Surface Plasmons

Abstract

The purpose of the experiment is observation of the optically-excited non-radiative plasma waves at the surface of a thin metal film (surface plasmons). Observation of surface plasmons provides a tool to measure the thickness of ultra-thin metal films.

Dispersion relation for surface plasmons

Maxwell's theory shows that the electromagnetic surface waves can propagate along a metallic surface with a broad continuous spectrum of frequencies from $\omega = 0$ to $\omega = \omega_p/\sqrt{2}$ depending on the wave vector $k$ [$\omega_p$ is the so-called plasma frequency, $\omega_p = (4\pi ne^2/m_e)$, $n$ is the electron density]. These electromagnetic surface waves are coupled to the oscillations of free electrons at a metal surface – the so-called surface plasma waves, or surface plasmons (SPs) (see Fig. 1). Oscillations of the charge density are localized in the $z$ direction within the Thomas-Fermi screening length of about 0.1 nm. The surface plasma waves are accompanied by a mixed transversal and longitudinal electromagnetic field which vanishes at $|z| \to \infty$ (see Fig. 2), and has its maximum at the surface $z = 0$, typical for the surface waves. One type of the solutions of the Maxwell's equations is the surface wave propagating along the interface between two media (Fig. 1):

$$
\begin{align*}
E_x &= E_0 \\
E_y &= 0 \\
E_z &= ikE_0 \left( k^2 - \varepsilon_2 \frac{\omega^2}{c^2} \right)^{-1/2} \\
\exp[i(kx - \omega t)] &\left[ \exp \left[ - \left( k^2 - \varepsilon_2 \frac{\omega^2}{c^2} \right)^{1/2} z \right] \right]
\end{align*}
$$

![Fig. 1. The structure of fields and charges in the surface e.m. wave at the dielectric/metal interface](image)
To be physically sensible, these solutions should decay exponentially at a large distance from the interface:

$$\left( k^2 - \varepsilon_1 \frac{\omega^2}{c^2} \right)^{-1/2} > 0 \quad \text{and} \quad \left( k^2 - \varepsilon_2 \frac{\omega^2}{c^2} \right)^{-1/2} > 0$$

The boundary conditions require continuity of the tangential components of $E$ and $B$ at $z = 0$. As the result:

$$\varepsilon_1 \left( k^2 - \varepsilon_2 \frac{\omega^2}{c^2} \right)^{-1/2} = -\varepsilon_2 \left( k^2 - \varepsilon_1 \frac{\omega^2}{c^2} \right)^{-1/2}.$$

This can only be true if $\varepsilon_1 < 0$ (see Appendix).

The wave vector $k_x$ is parallel to the $x$ direction; $k_x = 2\pi/\lambda_p$, where $\lambda_p$ is the wavelength of the plasma oscillations. The frequency $\omega$ of these longitudinal oscillations is coupled to its wave vector $k_x$ by a dispersion relation (DR), $\omega(k_x)$:

$$\omega = ck_x \left[ \frac{\varepsilon_1(\omega) + \varepsilon_2}{\varepsilon_1(\omega)\varepsilon_2} \right]^{1/2} = ck_x \left[ 1 + \frac{1}{1 - \left( \frac{\omega_p}{\omega} \right)^2} \right]^{1/2}.$$  \hfill (1)

For real $k_x$, one needs $\varepsilon_1 < 0$ and $|\varepsilon_1| > \varepsilon_2$, which can be fulfilled in a metal near the plasma frequency (see Appendix). The dispersion relation approaches the light line $\varepsilon_2^{1/2}\omega/c$ at small $k_x$ (see Fig. 3), but remains larger than $\varepsilon_2^{1/2}\omega/c$. Thus, the SP energy cannot be transformed into light (it is a “non-radiative” SP) and vice versa, the SPs won’t be excited if one shines light at the dielectric-metal interface in this simple geometry.
Spatial Extension of the SP Fields

Wave vectors $k_{z2}$ and $k_{z1}$ are imaginary due to $\omega/c < k_x$ and $\varepsilon_1 < 0$. The field amplitude decreases exponentially with increasing the distance from the surface. The value of the characteristic length (skin depth) at which the field is reduced by a factor $1/e$ is $\hat{z} = \frac{1}{|k_{z2}|}$, or in the metal with $\varepsilon_1$:

$$\hat{z}_1 = \frac{\lambda}{2\pi} \left[ \frac{\varepsilon_1(\omega) + \varepsilon_2}{\varepsilon_1(\omega)\varepsilon_2} \right]^{1/2}.$$  

For $\lambda = 600$ nm, one obtains for silver $\hat{z}_1 = 24$ nm.

Optical Excitation of SPs

The SP dispersion relation $\omega(k)$ lies to the right of the light line (see Fig. 4). This means that the SPs have a longer wave vector than light waves of the same frequency $\omega$, and they cannot be excited if only one interface is present. There is, however, a trick which allows coupling of the SPs to the light wave – we need another interface, very close to the first one, because the field decays very fast in the metal (see Fig. 3). The SPs will propagate along this second interface between the metal and a dielectric with the dielectric constant $\varepsilon_0 < \varepsilon_2$ - the second dielectric might be, e.g., air (see below).

The experiment on optical excitation of surface plasmons in thin metal films is shown in Fig. 3. The light polarized in the plane of incidence (important!) undergoes total internal reflection at the interface glass/metal. Surface plasma waves may be excited at the other interface, metal/air, by coupling to the evanescent field. The wave vector $k_x$ is continuous across the boundaries. Note that two interfaces are crucial for observation of SPs: by varying the angle of incidence, we adjust the wave vector $k_x$ at the glass/metal interface in order to fulfill the “resonance” conditions on the other (metal/air) interface for the SP excitation.
Formation of SPs in this device can be understood as follows. Since the excitation of SPs occurs in the region of total reflection at the glass/metal interface, an evanescent light wave with a phase velocity \( v = \omega / k_x = c / (\varepsilon_2^{1/2} \sin \theta_0) \) with \( \varepsilon_2^{1/2} \sin \theta_0 > 1 \) propagates along the interface with \( v < c \). The resonance condition for SPs at the metal/air interface:

\[
\frac{\omega}{k_x} = c \sqrt{\frac{\varepsilon_1(\omega) + 1}{\varepsilon_1(\omega)}} = \frac{c}{\sqrt{\varepsilon_2 \sin \theta_0}} \tag{1}
\]

can thus be fulfilled, particularly because the character of both waves is the same.

Fig. 3 Two different interfaces (glass/metal and metal/air) are required for optical excitation of the surface plasmon.

Another way to understand the formation of SPs is shown in Fig. 4. The dispersion relation for SPs propagating along the metal/air interface can be satisfied between the lines \( c \) and \( c / \varepsilon_2^{1/2} \).

Fig. 4. Dispersion relation DR of SPs for a glass/metal/air system (\( \varepsilon_2 \sim 1.5, \varepsilon_1 < 0, \varepsilon_0 = 1 \)). Since the light line in glass \( c / \varepsilon_2^{1/2} \) lies to the right of the DR up to a certain \( k_x \), light can excite SPs of the frequency \( \omega \) below the crossing point \( P \) for the metal/air interface. The SPs on the glass/metal interface cannot be excited, because their DR lies to the right of \( c / \varepsilon_2^{1/2} \).
Measurement of the thickness of ultra-thin silver films

By observing the surface plasmon resonance (SPR), one can study the optical properties of thin metal film and measure directly their thickness. The SPR can be characterized by the following three parameters (see Fig. 5): the reflection coefficient \( R \) at the minimum (without the metal film, \( R = 1 \) due to the total internal reflection), the angular position of the minimum, \( \alpha \), and the angular halfwidth \( \Delta \alpha \). By measuring these three parameters, we can find the complex dielectric permittivity \( \varepsilon = -\varepsilon_r + i\varepsilon_i \), and the thickness \( d \) of the metal film (in other words, the distance between totally-reflecting and plasmon-carrying surfaces).

![Fig. 5](image)

It is relatively easy to get a solution for \( R(\alpha) \) by considering Fresnel's reflection equation in a situation when a light wave with a plane wavefront is falling on optically flat interfaces. The inverse problem (to restore \( \varepsilon \) and \( d \) from \( R, \alpha \), and \( \Delta \alpha \)) is much more difficult. The exact analytical solution does not exist, and we can do some approximations following Kretschmann [1]. For the film thickness, we have:

\[
d = -\phi \ln \left[ \frac{\Delta \alpha}{4B} \right]
\]

where (below we assume that medium 3 is air with \( \varepsilon_3 = 1 \))

\[
B = \frac{\omega}{c} \frac{2}{\varepsilon_r + 1} \left( \frac{\varepsilon_3}{\varepsilon_r - 1} \right) \text{Im} r_{i2}
\]
\( r_{12} \) is the reflection coefficient of the in-plane polarized wave at the interface between layers 1 and 2, and

\[
\phi = 2 \frac{\omega}{c} \frac{\varepsilon_r}{\sqrt{\varepsilon_r - 1}}.
\]
Appendix. The dispersion of e.-m. waves in conductors.

The complex relative permittivity $\varepsilon_r^*$ in conductors can be written as follows:

$$\varepsilon_r^*(\omega) = \varepsilon_r(\omega) + i \frac{\sigma(\omega)}{\varepsilon_0 \omega}.$$ 

In principle, both $\varepsilon_r$ and the conductivity $\sigma$ are complex; thus, the imaginary part of $\varepsilon_r$ and the real part of $\sigma$ contribute to $\text{Im}\varepsilon_r^*$ (dissipation, absorption, dispersion), and the real part of $\varepsilon_r$ plus the imaginary part of $\sigma$ contribute to $\text{Re}\varepsilon_r^*$ (the index of refraction, the phase velocity, etc.).

Let’s consider sufficiently high frequencies $\omega \tau >> 1$, where $\tau$ is the electron scattering time. These frequencies correspond typically to the visible light range and ultra-violet. At such frequencies, $\varepsilon_r \sim 1$ (the bound electrons are too slow to respond), and $\sigma = i \sigma_0 / \omega \tau$, where $\sigma_0$ is the Drude conductivity at $\omega = 0$ (the inertia of mobile electrons make the conductivity pure imaginary at high frequencies). Thus,

$$\varepsilon_r^*(\omega) = 1 - \frac{\sigma_0}{\varepsilon_0 \omega^2 \tau} = 1 - \left( \frac{\omega_p}{\omega} \right)^2,$$

where $\omega_p = \left( \frac{4\pi n e^2}{m} \right)^{1/2}$ is the plasma frequency, $n$ is the electron density, $m$ – the electron mass.