation describing the interaction between the electrons and an external harmonic electric field ($\mathbf{E} = \mathbf{E}_0 \exp(-i\omega t)$) is the following

$$m_e \ddot{\mathbf{r}} + m_e \gamma \dot{\mathbf{r}} = -e \mathbf{E}_0 \exp(-i\omega t), \tag{8}$$

where $\mathbf{r}$ is the displacement of the electrons and the damping term γ accounts for the dissipative effects in the system, representing the collision frequency of the electrons. This parameter is proportional to v_f/l, where v_F is the Fermi velocity and l is the electron mean free path between scattering events [Hecht06]. Considering $\mathbf{r} = \mathbf{r}_0 \exp(-i\omega t)$ from equation (8) we obtain the following expression for the dielectric function:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}. \tag{9}$$

The parameter $\omega_p = ne^2/\varepsilon_0 m$ is the so called plasma frequency, n is the density of free electrons and γ depends on the conductivity σ of the metal through the relation $\gamma = ne/m_e\sigma$. If $\omega/\gamma \gg 1$, that is when metals retain their metallic character, the dielectric function assumes the form

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}. \tag{10}$$

When $\omega < \omega_p$, the dielectric constant becomes negative and the refractive index is a complex number, so that an electromagnetic wave can propagate inside the medium only up to a certain depth. If $\omega > \omega_p$, the dielectric constant is positive and the corresponding refractive index is a real quantity. In this regime of frequency the metal behaves like a dielectric material. Table II.1 lists the values of γ and ω_p for the metals generally used to support the plasma wave.

Metal	$\omega_\mathbf{p}$ $(10^{15}s^{-1})$	$\gamma \times 10^{12}s^{-1}$	λ_p (nm)
Gold	13.716	6.46	137.4
Silver	13.697	4.353	137.6
Aluminium	22.43	19.79	84.4
Platinun	7.816	16.73	241.1
copper	12.026	8.34	156.7

Table II.1: Plasma frequency (ω_o) and damping term (γ) for the most common metals used to support the plasma wave [Ordal95]

In figure II.1 is shown the comparison between the dielectric function of gold using the Drude model and the experimental values obtained by Johnson [Johnson72].

While the measured imaginary part of the dielectric function increases for energies higher than 1.9 eV (λ = 653 nm), the Drude model predicts a continuous decrease with energy. The experimental increase of $\varepsilon(\omega)$ with frequency is to be attributed to interband transitions in metals (d-band contribution), and can be described theoretically using the so called model of Lorentz [Trugler11][Serne01], where the electrons are assumed to be bound

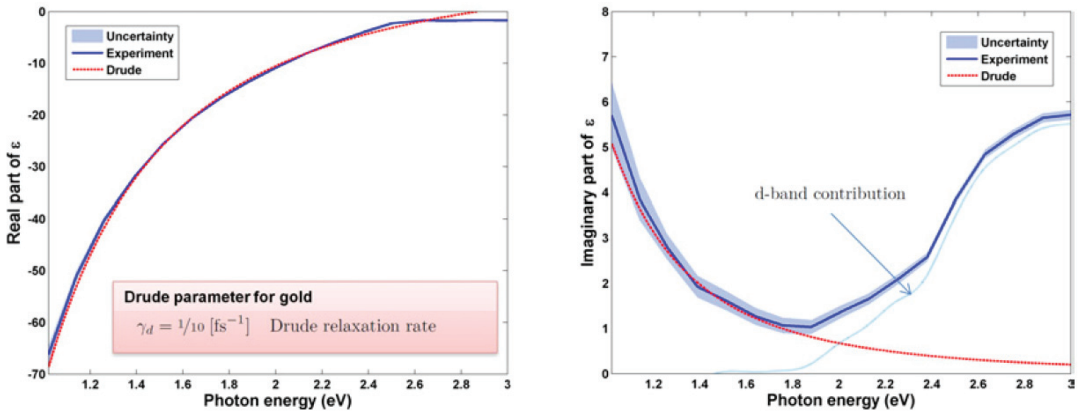

Figure II.1: Comparison between the theoretical values of $\varepsilon(\omega)$ of gold using the Drude model and the experimental datas obtained by Johnson. The damping term is 1/30 fs, the plasma frequency is $\omega_p = 45 \times 10^{14}$Hz [Trugler11]

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to the nucleus with forces obeying Hook's law. The interaction between the electrons and the nucleus is taken in account by the introduction of a resonance frequency ω_0,and the motion equation for the electrons becomes

$$m_e\ddot{\mathbf{r}} + m_e\gamma\dot{\mathbf{r}} + m_e\omega_0^2\mathbf{r} = \mathbf{E}_0 \exp(-i\omega t). \tag{11}$$

Solving equation (11) and considering that in a material may exist different types of oscillators [Marder00], we got the following expression for the contribution of bound electrons to the metal dielectric function:

$$\varepsilon(\omega) = \sum_i \frac{\omega_p^2}{(\omega_{0i}^2 - \omega^2) - i\gamma\omega}. \tag{12}$$

Indifferently from the model used to describe the response of electrons to an external electric field, we define the complex refractive index of a metal as $n'(\omega) = n(\omega) + i\kappa(\omega)$ with $n' = \sqrt{\varepsilon}$. This definition yields to the following relations between the real ε_R and the imaginary ε_{Im} parts of the dielectric function and the complex refractive index [Hecht06]:

$$n^2 = \frac{\varepsilon_R}{2} + \frac{1}{2}\sqrt{\varepsilon_R^2 + \varepsilon_{Im}^2}, \tag{13}$$

$$\kappa = \frac{\varepsilon_R}{2n}, \tag{14}$$

$$\varepsilon_R = n^2 - \kappa^2, \tag{15}$$

$$\varepsilon_{Im} = 2n\kappa. \tag{16}$$

In the complex dielectric function the real part is associated to the change in the phase velocity of the electromagnetic wave penetrating into the material, and the imaginary part is associated to power dissipation.

II.2 Electromagnetic waves at metal-dielectric interfaces

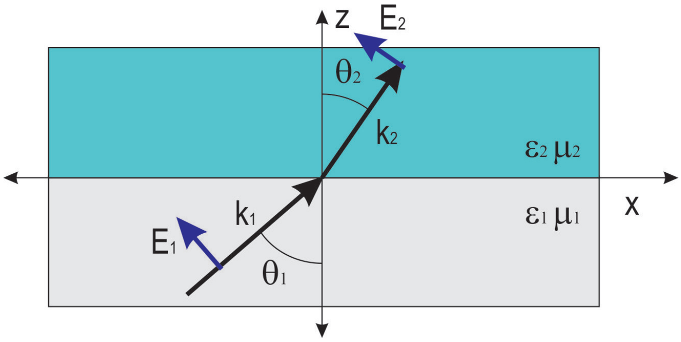

Figure II.2: Representation of the interface between two semi-infinite media. Note that the Electromagnetic field is considered TM polarized.

Now we want to find the condition that allows the existence of a surface electromagnetic wave propagating at the interface between two different media. We consider two semi-infinite media with complex dielectric functions ε_1 and ε_2 separated by a planar interface parallel to the X direction as is represented in figure II.2. Each of the electromagnetic fields must satisfy the Maxwell's equations and the boundary conditions for electromagnetic fields. It is necessary to consider two different possible states of polarization of the electromagnetic wave : transverse magnetic wave (TM) and transverse electric wave (TE), where the magnetic field or the electric field is respectively perpendicular to the plane of incidence.

(a) TM polarization

Since we are looking for traveling electromagnetic waves, a convenient way to express the fields in the two semi-infinite media is the following

$$\mathbf{E}_j = (E_{x,j}, 0, E_{z,j}) \exp\left(i(k_{x,j}x + k_{z,j}z) - i\omega t\right) \tag{17}$$

$$\mathbf{H}_j = (0, H_{y,j}, 0) \exp\left(i(k_{x,j}x + k_{z,j}z) - i\omega t\right), \tag{18}$$

where $j = 1, 2$.The following relations hold for the wavevector components as a consequence of the Maxwell's equations and boundary conditions:

$$k_x^2 + k_{z,j}^2 = \varepsilon_j k_0^2. \tag{19}$$

$$k_{x,1} = k_{x,2} = k_x = \beta \tag{20}$$

In (19) k_0 is the vacuum wave vector and β, called propagation constant, is the component of the wave vector parallel to the interface. Conceptually exist two types of travelling electromagnetic waves: nonradiative and radiative. If k_z is imaginary, the amplitude of the fields decreases exponentially perpendicularly to the interface, so that the wave does not transport any energy away from the boundary. Viceverse E_z has a oscillatory or radiative character if k_z is real [Raether77]. The boundary conditions of the electromagnetic fields want the component of **E** and **H** parallel to the interface and the component of **D** perpendicular to it to be continuous, that is $\mathbf{E}_{x,1} = \mathbf{E}_{x,2}$, $\mathbf{H}_{y,1} = \mathbf{H}_{y,2}$ and $\mathbf{D}_{z,1} = \mathbf{D}_{z,2}$. Using Maxwell's Equation (1) it is possible to demonstrate that

$$ik_{z,j}H_{y,j} = \omega D_{x,j} = \omega\varepsilon_0\varepsilon_j E_{x,j}. \tag{21}$$

Equation (21) together with the boundary conditions listed above lead to the equation

$$\frac{k_{z,2}}{\varepsilon_2} - \frac{k_{z,1}}{\varepsilon_1} = 0. \tag{22}$$

Substituting this condition in (19), we obtain the dispersion relation of the surface plasmon, that is

$$\beta = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}} = \beta' + i\beta''. \tag{23}$$

The expression for the normal component of the wavevector obtained replacing (23) in (19), and is written

$$k_{j,z} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_j^2}{\varepsilon_1+\varepsilon_2}}. \tag{24}$$

To obtain electromagnetic waves propagating along the interface, the normal components of the wavevector (24) have to be purely imaginary in both media, giving rise to exponentially decaying solutions [Hecht06]. It is easy to see that this condition is fulfilled only if $\varepsilon_1 < 0$ and $\varepsilon_2 > 0$ (or viceversa), that is only if one of the two media has a negative dielectric function. Materials with $\varepsilon_1 < 0$ are metals or semiconductor highly N doped. For most of the metals, $|\epsilon_{metal}| \gg |\varepsilon_{dielectric}|$, so that with a good approximation we can write that $\beta \geq k_0\sqrt{\varepsilon_{dielectric}}$. This relation demonstrates that the propagation constant of the surface plasmon is bigger than the wave vector of light inside the dielectric media.

The relations (23) and (24) are fundamental to understand the propagation length of the surface plasmon and the confinement of the electromagnetic fields in the two media. The confinement of the fields is related to the so called "skin depth", defined as the distance normal to the interface at which the amplitude of the evanescent field falls to $1/e$ [Homola06][Raether88]. The "skin depth" into the dielectric and metal media are respectively defined as

$$L_d = \frac{\lambda}{2\pi}\left(\frac{\varepsilon_m + \varepsilon_d}{\varepsilon_d^2}\right)^{1/2} \tag{25}$$

$$L_m = \frac{\lambda}{2\pi}\left(\frac{\varepsilon_m + \varepsilon_d}{\varepsilon_m^2}\right)^{1/2}, \tag{26}$$

while the propagation length along th interface can be defined as the length L_i after which the intensity decreases to l/e, and is given by [Raether88]

$$L_i = \frac{1}{2\beta''}. \tag{27}$$

Table II.2 shows the values of the "skin depth" and propagation length relative to SPP at different metal/air interfaces.

	Skin depth		Propagation
Metal	in metal (nm)	in air (nm)	length (μm)
Silver	24	216	19
Gold	29	162	3

Table II.2: Skin depth and propagation length of SPP in silver/air and gold/air at a wavelength of 630 nm

Figure II.3 represents an evanescent wave propagating at a metal/ dielectric interface.

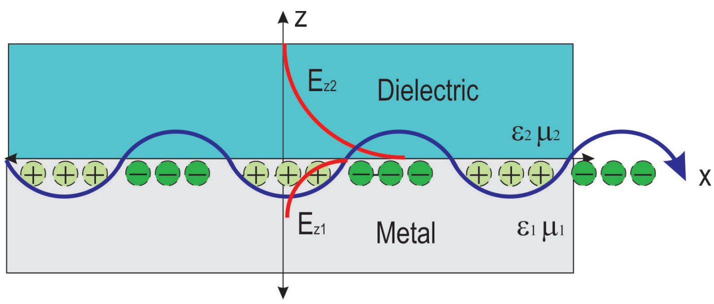

Figure II.3: Representation of the Surface Plasmon Polariton (SPP). The evanescent wave that propagates along the interface metal-dielectric interface.

(b) TE polarization

When the magnetic field is parallel to the incidence plane, the boundary conditions and Maxwell's equation lead to the relations

$$k_{z,1} + k_{z,2} = 0, \tag{28}$$

and

$$k_{x,1} = k_{x,2}, \tag{29}$$

which, together with(19), lead to the equation

$$k_1^2 = \left(\frac{\omega}{c}\right)^2 \varepsilon_1 = k_2^2 = \left(\frac{\omega}{c}\right)^2 \varepsilon_2. \tag{30}$$

It is easy to note that equation (30) has no solution, which means that surface electromagnetic waves do not exist for TE polarization [Palik98].

(c) Excitation of Surface Plasmons Polaritons (SPP)

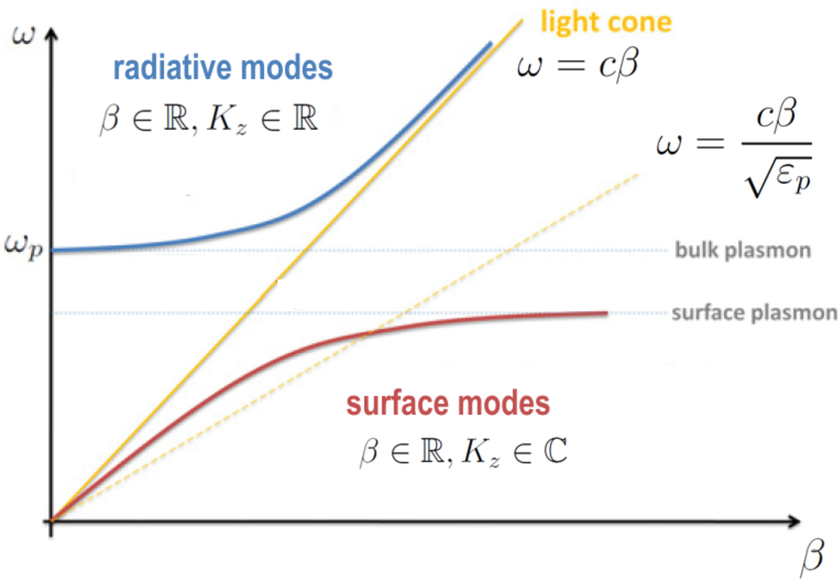

Figure II.4: Dispersion of plasma waves at an air-gold interface. The low energy modes are surface plasmons polaritons, the high energy modes are bulk propagating wave.

Figure II.4 shows in yellow the dispersion relations for photons in the free space and in the prism, while in red(blue) is shown the dispersion relation for the confined(radiative) plasma waves (23). Here the assumption of free electron gas for the metal has been taken for the real part of the dielectric function, and neglecting the damping, the imaginary part is zero . The dispersion relation shows two kind of modes, a high-energy (blue) and a low-energy mode (red). The high-energy , called the Brewster mode, does not describe surface waves, this is the radiation mode where k_z and k_x are real. The low-energy corresponds to a true interface wave, the surface plasmon polariton (SPP), with k_z imaginary and k_x real (see fig II.3).

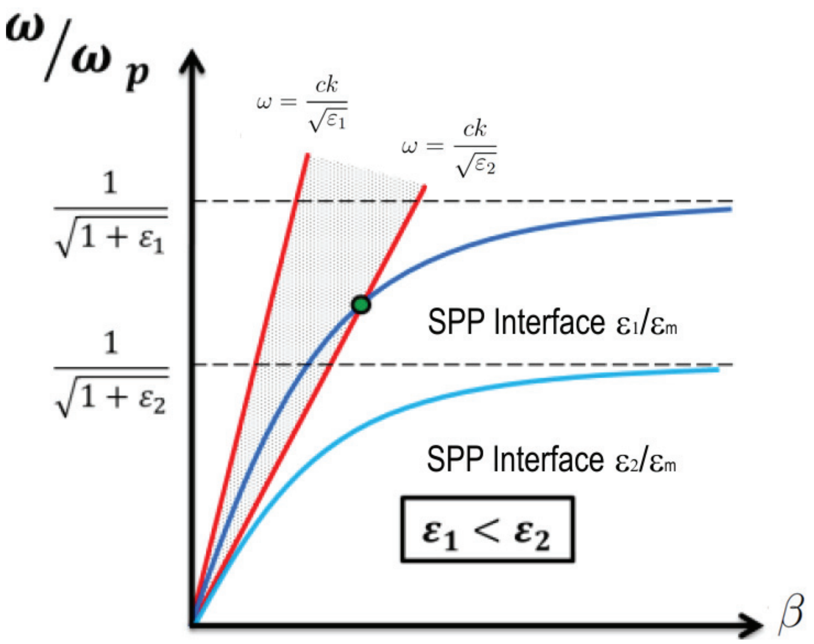

Figure II.5: Dispersion Relation for SPP in two different media.

Figure II.5 shows the dispersion relation for photon in free space (light curve) in two hypothetical media 1 and 2 and the SPP dispersion relation for interfaces between these media and a metal. There is no point where the SPP curve relative to one of the media and its light curve intersect. For a given frequency the wavevector β is always larger than the wavevector of light in free space. This means that Surface Plasmon Polaritons at the interface between a metal and dielectric media cannot be excited with light that is propagating in the same dielectric material.

Charged particle impact, optical grating coupling and prism coupling are the most common techniques used to excite the SPP [Maier07].

The first experimental schemes using an high index prism for SPP optical coupling were developed by Otto [Otto68], Raether and Kretschmann [Kret68]. In Kretschmann configuration a prism with refractive index $n_p > n_d$ (n_d is the refractive index of the dielectric at the external interface where we want to excite the SPP) is placed in contact with the metal-dielectric structure (see fig. II.6). An electromagnetic wave with TM polarization impinges on the base of the prism with an angle of incidence θ_{pt}. A variation in the angle of

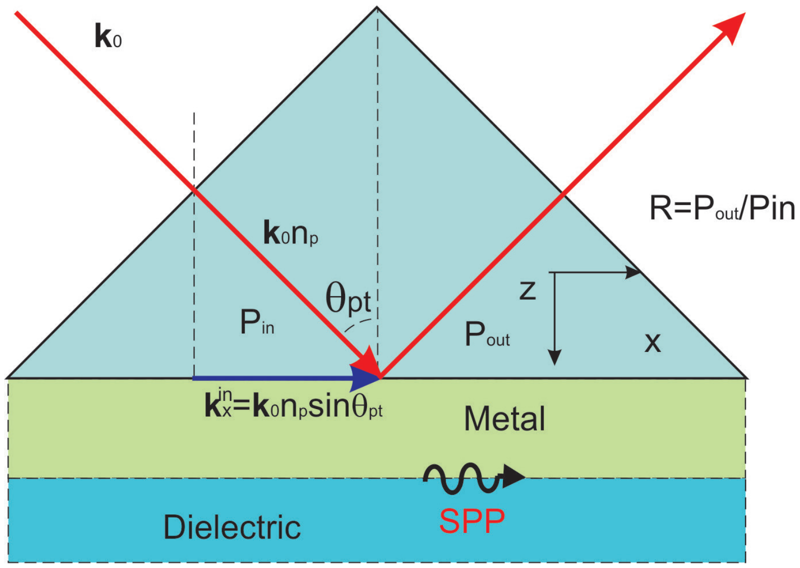

Figure II.6: Kretschmann configuration. $\mathbf{k}_0$ is the wavevector of the EM-field in air, $\mathbf{k}_{In_x}$ is the component of the wavevector of the EM-field in the prism parallel to the metal-dielectric interface, n_p is the refractive index of the prism, P_{Im} is the power of the EM-wave impinging on the base of the prism, P_{Out} is the power of the EM-wave reflected at the base prism, and R is the reflectivity of the structure.

incidence changes the component of the wavevector of electromagnetic wave parallel to the metal dielectric interface. At a certain angle of incidence, called angle of resonance, the photons in the prism couple to the SPP mode at the external metal-dielectric interface. Thin gold or silver films are often used as SPP supporting materials due to their low chemical reactivity and optical properties at visible wavelengths. The thin metal layer, approximately 50 nm thick, is usually deposited onto a glass slide and subsequently optically coupled to the prism by a high refractive index matching liquid. The wavevector of the electromagnetic radiation impinging on the base of the prism is given by

$$k_x^{In} = \frac{2\pi}{\lambda} n_p \sin\theta_{pt} \tag{31}$$

where λ is the wavelength of the incident electromagnetic wave and θ the angle of incidence. When this wavevector is equal to the propagation constant β of the SPP supported by the structure, the Surface Plasmon Resonance (SPR) condition is reached and the portion of light reflected by the structure is highly attenuated (Attenuated Total Reflection, ATR). The excitation of the SPP results in a dip in the curve of the reflectivity ($R = P_{out}/P_{in}$)of the structure versus the angle of incidence of the impinging beam.

It's important to observe that the use of the prism to couple light with SPPs introduces a perturbation to the simple model of two semi-infinite media, so that the value of the effective index of the surface plasmon mode is slightly different from the one of equation (23). To consider this situation, and also more complicated structures where various thin films of dielectric material are deposited onto the metal layer, is necessary to study the interaction between light and the multi layer system using a model that accounts for the multi reflections and interference of the electromagnetic radiation passing through the sample under analysis.

II.3 Reflectivity of multilayer planar systems

(a) Two layer system

Consider a system constituted by a single planar interface between two different homogeneous and isotropic media (1 and 2) in the absence of any charge or current. After a simple manipulation of the Maxwell´s equations (1), it is possible to demonstrate that the electromagnetic field satisfies the following wave equations [Pochi88]

$$\nabla^2\mathbf{E} - \mu\varepsilon\frac{\partial^2\mathbf{E}}{\partial t^2} = 0, \tag{32}$$
$$\nabla^2\mathbf{H} - \mu\varepsilon\frac{\partial^2\mathbf{H}}{\partial t^2} = 0. \tag{33}$$

These equations are the starting point to study the propagation of electromagnetic waves in any layered system. A general solution of these equations can be expressed as the superposition of forward and backward propagating plane waves of the form

$$\mathbf{E} = \begin{cases} \left(\mathbf{E}_1 e^{-i\mathbf{k}_1\cdot\mathbf{r}} + \mathbf{E}_1' e^{-i\mathbf{k}_1'\cdot\mathbf{r}}\right) e^{i\omega t}, & x > 0 \\ \left(\mathbf{E}_2 e^{-i\mathbf{k}_2\cdot\mathbf{r}} + \mathbf{E}_2' e^{-i\mathbf{k}_2'\cdot\mathbf{r}}\right) e^{i\omega t}, & x < 0 \end{cases} \tag{34}$$

where $\mathbf{E_1}$, $\mathbf{E_2}$, $\mathbf{E_1}'$ and $\mathbf{E}_2'$ are constant complex vectors. The system under study together with the model used to represent the electromagnetic fields are shown in figure II.7 where, for simplicity, only TM waves are considered.
Applying boundary conditions to the fields $\mathbf{E}_z$ and $\mathbf{H}_y$ at the interface between media 1 and 2 we obtain the equation

$$D_p(1)\begin{pmatrix} E_1 \\ E_1' \end{pmatrix} = D_p(2)\begin{pmatrix} E_1 \\ E_1' \end{pmatrix}, \tag{35}$$

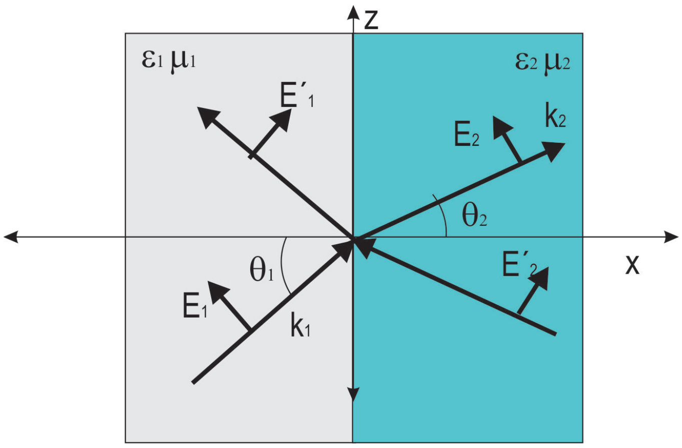

Figure II.7: Scheme of forwards and backwards propagating plane waves with TM polarization, used to model the reflection and transmission properties of a planar interface between two different media (1,2).

where $D_p(i)$ is called dynamical matrix of the TM-wave (or p-wave) of the medium i and is defined by

$$D_p(i) = \begin{pmatrix} \cos\theta_i & \cos\theta_i \\ \sqrt{\frac{\epsilon_i}{\mu_i}} & -\sqrt{\frac{\epsilon_i}{\mu_i}} \end{pmatrix}. \tag{36}$$

If the light is incident from medium 1, the reflection coefficient of a TM-wave in the case of a single interface is defined as

$$r_p = \left(\frac{E'_{1p}}{E_{1p}}\right)_{E'_{2p}=0}, \tag{37}$$

that is

$$r_p = \frac{n_1\cos\theta_2 - n_2\cos\theta_1}{n_1\cos\theta_2 + n_1\cos\theta_2}. \tag{38}$$

Equation (38) is known as Fresnel formula, and is valid for any two media, also absorbing media such as metals. This matrix formulation can be extended for the case of a general multilayer system with an arbitrary number of layers as described in [Pochi88]. Using this approach is so possible to find numerically the behavior of the reflectance $R = |r|^2$ as a function of the angle of incidence for any multilayer planar structure.

The reflectance of the multilayer structure fabricated during the work of this thesis has been computed using the free software *Winspall* 3.02, which has the further potentiality to fit the values of the thickness and index of refraction of each single layer of the structure by minimizing χ^2 (the difference between the experimental data and the simulation data) between the theoretical and the experimental curve of the reflectance in function of the angle of incidence on the first medium.

(b) Approximate analytical solution for a three layer system

In the case of a 3 layers system (i.e glass prism, metal with finite thickness, external infinite medium), the wave vector of the surface plasma wave suffers a perturbation Δk respect to the wave vector β (equation (23)) characteristic of two semi infinite media, and can be written as

$$\beta_r = \beta + \Delta k \tag{39}$$

The real part of Δk causes a displacement of the resonance position compared to Re(β), while its imaginary part is related with the presence of the prism and the finite thickness of the metal layer. This new term Δk can be approximated as the contribution of the intrinsic damping, which represents the joule loss in the metal, and the radiation damping which represents the energy lost by back-coupled radiation. For metals generally used in SPR experiments such as aluminum, gold or silver, it exists an analytic approximation of the SPR curve [Kret71][Pockrand78][Chen81] near the angle of resonance θ_{SPR} which is given by

$$R = 1 - \frac{4\,\mathrm{Im}(\beta)\,\mathrm{Im}(\Delta k)}{n_p^2 k_0^2 (\sin\theta - \sin\theta_{spr})^2 + \mathrm{Im}(\beta_r)^2}. \tag{40}$$

The minimum of R is reached when $\theta = \theta_{SPR}$ and can be expressed as

$$R_{min} = 1 - 4\frac{\frac{\mathrm{Im}(\beta)}{\mathrm{Im}(\Delta k)}}{\left(1 + \frac{\mathrm{Im}(\beta)}{\mathrm{Im}(\Delta k)}\right)^2}. \tag{41}$$

It´s easy to note that the value of the minimum is dictated by the ratio between the inner (Ohmic) and radiation damping and reaches 0 only when the 2 terms have the same value. This ratio depends on the thickness and dielectric function of the metal. Is possible to show that for wavelengths of electromagnetic waves in the visible range, and using noble metals such as gold or silver, the ratio of the losses terms reaches 1 when the thickness is approximately 50 nm. Further, it is possible to demonstrate that the full width half maximum (FWHM) of the curve of reflectivity is proportional to the imaginary part of the wave vector of the plasma wave, that is to the losses of the systems. Figure II.8 shows the

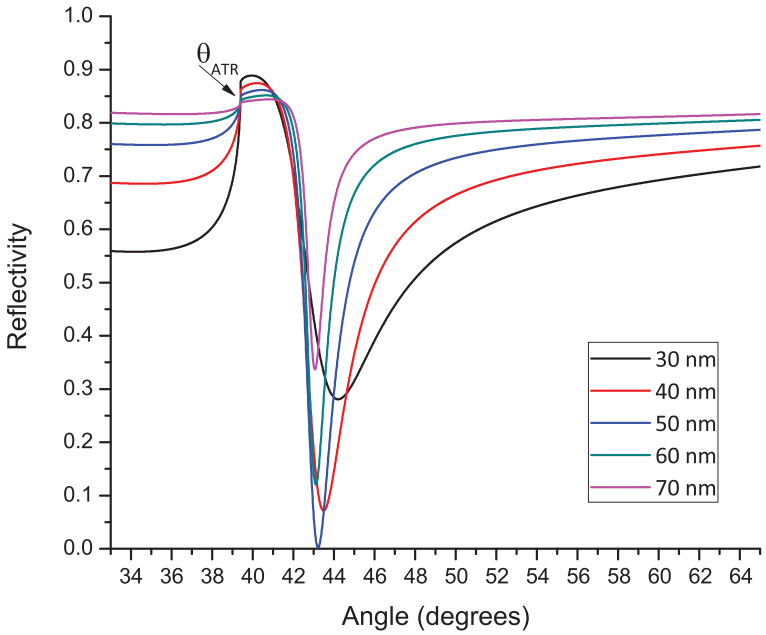

Figure II.8: SPR curve obtained using *Winspall* free software for gold films with different thickness at $\lambda = 632.8$ nm. The external medium is air and the prism is considered to be made of BK7.

dependence of the SPR curve in function of the angle of incidence for different thickness of a metal layer of gold, ranging from 30 nm to 70 nm. The calculus has been performed considering an impinging laser beam at the wavelength of 633 nm and considering an index of refraction of gold of $\varepsilon = -11.6 + i1.20$ [Johnson72]

(c) Four layer system: sensing applications

In a four-layered system (0-prism,1-metal,2-dielectric of finite thickness,3-external medium) it is impossible to obtain an approximate analytical form for the SPR curve. Nevertheless, if the dielectric coating is thin enough and it is not adsorbing, it is possible to link the thickness and the index of refraction of the dielectric coating to the angle of resonance of the system. If we define Δk_{min} as the shift in the wavevector of the plasma wave in the condition of resonance when the dielectric layer is deposited over the metal film, the following relation is valid [Peter96][Bruijn91][Pockrand78]

$$\Delta k_{min} \approx d_2 \left(\frac{2\pi}{\lambda}\right)^2 \frac{(\varepsilon_1\varepsilon_3)^{1/2}(\varepsilon_2\varepsilon_1 - \varepsilon_2\varepsilon_3 - \varepsilon_3\varepsilon_1 + \varepsilon_2^2)}{\varepsilon_2(\varepsilon_1^2 - \varepsilon_3^2)(\varepsilon_1 - \varepsilon_3)}, \tag{42}$$

where ε_1 is just the real part of the dielectric function of the metal. Equation (42) gives a set of possible solutions (ε_2, d_2) for the characteristics of the dielectric deposition. To determinate simultaneously the thickness and the index of refraction of this layer is so necessary to perform two independent measurements varying one of the following parameters:

1. The wavelength λ of the impinging radiation. This approach is called Two-Colors Method and requires the knowledge of the dispersion properties of the dielectric deposition[Peter96][Liang10].

2. The index of refraction of the external medium (air, water, other organic solvents)[Bruijn91][Damos05].

3. The metal used to support the surface plasma wave. Different metals can be deposited in different regions of the sample and subsequently the same dielectric layer can be deposited over them.

To our knowledge, the deposition of two different metals has never been used up to now to characterize a thin dielectric deposition. As described in chapter 4, this approach was used for the simultaneous determination of the thickness and index of refraction of a thin film of Alq_3 [Meyer05] deposited over gold and silver planar layers.

II.4 Alq_3

The metal-organic complex Tris(8-hydroxyquinolato)aluminum) (Alq_3) is a widely utilized component in organic electroluminescent devices. Alq_3 can act as a transport layer and fulfil part of the emission in an organic light emitting diode (OLED) because of its relatively good hole carriers mobility [Meyer05, Dalansinski04]. The molecular structure is given in figure II.9.

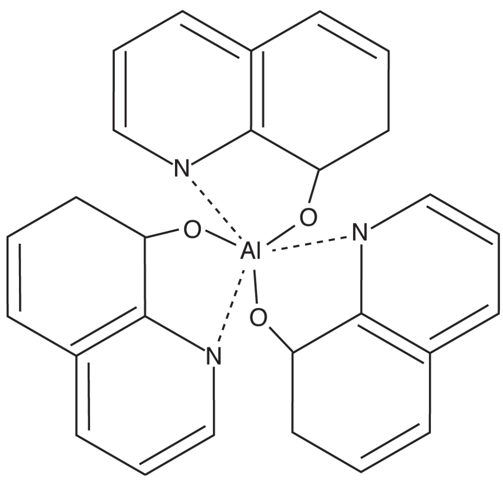

Figure II.9: Molecular structure of Alq_3.

One of the parameters to characterize the quality of an OLED is the external quantum efficiency η_{ext} [Hassan07], it is defined as the ratio of the number of photons emitted into the viewing direction to the number of every electron injected

$$\eta_{ext} = \frac{\eta_{in}}{2n^2} \qquad (43)$$

Where n is the refractive of the organic material, in our case Alq_3. η_{in} is the internal quantum efficiency, and corresponds to the total number photons emitted for every electron injected. Sometimes is defined the extraction efficiency $\eta_e = 1/2n^2$ and it specifies how much of the internal photon flux is transmitted out of the structure. Due the $\eta_{in} > \eta_{ext}$, it suggests that a lot of the light generated is lost within the material itself due to internal reflection and re adsorption leading to non radiative decay. As a result of measuring the refractive index the extraction efficiency of OLED can be encountered.