Optical Properties of Metals

The presence of an electric field **E**(**r**,*t*) causes a current, owing to the conductivity σ. Note that $\vec{j} = \sigma\vec{E}$ which is Ohm's law at the microscopic level. We can write Maxwell's equations for an homogeneous, isotropic medium containing charge carriers, such as electrons in a non-magnetic metal:

$$\vec{\nabla}\cdot\vec{E} = \rho/\varepsilon \quad \vec{\nabla}\cdot\vec{B} = 0 \quad \vec{\nabla}\times\vec{E} = -\frac{\partial\vec{B}}{\partial t} \quad \vec{\nabla}\times\vec{B} = \mu\sigma\vec{E} + \mu\varepsilon\frac{\partial\vec{E}}{\partial t}$$

We can easily manipulate the 3rd and 4th equations:

$$\vec{\nabla}\times\left(\vec{\nabla}\times\vec{E}\right) = -\frac{\partial}{\partial t}(\vec{\nabla}\times\vec{B}) = -\mu\sigma\frac{\partial\vec{E}}{\partial t} - \mu\varepsilon\frac{\partial^2\vec{E}}{\partial t^2}$$

Also, we will make use of the vector identity: $\vec{\nabla}\times\left(\vec{\nabla}\times\vec{A}\right) = \vec{\nabla}\left(\vec{\nabla}\cdot\vec{A}\right) - \nabla^2\vec{A}$

$$\vec{\nabla}\left(\vec{\nabla}\cdot\vec{E}\right) - \nabla^2\vec{E} = -\mu\sigma\frac{\partial\vec{E}}{\partial t} - \mu\varepsilon\frac{\partial^2\vec{E}}{\partial t^2} \quad \textit{and} \quad \vec{\nabla}\cdot\vec{E} = \rho = 0$$

$$\Rightarrow \quad \nabla^2\vec{E} = \mu\varepsilon\frac{\partial^2\vec{E}}{\partial t^2} + \mu\sigma\frac{\partial\vec{E}}{\partial t}$$

which is the wave equation in an uncharged conducting medium (i.e. a metal).

$$\textit{Since} \quad \vec{E} = \vec{E}_0 \exp i\left(\vec{k}\cdot\vec{r} - \omega t\right), \quad -\tilde{k}^2\vec{E} = -\mu\varepsilon\omega^2\vec{E} - i\omega\mu\sigma\vec{E}$$

$$\Rightarrow \quad \tilde{k}^2 = \mu\omega^2\left(\varepsilon + i\sigma/\omega\right); \quad \tilde{n} = \frac{c}{\omega}\tilde{k} = n_R - in_I\,; \quad \tilde{k} = \frac{\omega}{c}\left(n_R - in_I\right)$$

Thus, the wave equation for a metal gives a complex dispersion relation $k(\omega)$ in which k *(~ tilda)* here is complex; which leads to a complex index of refraction containing real (n_R) and imaginary (n_I) parts. Note that the last term in the wave equation is like a damping force and is responsible for absorption. Let's write the propagating wave as

$$\vec{E} = \vec{E}_o \cos\left(\omega t - ky\right) = \vec{E}_o \cos\omega\left(t - \frac{k}{\omega}y\right) = \vec{E}_o \cos\omega\left(t - \tilde{n}y/c\right)$$

Putting this in a more general form involving a complex exponential:

$$\vec{E} = \vec{E}_o \exp i\omega\left(t - \tilde{n}y/c\right) = \vec{E}_o \exp i\omega\left(t - (n_R - in_I)y/c\right)$$

$$= \vec{E}_o \exp\left(-\omega n_I y/c\right)\exp i\omega\left(t - n_R y/c\right)$$

$$\mathrm{Re}\,\vec{E} = \vec{E}_o \exp\left(-\omega n_I y/c\right)\cos\omega\left(t - n_R y/c\right)$$

$$\textit{Since} \quad I \propto \left|\vec{E}\right|^2 \qquad \textit{and} \quad I(y) = I_o \exp(-\alpha y) \qquad \textit{with} \quad I_o = I(0),$$

$$\textit{comparison} \quad \textit{gives} \quad \alpha \equiv 2\omega n_I / c$$

This is the absorption or attenuation coefficient α and $d = 1/\alpha$ is known as the skin or penetration depth. Note that α depends on the frequency or wavelength. For materials that are transparent, $1/\alpha >>$ thickness.

For metals, take Cu for example: $1/\alpha \approx 6$Å at $\lambda = 100$ nm (UV) and 60 Å at $\lambda = 10{,}000$ nm (IR). This explains the opacity of metals in which the penetration depth is very small and most of the energy is reflected.

Imagine the metal as a collection of driven and damped oscillators. Some of the electrons in the metal (valence electrons) are free to move and thus possess no restoring force. Other electrons are bound to the atoms such as in a dielectric material like glass. Remember for an oscillating dipole we derived the classical expression from Newton's second law:

$$F_E - k_s x = q_e E_o \cos\omega t - m_e \omega_o{}^2 x = m_e \frac{d^2 x}{dt^2}$$

$$\Rightarrow q_e E_o \cos\omega t - m_e \omega_o{}^2 x_o \cos\omega t = -m_e \omega^2 x_o \cos\omega t$$

$$\Rightarrow x_o = \frac{q_e E_o}{m_e\left(\omega_o{}^2 - \omega^2\right)}; \quad x = \frac{q_e E_o}{m_e\left(\omega_o{}^2 - \omega^2\right)}\cos\omega t; \quad x = \frac{q_e E(t)}{m_e\left(\omega_o{}^2 - \omega^2\right)}$$

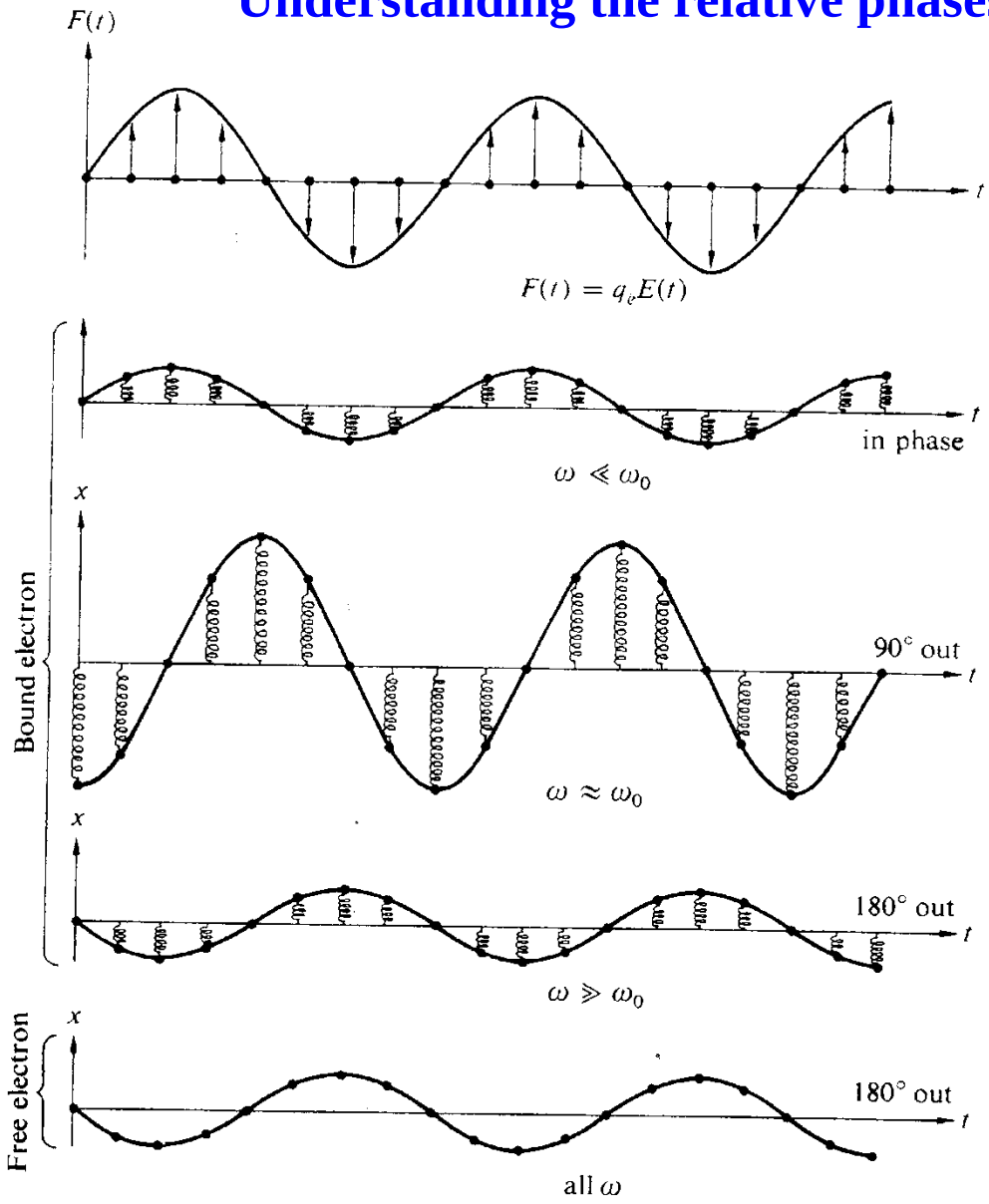
For the free electrons in a metal, there is no restoring force and $\omega_o=(k_s/m_e)^{1/2} \approx 0$. It is as though electrons are attached by very weak springs. Therefore we have

$$x(t) = -\frac{q_e E(t)}{m_e\omega^2} = -\frac{F_E}{m_e\omega^2}$$

The minus sign indicates that the free electrons oscillate 180° out-of-phase relative to the E-field of the incident light. This oscillation therefore creates light waves that will cancel (interfere destructively with the incident wave) when radiating in the same direction as the incident wave. The result is a rapidly decaying refracted wave, as we have just seen with the attenuation. We can extend the dispersion relation to include both types of electrons (bound and free valence e⁻'s):

$$\vec{P} = (\varepsilon - \varepsilon_o)\vec{E} \quad \Rightarrow \quad \varepsilon = \varepsilon_o + \frac{P(t)}{E(t)}, \quad n^2 = \frac{\varepsilon}{\varepsilon_o}$$

Understanding the relative phases for oscillating electrons



$$x = \frac{q_e E(t)}{m_e\left(\omega_o{}^2 - \omega^2 + i\gamma\omega\right)}$$

$$\exp(i\Delta\varphi) = \exp(i0) = 1$$

$$\exp(i\Delta\varphi) = \exp(i\pi/2) = i$$

$$\exp(i\Delta\varphi) = \exp(i\pi) = -1$$

$$\exp(i\Delta\varphi) = \exp(i\pi) = -1$$

Figure 4.57 Oscillations of bound and free electrons.

free e⁻'s bound e⁻'s

Therefore $$n^2(\omega) = 1 + \frac{q_e{}^2 N}{\varepsilon_o m_e}\left[\frac{f_e}{-\omega^2 + i\gamma_e\omega} + \sum_j\left(\frac{f_j}{\omega_{oj}^2 - \omega^2 + i\gamma_j\omega}\right)\right]$$

where N is the number of atoms per unit volume; f_e is the number of free valence electrons per atom. The second term involving the sum again refers to the bound electrons, as we have seen previously for dielectric materials.

If a metal has a particular color (Gold and copper are reddish yellow) it indicates that the atoms of the metal are involved with the selective absorption via bound electrons. We can approximate the above equation further by assuming a negligible contribution from bound e⁻'s and $\gamma_e \approx 0$ for large ω, i.e. a small dissipation at high frequencies:

$$n^2(\omega) = 1 - \frac{q_e{}^2 N}{\varepsilon_o m_e}\frac{1}{\omega^2} = 1 - \left(\frac{\omega_p}{\omega}\right)^2 \quad with \quad \omega_p = \sqrt{\frac{q_e{}^2 N}{\varepsilon_o m_e}}$$

Consider the behavior of $n(\omega)$ for limiting cases in metals:

(i) $\omega < \omega_p \Rightarrow n^2(\omega) < 0$ and n is complex. Since $\alpha = 2\omega n_I/c$, the absorption will be large.

(ii) $\omega > \omega_p \Rightarrow n^2(\omega) > 0$ and n is real, absorption is small and we observe a transparency condition. Notably, x-rays (100 Å > λ > 1Å) will penetrate metals.

(iii) Some metals, such as Alkali metals, are transparent even in the ultraviolet. The table below illustrates the calculated plasma frequencies and wavelengths for some Alkali metals.

TABLE 4.3 Critical Wavelengths and Frequencies for Some Alkali Metals

Metal	λ_p (observed) nm	λ_p (calculated) nm	$\nu_p = c/\lambda_p$ (observed) Hz
Lithium (Li)	155	155	1.94×10^{15}
Sodium (Na)	210	209	1.43×10^{15}
Potassium (K)	315	287	0.95×10^{15}
Rubidium (Rb)	340	322	0.88×10^{15}

In general, n is complex and so there is absorption in metals when there is a finite n_I.

Consider reflection from a metal surface at normal incidence ($\theta_i = 0$).

$$We \quad derived \quad R = \frac{I_r}{I_i} = r^2 = \left(\frac{n_t - n_i}{n_t + n_i} \right)^2$$

We derived this for a dielectric.

For an air-metal interface, take

$$n_i = 1 \quad and \quad n_t = \tilde{n} = n_R - i n_I$$

$$Since \quad r = \frac{n-1}{n+1} \quad \Rightarrow \quad R = |r|^2 = r^* r = \left(\frac{\tilde{n}-1}{\tilde{n}+1} \right) \left(\frac{\tilde{n}-1}{\tilde{n}+1} \right)^*$$

$$= \left(\frac{n_R - 1 - i n_I}{n_R + 1 - i n_I} \right) \left(\frac{n_R - 1 + i n_I}{n_R + 1 + i n_I} \right) = \frac{(n_R - 1)^2 + n_I^2}{(n_R + 1)^2 + n_I^2}$$

Typical values of n_R, n_I, and R at λ=589 nm

Notice that the reflectance of Na has a larger R despite its smaller n_I.

	Na	Sn	Ga
n_R	0.04	1.5	3.7
n_I	2.4	5.3	5.4
R	0.9	0.8	0.7

1) If the conductivity $\sigma \rightarrow 0$ which gives a dielectric with $n_I \approx 0$, $n_I << n_R$, and $\alpha \rightarrow 0$, $n_R \approx n_t$

2) If σ is large, n_I is large and $n_I >> n_R$ and $R \rightarrow 1$.

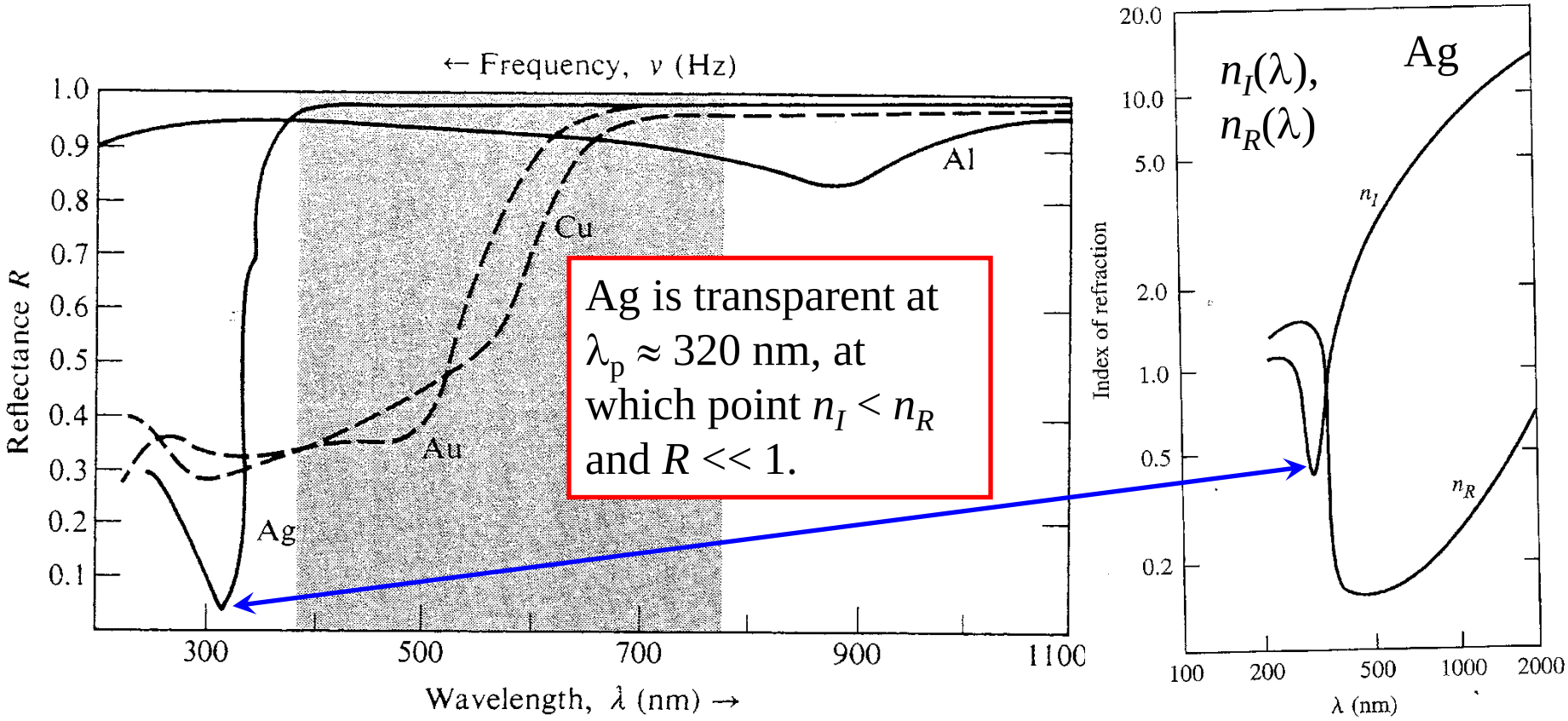


Figure 4.59 Reflectance versus wavelength for silver, gold, copper, and aluminum.

Note that Au and Cu exhibit an increasing R in the range 500 nm < λ < 700 nm, and this provides the reddish-yellow color when the metals are illuminated with white light.

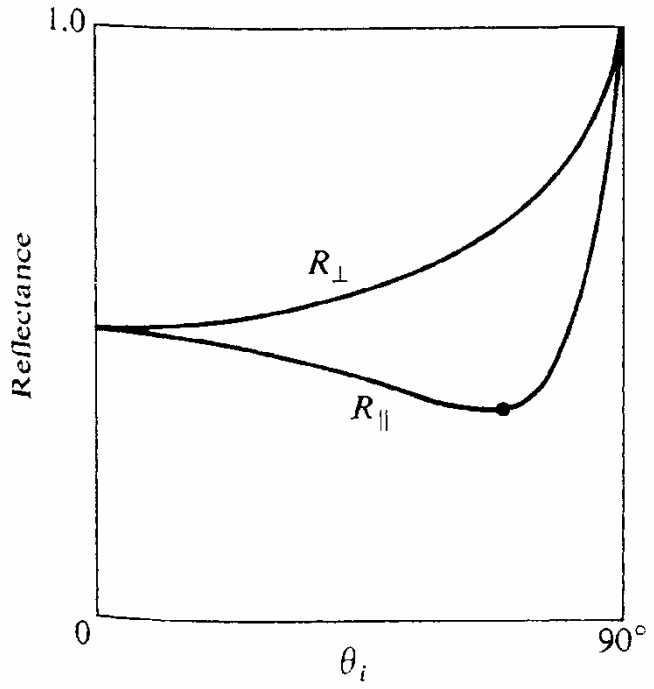


Figure 4.58 Typical reflectance for a linearly polarized beam of white light incident on an absorbing medium.

Note that the dip in $R_\parallel$ is similar to the case of Brewster's angle (θ_p) for dielectric interfaces except that $R_\parallel > 0$ at its minimum, as shown.

Phase shifts occur during reflection from a metal surface. Both $E_\parallel$ and $E_\perp$ experience phase shifts which are in general between 0 and 180°. When $\theta_i = 90°$, both $E_\parallel$ and $E_\perp$ experience $\Delta\varphi = 180°$.

Bulk Plasmons and the dispersion relation ω(*k*) for a metal

We can write the E-M wave equation as

$$\nabla^2 \vec{E} = \mu_o \frac{\partial^2 \vec{D}}{\partial t^2} \quad and \quad \vec{D} = \varepsilon(\omega, \vec{K})\,\vec{E}$$

$$and \quad \vec{E} = \vec{E}_o \exp i\left(\vec{K}\cdot r - \omega t\right) \quad \Rightarrow \quad \varepsilon(\omega, \vec{K})\mu_o\,\omega^2 = K^2$$

Note that ε(*ω*, **K**) can be complex in general and lead to **K** which is complex, as we have seen in FTIR. We saw already solutions in which we assumed that the contribution from bound electrons and damping were assumed negligible:

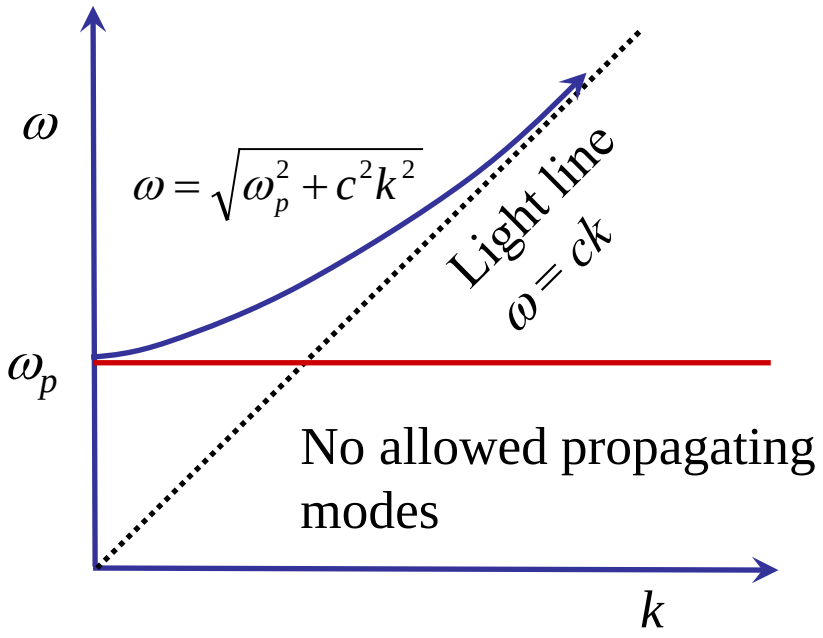
$$n^2 = \frac{\varepsilon(\omega)}{\varepsilon_o} = 1 - \frac{\omega_p^2}{\omega^2}$$

Inserting this into the first equation above, we get

$$\Rightarrow \quad \left(1 - \frac{\omega_p^2}{\omega^2}\right)\varepsilon_o \mu_o\,\omega^2 = k^2 \quad and \quad \omega^2 - \omega_p^2 = c^2 k^2$$

We assume propagating solutions in which *K*=*k* is real.

Bulk Plasmon Dispersion Relation



Solutions lie above the light line. Typical values for the plasmon energy are

$\hbar\omega_p \approx 10eV$ …Metals

$\hbar\omega_p < 0.5eV$...Semiconductors (depends on dopant concentration).

Surface Plasmon Polaritons

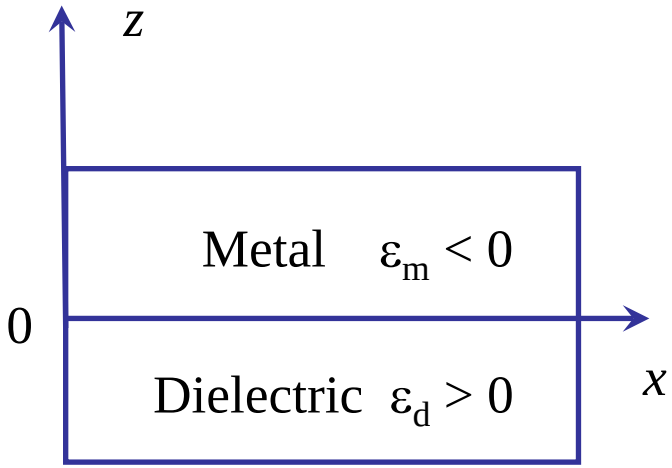
Consider an E-M wave that can propagate along the interface between metal and vacuum (i.e. the surface of a metal) or between the metal and a dielectric material. Again, we assume solutions to the E-M wave equation.

The solutions E(***r***,*t*) are of the form:

$$E_x = A\exp(ik_x x)\exp(-k_{zm} z), \quad E_y = 0, \quad E_z = B\exp(ik_x x)\exp(-k_{zm} z), \quad z > 0$$

$$E_x = C\exp(ik_x x)\exp(+k_{zd} z), \quad E_y = 0, \quad E_z = D\exp(ik_x x)\exp(+k_{zd} z), \quad z < 0$$

$$\vec{K}_m = k_x + ik_{zm} \quad and \quad \vec{K}_d = k_x - ik_{zd}$$



We need to invoke continuity conditions of $\mathbf{E}_{\|}$ and $(\varepsilon\mathbf{E})_{\perp}$, along with Gauss's law: $\vec{\nabla}\cdot\vec{E} = 0$

$$\vec{\nabla}\cdot\vec{E} = 0 \quad \Rightarrow \quad ik_x E_x = k_{zm} E_z \quad \Rightarrow ik_x A = k_{zm} B \quad (z > 0)$$

$$\vec{\nabla}\cdot\vec{E} = 0 \quad \Rightarrow \quad ik_x E_x = -k_{zd} E_z \quad \Rightarrow ik_x C = -k_{zd} D \quad (z < 0)$$

$$\Rightarrow \frac{k_{zm}}{k_{zd}} = -\frac{AD}{BC}$$

We can further remove the time dependence in the *E*-*M* wave equation by inserting $\vec{E} = \vec{E}(\vec{r})\exp(-i\omega t)$

$$\nabla^2\vec{E} = \mu_o\varepsilon(\omega,\vec{K})\frac{\partial^2\vec{E}}{\partial t^2} = -\omega^2\mu_o\varepsilon(\omega,\vec{K})\vec{E} \quad \Rightarrow \quad -k_x^2 + k_{zm}^2 = -\omega^2\mu_o\varepsilon_m(\omega,\vec{K})$$

$(z > 0)$ (1)

and $-k_x^2 + k_{zd}^2 = -\omega^2\mu_o\varepsilon_d(\omega,\vec{K})$ $(z < 0)$ (2)

Continuity of E_x requires $A = C$ and for E_z requires $\varepsilon_m B = \varepsilon_d D$. *Therefore*

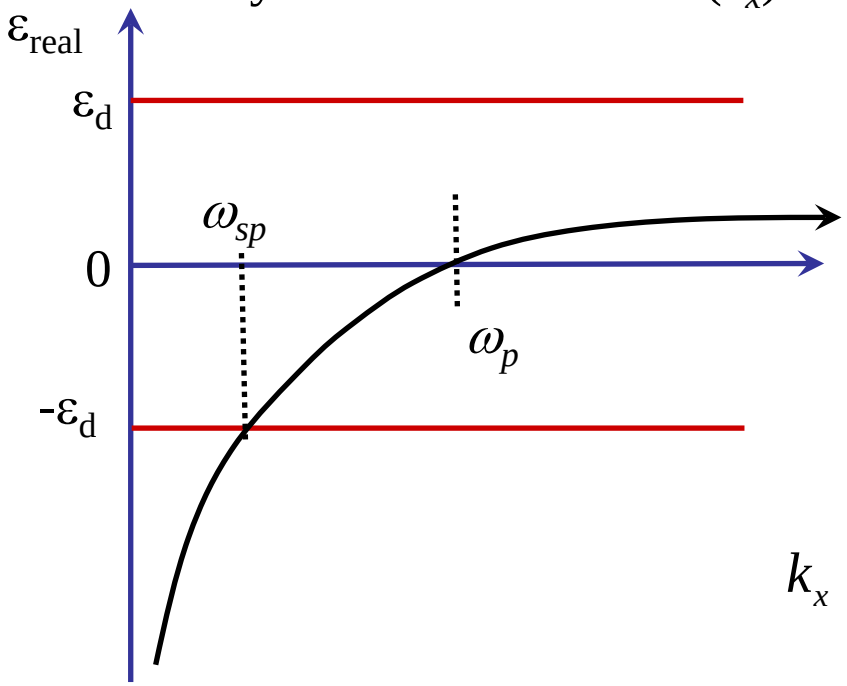
$$\frac{k_{zm}}{k_{zd}} = -\frac{AD}{BC} = -\frac{\varepsilon_m}{\varepsilon_d} \qquad (3)$$

Subtracting Eqs. (1) and (2) and eliminating k_{zd} using Eq. (3) we get

$$k_{zm}^2 = -\omega^2\mu_o\frac{\varepsilon_m^2}{\varepsilon_m + \varepsilon_d} \quad \text{and} \quad k_x = \omega\sqrt{\mu_o\frac{\varepsilon_m\varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$

$$k_x^2 = \frac{\omega^2}{c^2}n^2 = \frac{\omega^2}{c^2}\frac{\varepsilon_{\text{real}}}{\varepsilon_0} \qquad k_x^2 = \omega^2\mu_0\frac{\left(1 - \dfrac{\omega_p^2}{\omega^2}\right)\varepsilon_d}{\left(1 - \dfrac{\omega_p^2}{\omega^2}\right) + \varepsilon_d}$$

Examine the dielectric constants for both the dielectric and metal layers and determine $\omega(k_x)$ for surface plasmons.



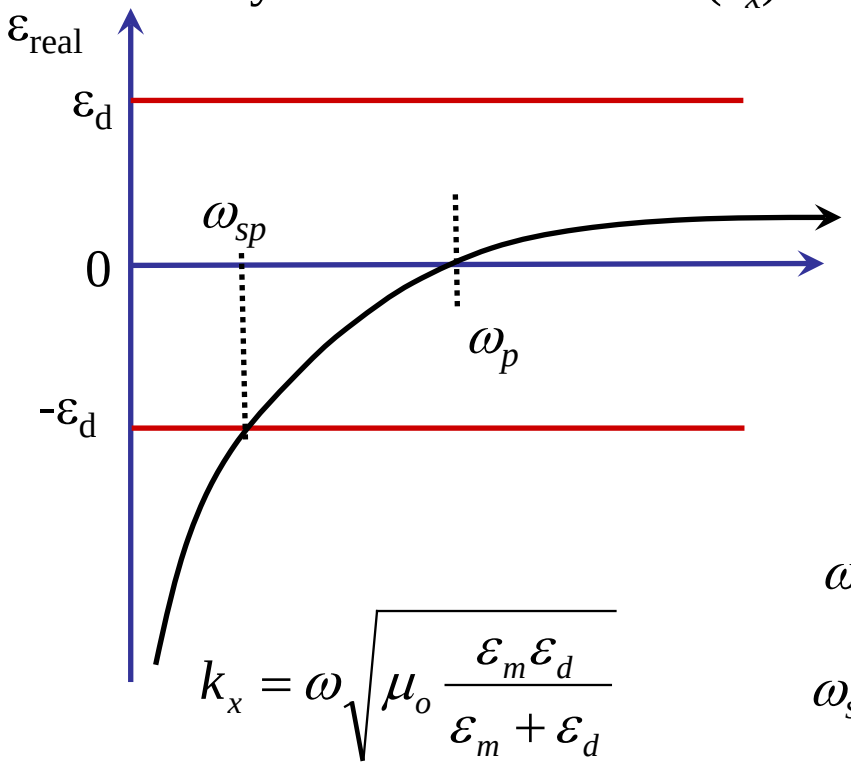
$$n^2 = \frac{\varepsilon_m(\omega)}{\varepsilon_o} = 1 - \frac{\omega_p^2}{\omega^2}$$

$$k_x = \omega\sqrt{\mu_o \frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} = \omega\sqrt{\mu_0 \frac{\left(1 - \frac{\omega_p^2}{\omega^2}\right)\varepsilon_d}{\left(1 - \frac{\omega_p^2}{\omega^2}\right) + \varepsilon_d}}$$

1) For small ω, $\varepsilon_m \rightarrow -\infty$ and $k_x \approx \omega(\varepsilon_d \mu_o)^{1/2} = \omega/v_d$

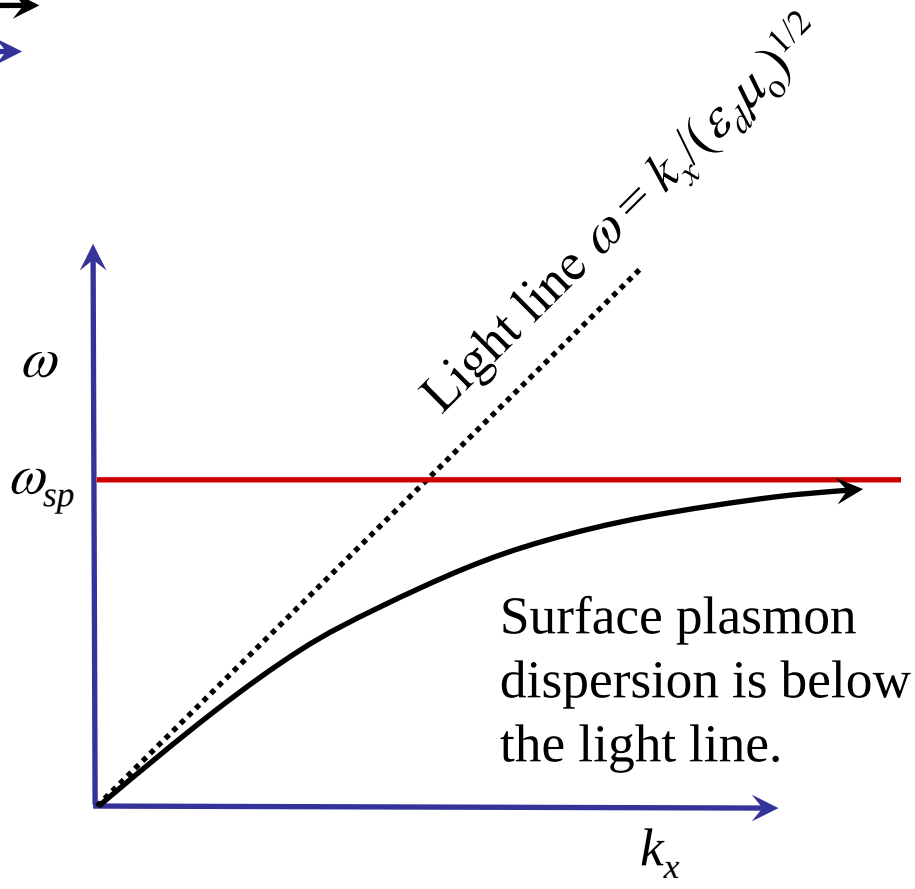
2) At $\omega = \omega_{sp}$, $\varepsilon_m \rightarrow -\varepsilon_d$ (from below) and $k_x \rightarrow +\infty$

Examine the dielectric constants for both the dielectric and metal layers and determine $\omega(k_x)$ for surface plasmons.



$$n^2 = \frac{\varepsilon_m(\omega)}{\varepsilon_o} = 1 - \frac{\omega_p^2}{\omega^2}$$

$$k_x = \omega\sqrt{\mu_o \frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$

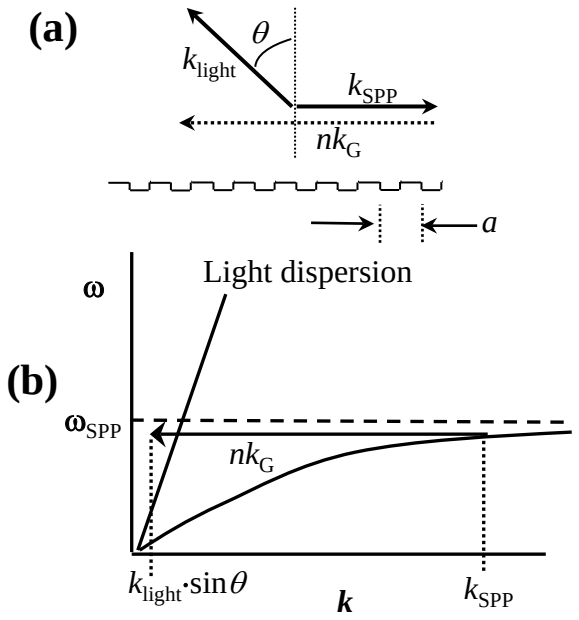


1) For small ω, $\varepsilon_m \rightarrow -\infty$ and $k_x \approx \omega(\varepsilon_d\mu_o)^{1/2} = \omega/v_d$

2) At $\omega = \omega_{sp}$, $\varepsilon_m \rightarrow -\varepsilon_d$ (from below) and $k_x \rightarrow +\infty$

Surface plasmon dispersion is below the light line.

Surface Plasmon polaritons (SPPs) in metal nanostructures: the optoelectronic route to nanotechnology, M. Salerno et. al., Opto-electronics Rev. 10(3), 217 (2002).



Light is injected from the left, creating surface plasmons (SPs) which propagate to the right. When they reach the end of the gold strip (point S), a transfer of momentum to the SPs causes energy to be transferred back to light, which is subsequently detected with a photon scanning tunneling microscope (PSTM).

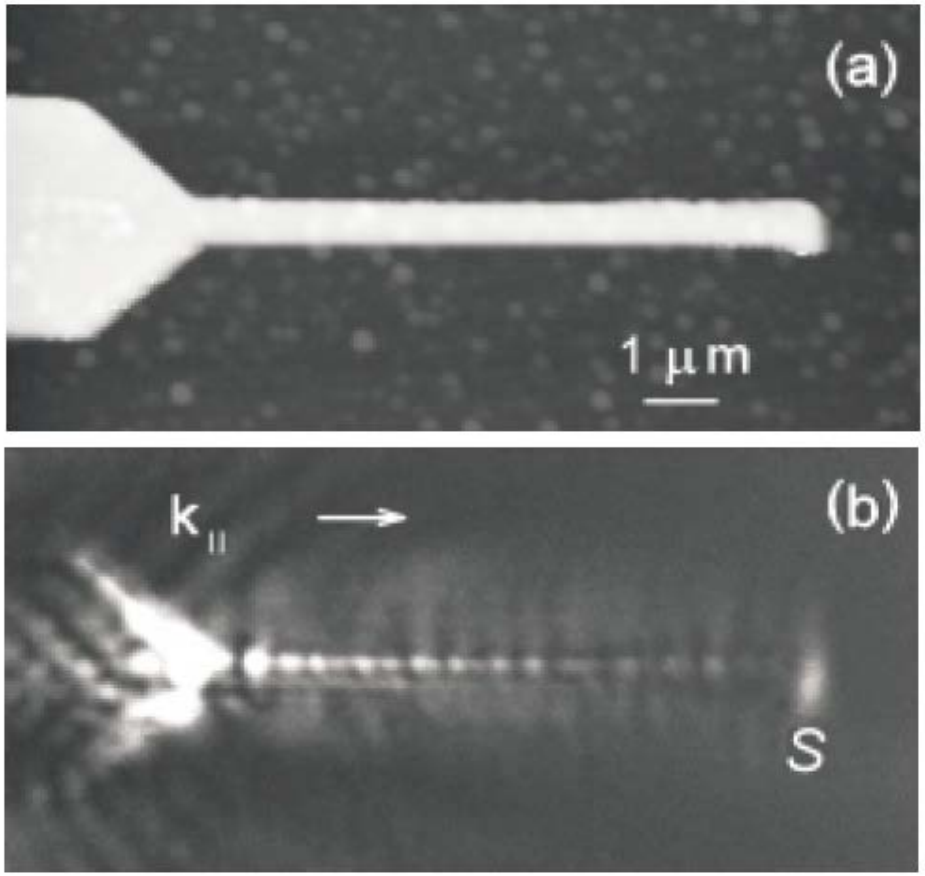


Fig. 6. A gold microstripe tapered down to a nanowire. Gold thickness: 50 nm; stripe width: 3 μm; wire width 200 nm. (a) shear-force topography, acquired simultaneously with (b); (b) PSTM measurement, (illumination conditions: $\lambda_0 = \lambda_{SP} = 800$ nm, TM-polarization, $\alpha = 42°$, injected light direction left to right). Image size: 15×7 μm^2. The letter *S* marks SP scattering at the nanowire termination.