# Surface plasmon resonance (SPR) based sensing

Objectives:

• In this laboratory experiment students have to get familiar with the concepts of surface plasmon resonance and use the underlying principle to demonstrate the sensitivity of **SPR** to surface phenomena for sensing.

• Experimental and theoretical values of the physical quantity of the detected materials will be compared to find the experimental error and the sensitivity of the sensor.

1. Introduction

Long before scientists started to investigate the optical properties of metal nanostructures and surface plasmons, they were used by artists to generate artistic colours in glass artefacts and artwork, where the inclusion of gold nanoparticles of different size into the glass creates a multitude of colours. Famous examples are the Lycurgus cup (Roman empire, 4th century AD), which has a green color when observing it in reflecting light, while it shines in red in transmitting light conditions, and church window glasses.
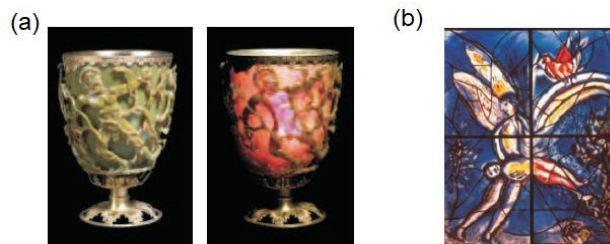
Figure 1. (a) Lycurgus cup. (b) colour windows made by Marc Chagall, St. Stephans Church in Mainz.

Today, the electromagnetic properties of metal–dielectric interfaces undergo a steadily increasing interest in science, dating back to the works of Gustav Mie (1908) [1] and others on small metal particles and flat surfaces. This is further motivated by the development of improved nano-fabrication techniques, such as electron beam lithography or ion beam milling, and by modern characterization techniques, such as near field microscopy.

Surface plasmon polariton (SPP) corresponds to a coherent oscillation of electrons at the interface between a metal and a dielectric medium. These are essentially electromagnetic waves that are trapped on the surface because of their interaction with the free electrons of the conductor (the term polaritons reflects this hybrid nature). In this interaction, the free electrons respond collectively by oscillating in resonance with the light wave. The first observation of SPPs was made by A. Otto in 1968 [2] and later the experimental setup was improved in 1971 by E. Kretschmann [3]. In the last few decades the properties of SPPs and its applications have been thoroughly studied giving birth to a research field called plasmonics. Today's applications of plasmonics include the utilization of metal nanostructures used as nanoantennas for optical probes in biology and chemistry, the implementation of sub-wavelength waveguides and they also allow to concentrate and channel light using subwavelength structures. This could lead to miniaturized photonic circuits with length scales much smaller than those currently achieved [4,5].

One of the most attractive aspects of SPPs is the ability to enhance the surface sensitivity of several spectroscopic measurements including Raman scattering, fluorescence, harmonic generations and so on. In their simplest form, reflectivity measurements can be used as sensors (bio-sensors) for chemical detection, monitor molecular adsorption (such as polymers, DNA or proteins) and become a very powerful tool for the study of interactions between different types of biomolecules (nucleic acids, receptors, peptides, proteins, antibodies, lipids). Moreover, SPP-based biosensors can also help to investigate different aspects of viral binding to functionalized surfaces and are also useful as anti-viral drug discovery tools. Many developments have been conducted for the design of commercial apparatus for these applications (Biacore followed by many others).

The manual begins with the basics of SPPs and their excitation mechanisms for sensing applications. The experimental setup and students' task are presented at the end.

2. *Theoretical background*

The interaction of metals with electromagnetic fields can be firmly understood in a classical framework based on Maxwell's equations [6]. Even metallic nanostructures down to sizes on the order of a few nanometres can be described without a need to resort to quantum mechanics, since the high density of free carriers results in minute spacings of the electron energy levels compared to thermal excitations of energy $k_B T$ at room temperature.

For frequencies up to the visible part of the spectrum, metals are highly reflective and do not allow electromagnetic waves to propagate through them. Metals are thus traditionally employed as cladding layers for the construction of waveguides and resonators for electromagnetic radiation at microwave and far-infrared frequencies. In the low-frequency regime, the perfect or good conductor approximation of infinite or fixed finite conductivity is valid for most purposes, since only a negligible fraction of the impinging electromagnetic waves penetrates into the metal. At higher frequencies towards the near-infrared and visible part of the spectrum, field penetration increases significantly, leading to increased dissipation, and prohibiting a simple size scaling of photonic devices that work well at low frequencies to this regime. Finally, at ultraviolet frequencies, metals acquire dielectric character and allow the propagation of electromagnetic waves, with varying degrees of attenuation, depending on the details of the electronic band structure. Alkali metals such as sodium have an almost free-electron-like response and thus exhibit an ultraviolet transparency. For noble metals such as gold or silver on the other hand, transitions between electronic bands lead to strong absorption in this regime. These dispersive properties can be described via a complex frequency dependent dielectric function $\varepsilon(\omega)$, which provides the basis of all phenomena discussed above.

A. OPTICS IN METALS

The interaction of metals with electro-magnetic fields can be completely described within the frame of classical Maxwell equations

$$
\begin{aligned}
\nabla \cdot \mathbf{D} &= \rho \\
\nabla \cdot \mathbf{B} &= 0 \\
\nabla \times \mathbf{E} &= -\partial \mathbf{B}/\partial t \\
\nabla \times \mathbf{H} &= \mathbf{J} + \partial \mathbf{D}/\partial t,
\end{aligned}
$$

which connects the macroscopic fields (dielectric displacement $\mathbf{D}$, electric field $\mathbf{E}$, magnetic field $\mathbf{H}$ and magnetic induction $\mathbf{B}$) with an external charge density ρ and current density $\mathbf{J}$.

In the limit of linear, isotropic and non-magnetic media, the constitutive relations read:

$$
\begin{aligned}
\mathbf{D} &= \epsilon_0 \epsilon \mathbf{E} \\
\mathbf{B} &= \mu_0 \mathbf{H}
\end{aligned}
$$

with a frequency dependent dielectric constant: $\varepsilon = \varepsilon(\omega)$, which is in general a complex function, $\varepsilon = \varepsilon' + i\varepsilon''$. It is furthermore connected to the complex index of refraction via $n + i\kappa = \sqrt{\varepsilon}$. Explicitly one can obtain the following expressions:

$$
\epsilon' = n^2 - \kappa^2, \qquad \epsilon'' = 2n\kappa,
$$
$$
n^2 = \frac{\epsilon'}{2} + \frac{1}{2}\sqrt{\epsilon'^2 + \epsilon''^2}, \qquad \kappa = \frac{\epsilon''}{2n}
$$

The real part of the refractive index $n(\omega)$ is responsible for dispersion, the imaginary part $\kappa(\omega)$ (extinction coefficient) determines absorption. Beer's law describes the exponential decay of the intensity I of a light beam (along the x-direction) in a medium: $I(x) = I_0\exp(-\alpha x)$, where $\alpha(\omega) = 2\kappa(\omega)\omega/c$ is the absorption coefficient.

B. BULK PLASMONS

The optical properties of metals can be described over a large frequency range using the Drude model, where an electron gas (effective electron mass m) of density N is assumed to freely propagate in a background of positively charged ions. These electrons will oscillate in the presence of an electromagnetic field $\mathbf{E}(t) = \mathbf{E}_0\exp(i\omega t)$ and are damped through collisions with a rate $\gamma = 1/\tau$ (typically $\tau = 10^{-14}$ s at room temperature). The equations of motion in the Drude model are thus:

$$
m\ddot{\mathbf{x}} + m\gamma\dot{\mathbf{x}} = -e\mathbf{E}(t)
$$

with the stationary solution

$$
\mathbf{x}(t) = \frac{e}{m(\omega^2 + i\gamma\omega)}\mathbf{E}(t)
$$

The electrons, which are displaced by $\mathbf{x}$ relative to the fixed ions, generate a polarisation $\mathbf{P} = -Ne\mathbf{x}$. It follows for the dielectric displacement and the dielectric constant:

$$\begin{aligned}
\mathbf{D} &= \epsilon_0\mathbf{E}+\mathbf{P}=\epsilon_0\epsilon\mathbf{E}\\
&= \epsilon_0\left(1-\frac{\omega_p^2}{\omega^2+i\gamma\omega}\right)\mathbf{E}\\
\Rightarrow \epsilon(\omega) &= 1-\frac{\omega_p^2}{\omega^2+i\gamma\omega}=1-\frac{\omega_p^2\tau^2}{\omega^2\tau^2+i\omega\tau},
\end{aligned}$$

where we introduced the plasmon frequency $\omega_p{}^2 = Ne^2/(\varepsilon_0 m)$.

At low frequencies the absorption coefficient becomes $\alpha = \sqrt{2\omega_p^2\omega\tau/c^2}$ and the penetration depth of the electromagnetic field, after Beer's law, becomes $\delta = 2/\alpha$ and it is called skin depth. However, at large frequencies, i.e. $\omega\,\tau \gg 1$, the damping term $i\omega\tau$ can be neglected and $\varepsilon(\omega)$ becomes approximately real:

$$\epsilon(\omega)=1-\frac{\omega_p^2}{\omega^2}$$

The dispersion relation of electro-magnetic fields can be determined from $\kappa^2 = \varepsilon\omega^2/c^2$.

$$\omega(k)=\sqrt{\omega_p^2+k^2/c^2}$$

As can be also seen in Figure 2, there is no propagation of electromagnetic waves below the plasmon frequency $\omega < \omega_p$. For $\omega > \omega_p$ waves propagate with a group velocity $v_g = d\omega/dk < c$. Of further interest is the special case $\omega = \omega_p$, where for low damping $\varepsilon(\omega_p) = 0$. One can show that here a collective longitudinal excitation mode ($k \,//\, E$) is formed (see Ref. [6]).
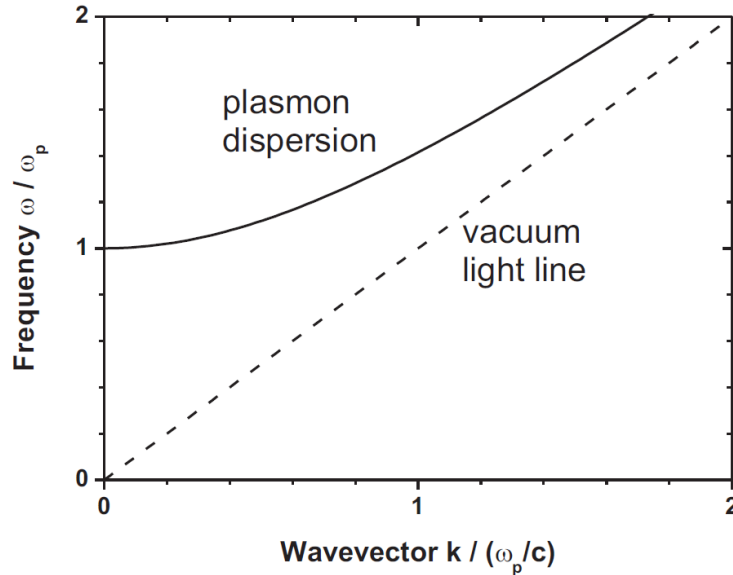

Figure 2. Dispersion relation of the free electron gas.

The physical interpretation is that there is a collective oscillation of the conduction electron gas with respect to the fixed background of positive ions. The quanta of this charge oscillation are called plasmons (or bulk plasmons, for better discrimination with surface plasmons in the later sections). As these are longitudinal waves, bulk plasmons cannot couple to transverse electromagnetic fields and thus cannot be excited from or strayed to direct radiation. In most metals,

the plasma frequency is in the ultra-violet regime, with energies within 5-15 eV, depending on the metal band structure.

C. SURFACE PLASMON POLARITONS

Surface plasmons polaritons (SPPs) are electromagnetic excitations that propagate along the interface between a metal and a dielectric medium. For the derivation of these excitation we again start with Maxwell's equations, which have to be separately solved for the metal and dielectric parts. Let us first start with a metal surface that extends infinitely in the xy-plane at $z = 0$ (see Fig. 3)
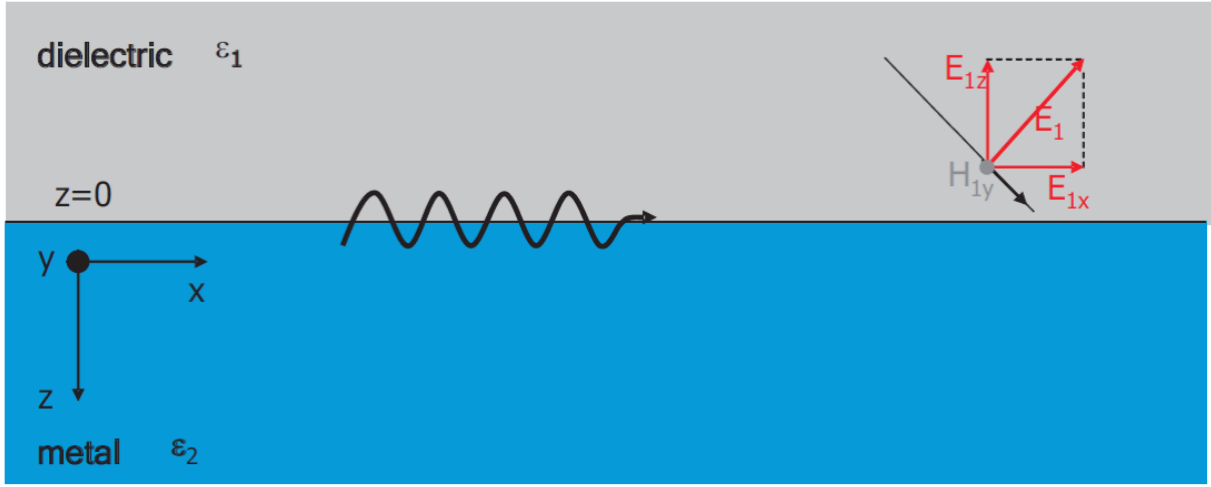
Figure 3. Interface along the xy-plane between a dielectric (top, index 1), and a metal (bottom, index 2).

The conditions for the continuity of the normal and transversal field components on this interface (see e.g. J.D. Jackson, "`Classical Electrodynamics"') are given by:

$$D_{1,z} = D_{2z}, \qquad B_{1,z} = B_{2,z}$$
$$E_{1,x/y} = E_{2x/y}, \qquad H_{1,x/y} = H_{2,x/y}$$

where the indices (1) and (2) indicate dielectric and metal, respectively. One can show (see Ref. 6) that under these conditions no transverse-electric (TE) modes can exist. Instead we directly start with an *ansatz* for a transverse-magnetic (TM) mode, which propagates along the x direction ($i = 1,2$):

$$\begin{aligned} \mathbf{E}_i &= (E_{i,x}, 0, E_{i,y})e^{i(\mathbf{k}_i \cdot \mathbf{r} - i\omega t)} \\ \mathbf{H}_i &= (0, H_{i,y}, 0)e^{i(\mathbf{k} \cdot \mathbf{r} - i\omega t)} \\ \mathbf{D}_i &= \epsilon_0 \epsilon_i \mathbf{E}_i, \qquad \mathbf{B}_i = \mu_0 \mathbf{H}_i \end{aligned}$$

The wave vector is given by $\mathbf{k}_i = (\beta, 0, k_{i,z})$, where $\beta = k_x$ indicates the propagation constant along x. Using this approach with the conditions of continuity from above and the Maxwell's equation in absence of charges and currents ($\rho = 0$, $\mathbf{J} = 0$), we obtain the following relations between the $k_{i,z}$ components:

$$\frac{k_{1,z}}{\epsilon_1} = \frac{k_{2,z}}{\epsilon_2}$$

We are looking for solutions that describe modes bound to the interface. Thus, the $k_{i,z}$ components have to be imaginary and of opposite sign:

$$k_{1,z} = +i\kappa_1$$

In this way, the fields decay exponentially into the respective half spaces: $E_i \propto \exp(\pm i k_{i,z}) = \exp(\pm k_{i,z})$, as also symbolized in Fig. 4. Comparing the above two relations, one can directly see that this is fulfilled only, if the dielectric constants of the two materials are of opposite sign (i.e. $\varepsilon_1 = -\varepsilon_2$). Surface plasmons can thus indeed only exist at the interface between a metal ($\varepsilon < 0$) and a dielectric medium ($\varepsilon > 0$).
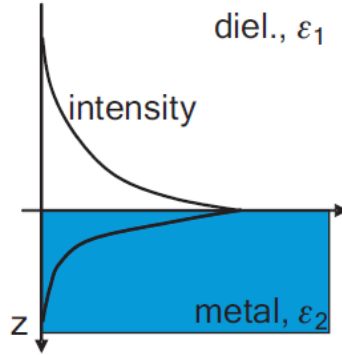
Figure 4. Evanescent field that decays exponentially into the two half spaces.

Altogether, one obtains a system that is composed of an electromagnetic wave in the dielectric medium and an oscillating electron plasma in the metal, where both modes have an exponentially decaying evanescent character (see Fig. 5 and Ref. 7).

Let us now derive the dispersion relations for surface plasmons. For the wave vector we get:
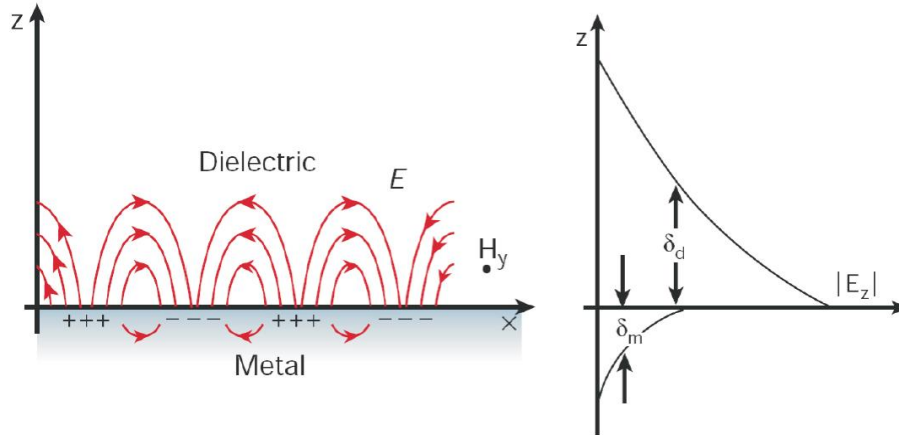
$$|\mathbf{k}_{1(2)}|^2 = \epsilon_{1(2)} k_0^2 = \beta^2 + k_{1(2),z}^2 = \beta^2 - \kappa_{1(2)}^2$$

here, $k_0 = \omega/c$ is the vacuum wave vector of light with frequency ω. Hence our previous relation

$$\frac{k_{1,z}}{\epsilon_1} = \frac{k_{2,z}}{\epsilon_2}$$

takes the form

$$\beta = \frac{\omega}{c} \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \tag{1}$$

Figure 5. Schematics to summarize the nature of SPPs. They are a coherent oscillation of electrons at the interface between a metal and a dielectric material. SPPs are transverse magnetic in character (H is in the y-direction), and the generation of surface charge requires an electric field normal to the surface (left). The combined character also leads to the field component perpendicular to the surface being enhanced near the surface and decaying exponentially with distance away from it. The field in this perpendicular direction is said to be evanescent, reflecting the bound, non-radiative nature of SPPs, and prevents power from propagating away from the surface. In the dielectric medium above the metal, typically air or glass, the decay length of the field, δd, is of the order of half the wavelength of light involved, whereas the decay length into the metal, δm, is determined by the skin depth (right).

Together with the information of the frequency dependence of $\varepsilon_{1(2)}(\omega)$, one can derive for the dispersion relation $\omega(k_{SPP})$. Under the assumption that $\varepsilon_1(\omega)$ in the dielectric is approximately constant and using the Drude approximation for ε_2, one obtains a dispersion relation as shown in Fig. 6.
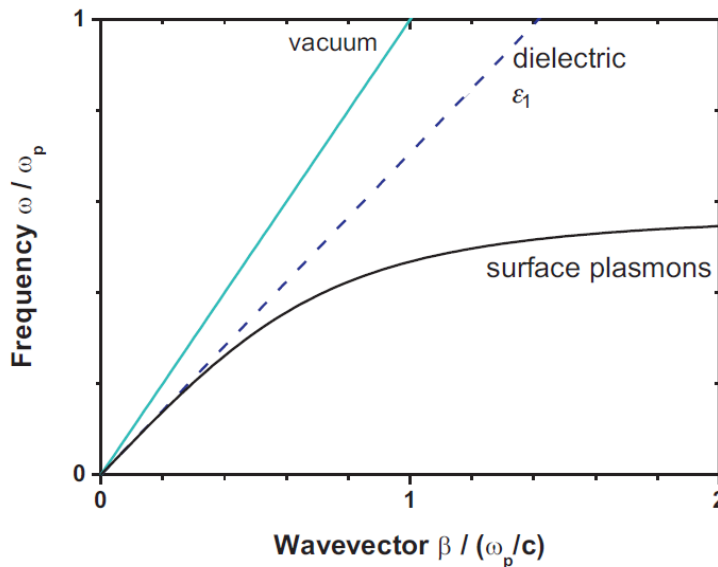
Figure 6. Dispersion relation of surface plasmons compared to light in vacuum and in the dielectric medium.

One realizes that the SPP dispersion relation completely resides below the light cones and thus SPPs cannot be excited by direct illumination, as energy and momentum conservation ($\omega_{light} = \omega_{SPP}$ and $k_{light} = k_{SPP}$) cannot be fulfilled at the same time. Instead, in order to excite SPPs, a momentum transfer has to be established. Techniques to achieve this will be discussed in the following.

3. *Experimental background*

A. COUPLING LIGHT TO SURFACE PLASMON POLARITONS AND SENSING

To couple light to the SPP mode energy and momentum conservation must be maintained. Therefore, the incoming beam has to match its momentum to that of the SPP. In the case of p-polarized light (polarization occurs parallel to the plane of incidence), there are three main techniques by which the missing momentum can be provided. The first makes use of prism coupling to enhance the momentum of the incident light. The second involves scattering from a topological defect on the surface, such as a subwavelength protrusion or hole, which provides a convenient way to generate SPPs locally. The third makes use of a periodic corrugation in the metal's surface. S-polarized light (polarization occurs perpendicular to the plane of incidence) cannot excite SPPs.

Otto and Kretschmann configurations are the two well-known simple methods to achieve coupling using a prism. In the Otto setup [2], light illuminates the wall of a prism and it undergoes total internal reflection. An air gap (or a spacer of low index) less than a few optical wavelengths thick) provides the tunnel barrier across which radiation couples, via the evanescent component of the totally reflected wave, to SPPs at the air (dielectric) metal interface (e.g. gold), as shown in Fig. 7(a). By varying the angle of incidence of p-polarized radiation at the prism/dielectric interface, one can vary the momentum in the *x*-direction and this allows for simple tuning through the coupling condition, called surface plasmon polariton resonance (SPR). The other alternative and simpler geometry was realized by Kretschmann [3]. Rather than using a dielectric spacer the metal itself could be used as the evanescence tunnel barrier provided it is thin enough to allow radiation to penetrate to the other side. All that is now needed is a prism with a thin coating of some suitable metal, as shown in Fig. 7(b).
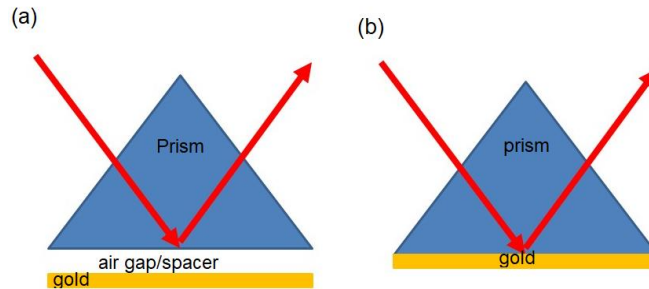

Figure 7. (a) Otto configuration. (b) Kretschmann configuration.

The sensing activity can be performed once efficient coupling is obtained. A schematic of a SPR-based sensor is depicted in Fig. 8. A glass prism is coated with a thin layer of a noble metal (or brought near to using Otto configuration) to create a biosensor surface. Antibody or another type of biomolecules (chemicals) immobilized on the sensor surface is also shown. At a particular angle (θ_o) the incoming wave couples to SPP. This special incidence angle is called SPR angle. At the SPR angle reflectivity hence drops to a minimum as shown in the figure (right). However, the

binding of biomolecules onto the sensor's surface affects the SPR condition: the refractive index of the dielectric component increases and shifts the SPR angle to another value (θ_1). The measurement of the SPR-angle shift offers an opportunity to measure molecular binding to the sensor's surface or other physical quantities (e.g. index of refraction) [8].
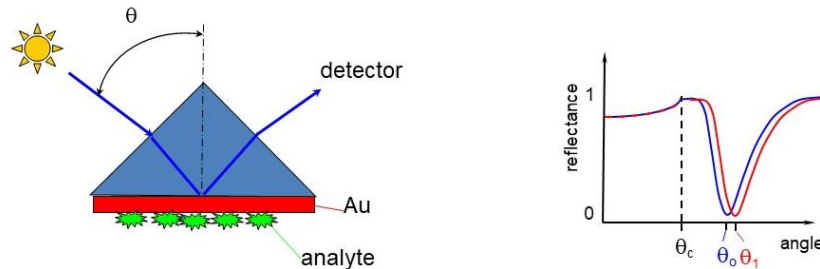
Figure 8. Schematics of a SPR-based sensor. The SPR-angle shift provides information about the efficiency of binding to the sensor's surface or directly measure the physical quantities under investigation.

B. EXPERIMENTAL SETUP FOR DETECTING SPR

The optical setup to measure the SPR of thin gold films (50 nm-thick) is depicted in Fig. 9 and it has the following elements:


Figure 9. Optical setup for directly measuring the plasmon extinction.

Light source: A He–Ne laser ($\lambda = 632.8$ nm) with 2 mW output power. The polarization of the laser can be manipulated by using a linear polarizer and a half-wave plate.

Prism and gold thin film: A high-index prism (index of refraction $n_p = 1.62$) is used to couple light to the SPP mode. Instead of depositing a thin film of gold on the prism, glass slides are already prepared and adapted on one side of the prism with an index matching liquid (index of refraction $n_L = 1.52$).

Manual rotation stage and light path: A manual rotation stage with an accuracy of $1°$ is used to measure the angle θ_{ext} as shown in Fig. 10. The prism is positioned on the stage so that the $180°$ angle corresponds to the laser beam being back reflected to the laser. This allows us to directly measure the angle marked θ_{ext}.
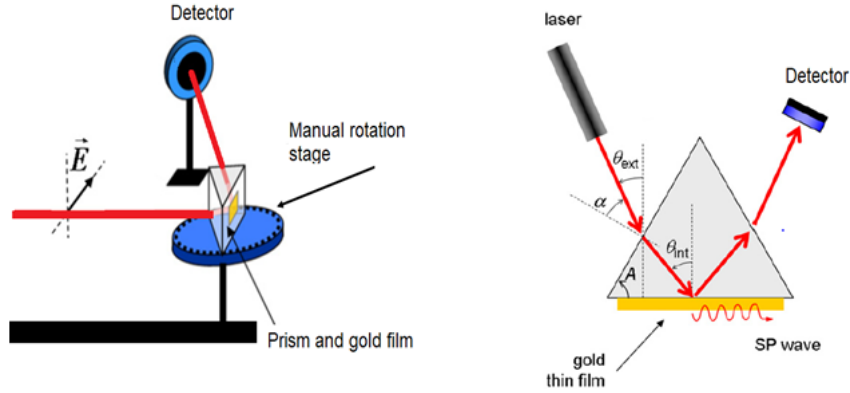
Figure 10. Monochromatic p-polarized light impinges on a prism in a total reflection configuration. An ultrathin gold film (thickness around 50 nm) is placed on the prism so that it collects the evanescent waves produced by total internal reflection and the SPP wave is launched at the gold/air interface if the angle is set at the right values. The light intensity reflected by the prism is measured with a photodiode, which shows a minimum when the coupling with the SPP wave occurs.

The value of θ_{int} is obtained by the following relation, where the angles are oriented according to the counter-clockwise orientation of the plane, as indicated in Fig. 10 (right).

$$\theta_{\text{int}} = \arcsin \frac{\sin (\theta_{\text{ext}} - A)}{n} + A. \tag{2}$$

According to the discussion in the previous session (see equation 1), the condition for coupling the excitation wave with the SP wave now takes the form:

$$(n \sin \theta_{\text{int}})^2 = \frac{\varepsilon_1(\omega) \cdot \varepsilon_2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)}. \tag{3}$$

Note that in the case of gold/air interface, $\epsilon_2 = 1$, but in more general cases medium 2 is a dielectric medium such as a liquid or molecules adsorbed on the gold surface.

Remember that in the experiment one measures the external angle θ_{ext} and using equation (2) the internal angle θ_{int} is determined. Equation (3) helps to relate the internal angle with the dielectric constants.

Detection: The reflected beam is collected with a photodiode and the photodiode is chosen so that the sensor area is greater than the cross-section of the laser beam. The detector is moved manually for each value of the incidence angle.

4. Procedures (Students activity)

A. EXCITATION OF SPP

Step 1. Check the setup and the necessary equipment required for the experiment, measure the power of the laser and check the polarization orientation.

Step 2. Verify that s-polarized incident radiation does not excite SPPs.
Step 3. Find the SPR angle for p-polarized light as shown in Fig. 11. Repeat the measurement for 10 times only near the transmission dip, in order to be able to apply statistics for the error analysis.
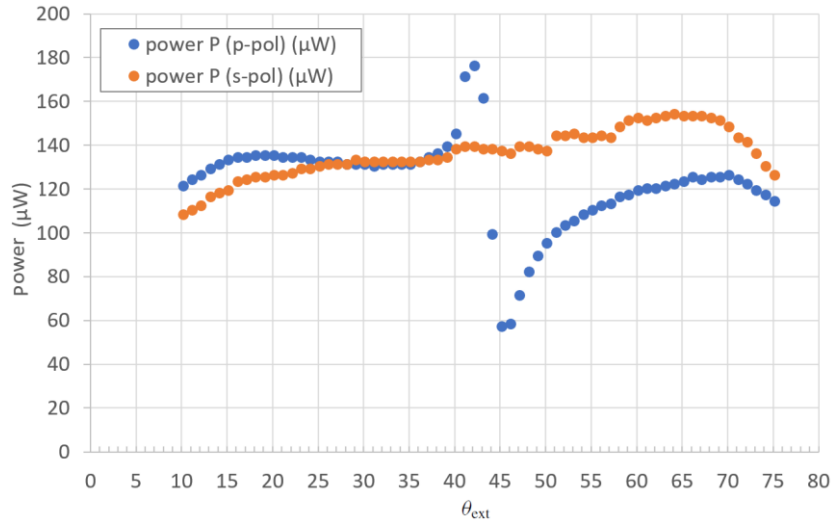
Figure 11. Excitation of SPPs using p-polarized incident light.

B. SENSING OF FLUID (DETERMINING THE INDEX OF REFRACTION OF WATER)

Step 1. Put droplet of water on the measured gold film. Carefully follow the procedures as described by your supervisor.

Step 2. Measure the shift in the SPR angle due to the water layer. Repeat the measurement 10 times around the transmission dip. Use this information to determine the index of refraction of water. Discuss the source of errors, analyze the data accordingly (e.g., standard deviation, error propagation) to estimate the experimental error on the measured refractive index. Compare the theoretical value of the index of refraction of water (n_w = 1.33) with the measured one.

C. DATA ANALYSIS AND REPORT FORMAT

A good lab report does more than presenting data; it demonstrates the writer's comprehension of the concepts behind the data. Merely recording the expected and observed results is not sufficient; you should also identify how and why differences occurred, explain how they affected your experiment, and show your understanding of the principles the experiment was designed to examine.

Bear in mind that a format, however helpful, cannot replace clear thinking and organized writing. You still need to organize your ideas carefully and express them coherently. Typical components to be fulfilled are: Title Page, Abstract, Introduction, Methods and Materials (or Equipment), Experimental Procedure, Results, Discussion, Conclusion, References.

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